# Russian Chemical Reviews, Volume 34 (1965)

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# THE ASYMMETRIC NON-CARBON ATOM

V.I. Sokolov and O.A. Reutov

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The stereochemistry of compounds with asymmetric carbon was long ago consolidated into a unified system which rests on numerous correlations of the configurations of important classes of compounds and received its principal consummation after the establishment of the absolute configurations. Later, in the fifties, the stereochemistry of compounds exhibiting molecular dissymmetry (without an asymmetric atom) was formulated: substituted biphenyls, allenes, etc. This process is still not completely finished, although there has been great progress in the last decade. It must also be noted that in this period great interest was aroused in the theory of optical activity in general and the method of optical rotatory dispersion was vigorously developed as a tool for the investigation of organic and inorganic compounds.

Until recent years much less attention was paid to molecules containing an asymmetric atom other than carbon. Meanwhile the great diversity of types of such compounds is of great interest for stereochemistry. This region of investigation, which has been exploited particularly intensively during the last 5–6 years, has not been surveyed in the review literature known to us.

## 1. GENERAL OUTLINE OF THE HISTORY OF THE PROBLEM

In the history of this problem it is possible to distinguish several periods, the start of each being indicated by the origination of a certain idea (naturally, it is impossible to draw sharp boundaries between these periods). The start of the stereochemistry of the non-carbon asymmetric atom can be ascribed to the time when one of the founders of stereochemistry, LeBel[1], obtained an optically active salt (the chloride) of the ethylisobutylisopropylmethylammonium cation by a microbiological method (1891). In the first period the main interest of chemists was in the demonstration of the possibility of the existence of tetra- and tri-substituted non-carbon atoms in an optically active form. This was evidence of the generality of the tetrahedral model and of its applicability also to elements other than carbon. The most important works in the years 1900–1910 were completed by the English stereochemical school (Pope and Peachey): ammonium[2] and sulphonium[3] salts, etc., were separated into antipodes. At the end of the twenties optically active esters of sulphinic acids[4], sulphoxides, and related compounds were obtained. Exhaustion of the possibilities in this direction appeared to be the reason for the considerable reduction in the number of publications (up to the fifties). However, the description work retains significance, for example, a quadruply-substituted sulphur derivative[6] was obtained in the optically active state in 1960, and an amine oxide[7] only in 1963.

The start of the second period can be considered to be the work of Meisenheimer[8,9] (1911–1926). At this time a persistent interest commenced in the nature of optical

activity, which first arose, of course, in the stereochemistry of carbon (beginning with Chugaev). Meisenheimer took up an idea of Werner [10] about the role of the central atom in complexes and introduced it into organic chemistry. He was not only the first who posed the problem of the influence of the nature of the asymmetric central atom on the magnitude of the rotation, but he also carried out experimental work that was a model in its execution. His work retained a demonstrative character (for the semipolar bond in amine oxides and phosphines), but the general statement of the question was elegant. After Meisenheimer, interest in this aspect of the problem was lost for a long time, being maintained only in the laboratory of Mann [11] (Cambridge), where unusual refraction was obtained.

The third period starts at the end of the fifties: compounds with an asymmetric non-carbon atom are used as models for studying reaction mechanisms, in which it is already necessary to take into account differences between carbon and other elements. In recent years the stereochemistry of Si, P, Ge, and As has been practically established and information obtained on the mechanisms of substitution at phosphorus and silicon. The greatest success is the establishment in certain instances of the absolute configuration of non-carbon asymmetric centres, which is one of the main tasks of static stereochemistry. A second task presents much greater difficulty: the determination of the magnitude of the optical rotation as a function of structure. This is still far from solution.

Specific interest in the limits of the problem under review is the problem of the dependence of rotation on the nature of the asymmetric atom. In compiling this review this has received the greatest attention. On the other hand we have not aimed at an exhaustive treatment of the problem of dynamic stereochemistry. Of the older works (which can be found in the well-known handbooks on stereochemistry) we consider in detail only those which are of significant importance in the aspect referred to; the others are simply mentioned. The most recent literature used in the review appeared in Autumn 1963. [The authors have added some more recent references at the end of the bibliography (Ed. of Translation).]

At present, optical activity due to asymmetric atoms of the following elements (other than carbon) has been established: Si, Ge, N, P, As, Sb, S, Se, Te. The material will be considered according to the Groups of the Periodic System, beginning in greater detail with Groups V and VI, whose stereochemistry has a greater history, and then reverting to the more recent work on Group IV. A special Section deals with spirans with a hetero-spiro-atom. The last part of the review contains an attempt to analyse the published material using the semiempirical method of calculating optical rotation developed by Brewster [12-14] for compounds with asymmetric carbon.

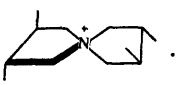
## 2. GROUP V

Salts of quadruply-substituted ammonium were long ago separated into antipodes [2]; in most instances their optical stability is small on account of the ease of the reverse reaction:

$$R_1R_2R_3R_4\overset{+}{N}\overset{-}{X} \rightleftarrows R_1R_2R_3N + R_4X.$$

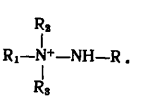
Greater optical stability is exhibited by the spiran systems with a bicyclic nitrogen, first resolved by Mills [15]. Their racemisation is hindered by the necessity for breaking two carbon–nitrogen bonds. [This does not follow (Ed. of Translation).]

There are two interesting points in connection with these systems. Firstly, there are the very rare instances of self-produced resolution observed by Havinga [16,17]: on long standing in a sealed ampoule benzylethylmethylphenylammonium iodide deposited crystals of an (-) enantiomer containing chloroform. Secondly, to this class belongs the only known example of a molecule which is optically inactive, since it is superimposable with its mirror image, although it does not possess a planar centre of symmetry [18]:



Here a rare symmetry element is realised — a fourfold axis of rotation-inversion, the absence of optical activity for such molecules had been suggested earlier [19].

A unique isologue of ammonium has been described in an optically active form — the hydrazonium salt (I) [20]:



(I)

In contrast to ammonium salts, phosphonium and arsonium salts could not be resolved into antipodes for long on account of rapid racemisation. Earlier works [21-23] were unsuccessful but sometimes slight and rapidly disappearing rotation was observed. Enantiomers of phosphonium salts were obtained only in the last decade by a few groups of investigators, especially Vanderwerf and McEwen [24-26]. Certain arsonium salts have also been obtained in an optically active form [27,28]. Of particular interest is the successful use by Kamai and Klabunovskii [29] for the separation of benzylethyl-n-pentylphenylarsonium bromide by selective adsorption of one of the antipodes on dissymmetrical crystals of quartz, for the effectiveness of this rather simple operation was greater than laborious multistage crystallisations.

The optical activity of stibonium salts has still not been observed experimentally, but there can be little doubt about its possibility.

The increase in the valency of the central atom on passing from carbon to the elements of Group V brings about the appearance of new types of asymmetric molecules. Here a new geometrical model is encountered — a distorted tetrahedron with a double bond directed to one of the vertices (Fig. 1). When the three remaining substituents are different, the molecule does not possess a plane of symmetry. This structural type in a pure form is represented in the sulphides of phosphines and arsines, $R_1R_2R_3P{=}S$ and $R_1R_2R_3As{=}S$. Evidently in these molecules a genuine double bond is present. Significantly there is a difference in the properties of the oxides and sulphides: phosphine sulphides, unlike phosphine oxides and amine oxides, do not add on hydrogen halides, which probably indicates the absence of an appreciable negative charge on the sulphur. The essential reason is that sulphides of tertiary amines do not exist [30]; evidently sulphur cannot be the negative end of the dipole of a semipolar bond (in the sense of $E^+-S^-$), and a double bond is impossible in the case of nitrogen.

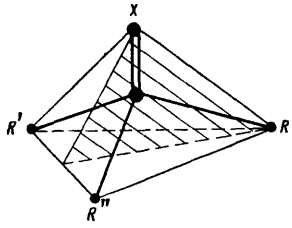
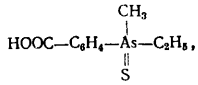
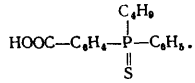



Fig.1.

Sulphides of a tertiary arsine (II*a*) was resolved into antipodes by Mills and Raper[31] in 1925, and its phosphorus analogue (II*b*) by Davies and Mann[32] in 1944. They then posed the question of comparison of the optical rotation of corresponding oxides, sulphides, and selenides, which has still not been investigated experimentally.



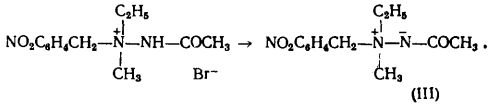
(IIa)



(IIb)

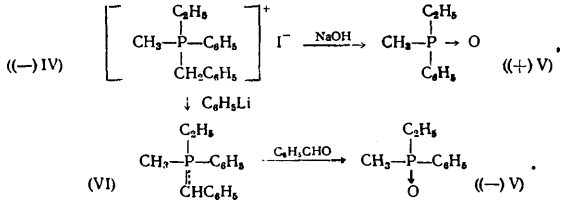
Oxides of ternary phosphines and amines were studied in the classical works of Meisenheimer and coworkers[8,9,33]. As a result of prodigious labour they succeeded in obtaining in an optically active form more than 20 compounds, of which they studied in detail the compounds containing the radicals methyl, phenyl, and ethyl (or benzyl). In many instances the work was restricted to the separation of diastereomers, since the exchange of the optically active anion led to racemisation. The results relating to the influence of the structure and solvent on the molecular rotation will be discussed in the final Section of this review.

Wawzonek[7] obtained a nitrogenous analogue of an amine oxide (III) from the corresponding hydrazonium salt:



(III)

Papers on optically active phosphine oxides appeared again only after 30 years had elapsed. In a series of papers[24,34-37] Vanderwerf and McEwen and their coworkers described various transformations of compounds with asymmetric phosphorus, which enabled them to establish a connection between the relative configurations (IV) and (V):



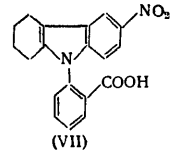
The ready detachment of the benzyl group in an alkaline medium leads to the phosphine oxide with opposite rotation. The transition state has the configuration of a trigonal bipyramid and the stereochemical result is the reversal of the configuration[38]. The action of phenyllithium on the benzylphosphonium salt (IV) gives an optically active Wittig reagent (VI), naturally of the same configuration. With (VI), benzaldehyde gives ((-)IV) as this stage, in accordance with the four-membered cyclic mechanism of the Wittig reaction[39], must involve retention of configuration. This enables the same configuration to be ascribed to the phosphorus atoms in ((-)IV) and ((-)V).

For a long time great interest was aroused in the problem of the possibility of the existence of stable enantiomers of triply-substituted nitrogen, phosphorus, arsenic, and antimony. Meisenheimer[40] did not succeed in resolving phenyltolyl-*o*-carboxyphenylamine into antipodes. At the end of the thirties the frequency of inversion of the pyramids of the hydrides of the Group V elements was evaluated from spectroscopical data[41] (Table 1).

The frequency decreases appreciably as the mass of the substituent is increased, which gave the possibility of stability of the configuration on passing to organic radicals. Mann assumed that the existence of optical antipodes is possible for all elements of the principal subgroup, excluding nitrogen. In 1954 Weston[42] evaluated by quantum chemical methods the configurational stability of the pyramid for $(CH_3)_3E$, by calculating the "racemisation temperature" — the temperature at which the half-period for inversion of the pyramid equals 2 h (Table 2).

According to Weston, the configurations of arsenic and antimony are sufficiently stable at room temperature, but phosphorus at somewhat lower temperature. However, it is not at all clear how $T_{rac}$ changes with change of radicals. For the trialkylsulphonium cation an incorrect result was obtained, since the sulphonium salts are completely stable optically. Evidently care must be taken in using this prediction.

The optical activity of certain aromatic systems with tervalent nitrogen, for example (VII)[43],



(VII)

is probably due to the hindrance of rotation. A stable structure with tervalent nitrogen atoms also occurs in

TABLE 1.

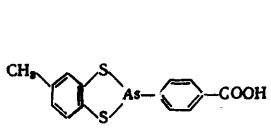
| | $NH_3$ | $PH_3$ | $AsH_3$ | $PD_3$ | $AsD_3$ |
|---|---|---|---|---|---|
| Frequency of inversion, $s^{-1}$ | $2\cdot10^{10}$ | $5\cdot10^{6}$ | $16\cdot10^{4}$ | $6\cdot10^{3}$ | 30 |

TABLE 2.

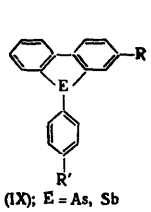
| | $(CH_3)_3N$ | $(CH_3)_3P$ | $(CH_3)_3As$ | $(CH_3)_3Sb$ | $(CH_3)_3S^+$ |
|---|---|---|---|---|---|
| $T_{rac}$, °K | 105 | 280 | 380 | 340 | 210 |

Troger's base, which was separated into antipodes by Prelog and Wieland[44], who for this made the first use of an asymmetric adsorbent, *d*-lactose.

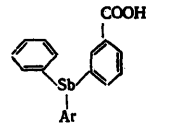
In the fifties Campbell and coworkers[45-49] published a series of papers in which they described optically active derivatives of arsenic, phosphorus, and antimony. The hetero-atom was included in a cyclic system condensed with benzene rings (VIII)–(X).



(VIII)

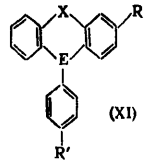


(IX); E = As, Sb



(X); Ar = α-$C_{10}H_7$ or (2-$C_6H_5$)$C_6H_4$

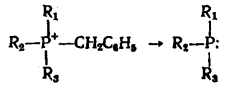
Earlier, structures of similar types were separated into antipodes by Lesslie and Turner[50-52], their distinguishing feature being the presence of two hetero-atoms, uniting aromatic rings (XI).



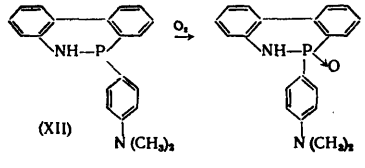
(XI)

Thanks to the specificity of these structures, doubt arose as to whether their optical stability was the result of steric hindrance due to the congestion of the rigidly bound aryl groups or the stability of the folded conformation (along the E–X axis); Mann[53] defended such a point of view. The problem of the asymmetry of the hetero-atom in a ring remained open.

This old problem of stereochemistry was recently solved in Horner's laboratory. Success was achieved in obtaining stable enantiomers of tertiary phosphines[54] and arsines[55] of completely normal structure: with one aryl and two alkyl radicals. An original method was used for this — the detachment of a benzyl† group in the reduction at the mercury cathode of the enantiomorphs of the corresponding phosphonium



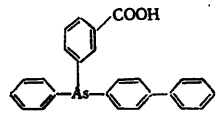
or arsonium salts. These compounds are extremely stable optically, some of them withstanding boiling in solution for many hours without the slightest racemisation! The German investigators found that electrolytic reduction of the onium salts of phosphorus and arsenic and also alkylation, oxidation, and addition of sulphur to $R_1R_2R_3E$ takes place with complete retention of the configuration[56-58]. Campbell[49] also observed retention of the configuration in the oxidation of tervalent phosphorus in the complex (XII)[49]:



(XII)

† It was found subsequently that the allyl group can also be split off electrolytically[57].

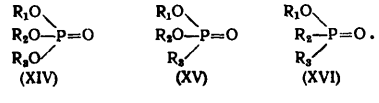
In 1963 Mislow[59] showed that the optical activity of the Lesslie–Turner compounds (XI) is due to the configurational stability of the arsenic atom, whereas these molecules are quite labile conformationally (the energy barrier for the "folding" of the molecule about the E–X axis totals ~ 6 kcal × × mole$^{-1}$). In this work the triarylarsine (XIII) was also separated into antipodes:



(XIII).

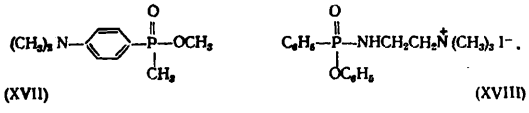
It is free from steric hindrance; optical rotatory dispersion curves without the Cotton effect (up to 310 mμm) are obtained. Hence the question of the possibility of the existence of three-covalent derivatives of the elements of the main subgroup of Group V in an optically active state is confirmed for phosphorus, arsenic, and antimony. The stability of the nitrogen pyramids is evidently too low: for example, the NMR spectra[60] show that for an *N*-alkylethyleneimine the inversion of the nitrogen configuration takes place with a frequency of 60 s$^{-1}$ at room temperature.

In addition to the classes of compounds considered, the elements of Group V form other molecules with a tetrahedral structure: derivatives of acids, for example, (XIV)–(XVI) for phosphorus, and various analogues with sulphur, halogen, or nitrogen instead of oxygen.



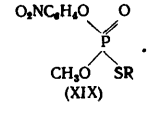
(XIV) (XV) (XVI)

It seems that the first compounds with an asymmetric acidic phosphorus (XVII) and (XVIII) were resolved into antipodes by McEwen and Vanderwerf[61,62], and also by Aaron *et al.*[63]:



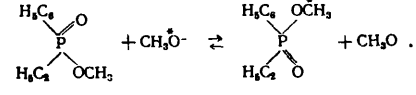
(XVII) (XVIII)

Then Hilgetag and Lehmann[64,65] obtained in an optically active state the ether (XIX), which does not contain a phosphorus–carbon bond.



(XIX)

In addition to the investigators mentioned, Green and Hudson in Switzerland and Michalski in Poland are now working on this problem. Most of the work has been carried out on derivatives of thiophosphoric acid; the main aim is to study the mechanisms of the reactions involving phosphorus[38]. For example, by studying the isotopic exchange:

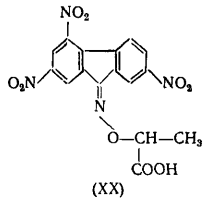


Green and Hudson[66] found that the rate of racemisation is exactly twice the rate of exchange. This is the application to phosphorus of the classical proof of the strict reversal

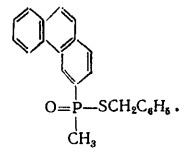
of the configuration for nucleophilic substitution of the $S_N2$ type, given for carbon (halogen exchange) by Hughes[67].

In Aaron and Miller's laboratory antipodes of esters of phosphonic acids have been used for studying the mechanism of action of cholinesterase[68]; the inhibition constants differ by a factor of ten. This can be of interest to enzymology.

The elegant use[69] of Newman's reagent (XX) for the optical separation of compound (XXI) and the 2-naphthylmethyl ester of methylphosphonic acid is worthy of note:



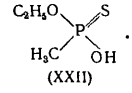
(XX)



(XXI)

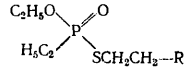
The geometric requirements are evidently very strict, for ester of 2-naphthylphosphonic acid does not give a molecular complex with (XX).

The configurations of the compounds with asymmetric acidic phosphorus are completely unknown; by the example of compound (XXII) it has been established[70] that changing the alkyl radical in the ester part of the molecule does not change the sign of rotation:



(XXII)

One of Michalski's papers[71] shows that the stereochemical course of reactions can depend on fine details of the structure: (XXIII*a*) and (XXIII*b*) with the same configuration



(XXIII) *a*: R = H; *b*: R = Cl,

give with $SO_2Cl_2$ chlorides with rotations of different sign. It is not possible to discuss in detail all the papers devoted to these systems, and we will merely mention a few[72-76].

The correlation of the configuration of the phosphorus atom in acids with other types of phosphorus compounds is an important and fascinating task. The most convenient method is the replacement of a chlorine atom or alkoxy--group on a hydrocarbon radical by the action of a Grignard reagent, with conversion into the oxide of a tertiary phosphine.

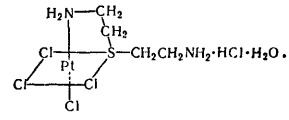
The optical isomerism of analogous derivatives of arsonic acids has not yet been investigated experimentally.

## 3. GROUP VI

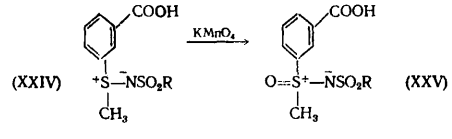
Many types of structure containing an asymmetric sulphur atom are known; the optical activity has usually been observed experimentally. On the other hand, with selenium and tellurium the only type of molecule obtained in an optically active form are onium compounds[77,78]. The case of oxygen is of interest. Meerwein's oxonium compounds[79] hardly merit attention on account of their low stability. There remain Nesmeyanov and Tolstaya's triaryloxonium salts[80,81], for which it is not known precisely whether they have pyramidal or planar structure. According to Syrkin[82] they are compounds of "oxanic" type, as with the salt $[O(HgCl)_3]^+Cl^-$, and therefore should be planar. X-Ray structural analysis of triphenyloxonium salts has still not been completed[83]. Meanwhile a repeat investigation[84] of the salt $[O(HgCl)_3]^+Cl^-$ has recently been made, which showed that the cation has the structure of a pyramid with height $\sim 0.5$ Å. The problem still remains unsolved; in the case of a pyramidal structure for the triaryloxonium salts, obviously separation of $Ar_1Ar_2Ar_3O^+$ into antipodes could be expected.

Optical activity is observed in compounds where the sulphur is bonded to three or four different groups. First of all, Pope and Peachey[3] in 1900 resolved the methoxycarbonylethylmethylsulphonium cation. Then Philipps and coworkers obtained esters of sulphinic acids[4], sulphoxides[5], and sulphimines[85] in the optically active state. At that time this played a large part in establishing the fact of the existence of the semipolar bond. The optical activity of sulphoxides, distinct from detones, was considered to be the conclusive proof of the tetrahedral configuration of sulphur. Strictly speaking, the tetrahedral structure is still not a proof of the semipolar nature of the sulphur–oxygen bond[86], since a decisive role could be played by the free pair of electrons (absent from the carbonyl carbon of the ketone molecule); geometrically the molecule could resemble an arsine sulphide.

Mann[87] synthesised an interesting structure in 1930: an asymmetric sulphide sulphur atom is produced as a result of coordination with a platinum central atom in a complex. This complex shows quite a large angle of rotation but is rapidly racemised:



Oxidation of coordinationally unsaturated sulphur of sulphoxides leads to symmetrical sulphones, but that of sulphimines to the slightly studied sulphoximines which have four different substituents at sulphur. Only in 1960 did Barash[6], by separating the diastereomers, show that sulphoximines can exist in an optically active form. In 1962 a detailed investigation[88] of the stereochemistry of oxidation of the sulphimine (XXIV) to a sulphoximine was completed:

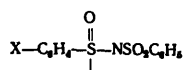


(XXIV) $[\alpha]_D^{20} + 254°$ (XXV). $[\alpha]_D^{20} + 143.5°$

Each compound was resolved into antipodes and during the oxidation complete preservation of the optical activity and configuration was observed which is confirmed by the proximity of the optical rotatory dispersion curves for enantiomers (XXIV) and (XXV) of the same sign. We note that in sulphones and sulphoximines only one bond is

(formally) semipolar, and sulphur has a decet of electrons and a single positive charge (in accordance with the principle of electrical neutrality [89]).

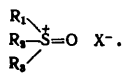
A second example of an optical isomerism of derivatives of quadruply-substituted sulphur was described at the end of 1963, by Levchenko and Kozlov [90]:



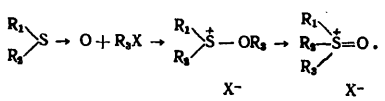
*a*: X = H, $[\alpha]_D^{24} \pm 16.6°$,
*b*: X = $NO_2$, $[\alpha]_D^{24} \pm 5.5°$.

The enantiomers were obtained, probably, in an optically pure state through salts with (-)-1-phenylethylamine.

Optical activity should also be shown by an original class of compound discovered by Kuhn and Trischmann [91] and also by Smith and Winstein [92], namely sulphoxonium salts:



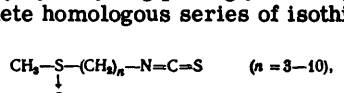
It is remarkable that they contain a true double bond S=O, as is shown by the infrared spectra and also the impossibility of obtaining them by direct oxidation of sulphur in sulphonium salts, although the existence of a positive charge on the sulphur does not hinder the "analogous" formation of sulphones and sulphoximines. The formation of a true double bond in this instance is the only means of fulfilling the principle of electroneutrality. The synthesis of sulphoxonium salts proceeds as follows:



The second stage obviously has a similarity to the regrouping of sulphinic esters and sulphones [93]. Starting with the optically active sulphoxide would probably give an enantiomer of the sulphoxonium salt; this has not yet been described. It is especially interesting that the geometry of the cation is evidently the same as in the sulphides of the Group V elements.

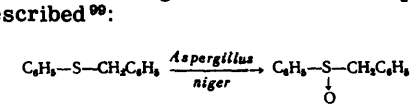
Optically active sulphoxides are encountered in nature, for example, biotin sulphoxide [94], alliin [96], and sulphorafan [95].

Kjaer [97,98], by hydrolysing plant glycosides, isolated almost a complete homologous series of isothiocyanates



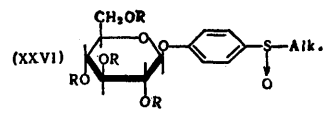
exhibiting strong laevo-rotation, as do most natural sulphoxides.

Several interesting specific methods have been used for preparing optically active sulphoxides. Thus a case of stereospecific microbiological oxidation of simple sulphides has been described [99]:

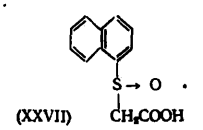


The authors consider that the substance is not optically pure.

Wagner and Böhme [100] obtained glycosidic derivatives of 4-hydroxyphenylsulphoxides (XXVI), and the diastereomers were then subjected to the action of an enzyme, which cleaved only the $\beta$-glycosidic bond:

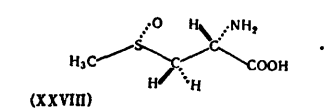


In Poland, Janczewski is working with the oxides of arylcarboxymethyl sulphides [101,102], which are interesting for the large angle of rotation in the visible region, for example, (XXVII) has $[\alpha]_D^{20} = \pm 480°$.

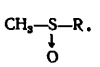


In particular, he described the first case of a pseudoasymmetric non-carbon atom [103].

An asymmetric sulphur atom was the first of the non-carbon atoms whose absolute configuration was established by X-ray analysis [104,105]. The sulphoxide of *S*-methylcysteine contains a carbon atom of known configuration, therefore the configuration of the sulphur was easily determined relative to carbon: ((+)-XXVIII) has sulphur in absolute configuration S:

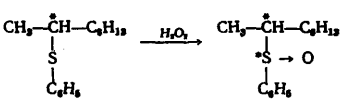


However, this method is not applicable to determining the configuration of sulphur in other compounds. In recent years rather a large number of investigations on asymmetric sulphoxides have been carried out [106-109]. A partial asymmetric synthesis took place by the action of optically active per-acids on sulphides. Using the rule of asymmetric induction this enables the absolute configuration to be described: the S configuration for the (-)-enantiomer:



Let us consider in detail an example from the work of Cram and Pine [110]. In the oxidation of optically active 2-octyl phenyl sulphide with hydrogen peroxide, two diastereomeric sulphoxides were isolated:

I $[\alpha]_D^{25} - 155°$
II $[\alpha]_D^{27} + 140°$



The ratio of the quantities of the diastereomers formed was I : II = 1.6 : 1. Since the absolute configuration of the carbon centre is known, the sulphide can be represented in the Newman projection (Fig. 2).

According to Cram's rule [111], oxygen will be attached preferentially to the least screened electron pair, adjacent to the hydrogen atom in the projection. If conformations

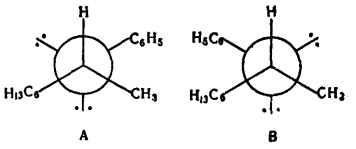



Fig. 2.

A and B were equally probable, then as a result both diastereomers would be formed in equal amounts. However, the effective volume of the n-hexyl group is greater than that of the methyl group, therefore the position adjoining it is less favourable for phenyl. This signifies that conformation A is the more stable, from which one can draw conclusions about the electron pair which can be preferentialy attacked and about the configuration of the asymmetric centre which is produced.

The following reaction enables sulphoxides to be obtained from the esters of sulphinic acids [112]:

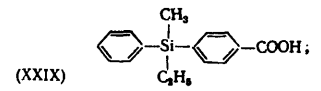
$$R{-}\underset{\underset{O}{\downarrow}}{S}{-}OR' + R''MgX \rightarrow R{-}\underset{\underset{O}{\downarrow}}{S}{-}R'' + Mg(OR')X.$$

It is a convenient method for the synthesis of optically active sulphoxides [113], starting from diastereomeric sulphinic esters, for example, the *l*-methyl ester. It is quite probable that in this reaction there is an inversion of configuration at the sulphur atom; in support of this there are the recently obtained optical rotatory dispersion curves of these classes of compounds [114]. The reversal of the configuration during substitution at the sulphur atom in sulphonic acids has also been established recently [115].

## 4. GROUP IV

A few compounds of silicon were resolved into antipodes by Kipping [116] at the start of the century. About this time Pope and Peachey [117] resolved ethylhalogenomethylpropyltin. In the thirties their result was confirmed by Manulkin [118], who also described an optically compound of germanium [119], In all three instances a very small angle of rotation was observed, so that the experiments cannot be considered completely reliable.

The first trustworthy example is the resolution of the organosilicon compound (XXIX) recently described by Eaborn and Pitt [120]:




(XXIX)

but the stereochemistry of silicon began in earnest with the work of Sommer's laboratory [121-123], where success was achieved in separating the diastereomers $R_1R_2R_3SiOR^*$, and then isolating optically pure $R_1R_2R_3SiX$, where $R_1$ = 1-naphthyl, $R_2$ = phenyl, $R_3$ = methyl, and X = various substituents, including H, F, Cl, Br, OH, $OCH_3$, $C_2H_5$, etc. The American investigators used these enantiomers for a broad study of the stereochemistry and mechanism of substitution at the silicon atom [124-126].

Without dwelling in detail on this work, we will note the cases when the results differ from the corresponding ones for the carbon atom. For example, homolytic replacement of hydrogen by molecular chlorine takes place with retention of the configuration:

$$R_1R_2R_3SiH \xrightarrow{Cl_2} R_1R_2R_3SiCl.$$

Significantly, the configuration is also retained in some, but not all, reactions of nucleophilic substitution reactions of type $S_N2$:

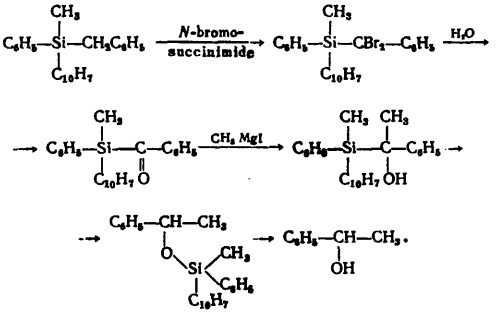
$$R_1R_2R_3SiOCH_3 \xrightarrow{LiAlH_4} R_1R_2R_3SiH,$$
$$R_1R_2R_3SiOCH_3 \xrightarrow{Bu^tMgCl} R_1R_2R_3SiH.$$

This agrees with earlier results about the readiness of the $S_N2$ reaction at the silicon atom at the head of the bridge [127] which certainly proceeds with retention of the configuration. In comparison with carbon, the anomalous, behaviour of silicon in nucleophilic substitution reactions is explained by the presence in silicon of a vacant *d* orbital, which also serves as an acceptor of the electron pair of the substituting agent at the rate-determining stage of the process.

There is special interest in the asymmetric silicon atom, for this is the first isolated non-carbon atom whose configuration has been determined. Two groups of research workers established simultaneously by different methods the absolute configuration of $R_1R_2R_3SiX$: Pepinsky [128] by means of X-ray analysis of isomorphic crystals of silane and fluorosilane, and Brook and Limburg [129] by chemical means (Fig. 3).

The relative configurations were established earlier by the method of quasiracemates and optical rotatory dispersion [124]: (-)-$R_1R_2R_3SiH$, (-)-$R_1R_2R_3SiF$, and (+)-$R_1R_2R_3SiCl$ have the same configuration.

The following scheme shows the succession of reactions which Brook and Limburg used [129] to establish the configuration:




The regrouping of an $\alpha$-hydroxysilane into a silicon ether of the corresponding alcohol used here was discovered earlier [130]. Cram's rule, which determines which of the

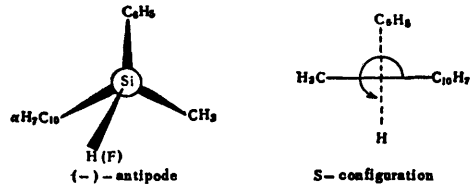
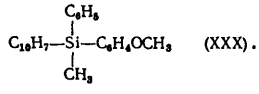



Fig. 3.

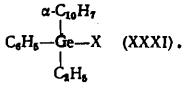
diastereomers is formed in excess, depending on the configuration of the neighbouring asymmetric silicon atom, applies at the stage of addition of the Grignard reagent at the carbonyl group. Finally, from the sign (and configuration) of the 1-phenylethanol the configuration of the silicon atom can be determined unambiguously if it is assumed that regrouping of the $\alpha$-hydroxysilane (under alkaline conditions) occurs with retention of the configuration.

Eaborn [131] used the optically active compound (XXX) for studying the replacement of an aryl radical by a halogen, with retention of the configuration:



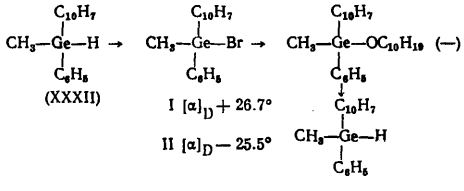
(XXX).

There has been an extremely rapid development of the stereochemistry of the elements of Group IV in the last few years. Following Sommer's method, Bott *et al.* [132] first made a reliable resolution of compound (XXXI) with an asymmetric germanium atom:



(XXXI).

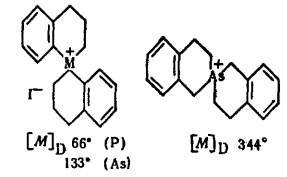
Immediately after this Brook and Peddle [133] published a detailed investigation of the reactions of optically active methyl-1-napthylphenylgermane and its derivatives. The scheme of separation into antipodes, which is similar for silicon and germanium, is:



The second reaction, carried out by Sommer and coworkers for silicon, was found by Brook and Peddle [133] to be completely analogous in steric course for germanium, except for the replacement of hydrogen by bromine, which occurred with racemisation (in the case of silicon there was retention of the configuration). They also established the absolute configuration of the germanium atom, using the structural identity of compound (XXXII) and the analogous silane and employing the method of quasiracemates. As expected, the enantiomers of silane and germane of the same configuration have the same sign of rotation.

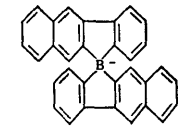
## 5. SPIRANS WITH A NON-CARBON SPIRO-ATOM

There is a limited group of spiro-compounds containing a hetero-spiro-atom which exhibits optical activity because of the asymmetry of the molecule as a whole. Formally, they are not within the scope of this review, but they are closely connected with the problem of the influence of the nature of the non-carbon atom on the magnitude of the optical rotation. The synthesis and resolution of these compounds was carried out in Mann's laboratory in Cambridge [134-136].



These compounds form a "eutropic series" (unfortunately, of only two members), in which there is an increase in the molecular rotation with the atomic weight (from phosphorus to arsenic).

Torsell [137] described the opposite case (when the spiran system forms an anion, not a cation), the spiro-position being occupied by a boron atom:



(XXXIII).

The molecular rotation of this anion, calculated from the rotation of its salt with an optically active ammonium cation, is -338°. It was first shown that the rotation of the cation (benzylmethylphenylpropylammonium) is independent of the anion and amounts to -258°.

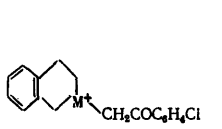
## 6. INFLUENCE OF THE ASYMMETRIC ATOM ON THE OPTICAL ROTATION

The problem of the optical activity of compounds with an asymmetric non-carbon atom must find a complete solution within the framework of the general problem of the optical activity of both organic and inorganic molecules. However, a general theory has not yet been established. The contemporary theoretical concepts relate mainly to compounds with asymmetric carbon and *a priori* it is not obvious what will be the effect of a change in the nature of the asymmetric centre. The absence of a general theory makes it desirable to seek partial rules applicable to restricted groups of compounds.

An essential obstruction in the path of a quantitative study of the problem is that the limiting value of the angle of rotation is often unknown. The absence of a definite criterion of optical purity was for long a general deficiency in stereochemistry. The main argument was the production of antipodes with rotations identical in magnitude but opposite in sign, but this was not always reliable. It was only in 1959 that Berson and Ben-Efraim [138] proposed an absolute method for the determination of optical purity and maximal rotation, apparently without limitations in principle. However, as yet it has hardly been used, even for carbon compounds (probably on account of the necessity for working with isotopes).

After Meisenheimer, whose work will be further considered below, the dependence of optical rotation on the asymmetric atom became of interest to Mann, who constructed the only example of a "eutropic series" [77] in which

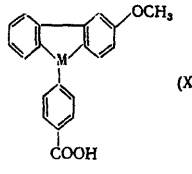
there has been observed a significant increase in molecular rotation in the series: sulphur < selenium < tellurium.



| | $[M]_D$ picrate |
|---|---|
| S | 250° |
| Se | 530° |
| Te | > 750°. |

A second example is provided by the spiro-derivatives of phosphorus and arsenic referred to above [136].

The insignificant increase in $[M]_D$ found by Campbell [45-49] for compounds (XXXIV) on replacing As by Sb cannot be considered conclusive, because the rotations of pyridine solutions of the acids were compared.



(XXXIV)

There is no guarantee that the extent of salt formation was the same; it is also completely unknown how the angle is affected by the increase of electron density on the arsenic or antimony atom due to the influence of the substituent through the benzene ring.

Subsequently we will attempt to analyse the published information relating to molecules of comparatively simple structure, on the basis of the system proposed in 1959 by Brewster [12-14]. It was found that this semi-empirical method successfully predicts the sign and magnitude of the rotation of wide circle of compounds with asymmetric carbon atoms (assigned configuration), when steric hindrance and strain do not play a large part [139]; in particular, the method is also applicable with a metal atom as the asymmetric centre [140]. Interesting work on the calculation of the rotation of polymeric hydrocarbons has been published [141].

According to the rule of conformational asymmetry, the contribution to the molecular rotation of the dissymmetrical structural unit represented in Fig. 4 is given by the expression:

$$\Delta [M]_{XY} = + k\,(X{-}H)\,(Y{-}H) = + 160\,(R_X^{1/2} - R_H^{1/2})\,(R_Y^{1/2} - R_H^{1/2}).$$

This is based on the idea of the rotational capacity being proportional to the square root of the atomic refraction, after which the additivity principle applies. The quantities $\Delta[M]_{XY}$ are determined from experimental results and in almost every case they agree well with calculation by the right-hand side of the equation. It can be assumed, as Brewster does in a footnote to one of his papers [14], that the constant $k$ is linked in some manner with the nature of the asymmetric centre and retains a constant numerical value (160–165) only in dealing with carbon. Brewster suggested the possibility of a change in $k$ when the central atom had a polarisability differing greatly from that of carbon. It is completely unknown whether the form of the function is then retained (that is, $k = \beta R_0^{1/2}$, where $R_0$ is the refraction of the central atom), or whether, within the framework of the stated approximate method, the nature of the asymmetric centre is allowed for in the numerical value of $k$ in another way. It should be noted that in the calculation of $\Delta[M]$ by the conformational asymmetry rule, constant $k$ should be a function of the parameters of two atoms $k = f(1, 2)$, and not $k = f(1)$, where 1 is an asymmetric atom and 2 a neighbour which participates in the formation of an axis of the Newman projection. Since atom 2 is known to be carbon it must be expected that the value of $k$ would only change slightly on changing the asymmetric atom, so that this change would not be experimentally observable at every $R_0$.

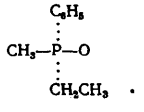
It is significant that when Brook and Limburg established the absolute configuration of silicon in methyl-1-naphthylphenylsilane, in 1963, they noted the agreement of the sign of the rotation for three substances with that predicted by Brewster's method. That showed for the first time the applicability of the atomic asymmetry rule to a non-carbon centre (qualitative aspect).

We calculated [142] the rotation of ethylmethylphenylphosphine by the conformational asymmetry rule using the value of $\Delta[M]_{XY}$ which is used for carbon compounds. Two antipodes are obtained experimentally [9,24], with $[\alpha]_D = \pm 22.8$, $[M]_D = 37.8 \pm 1.7°$. Fig. 5 shows two permissible conformations of this compound. Assuming them to be equally probable [12], we obtain:

$$[M]_D = \frac{-k(C{-}H)(C_{Ar}{-}H) - k(C{-}H)(O{-}H) + k(C{-}H)(O{-}H) + k(C{-}H)^3}{2} = -\frac{140-60}{2} = -40°.$$

For this calculation, it is necessary to know the rotational constant for oxidic oxygen (although it can also be calculated from refractometric data). The only assumption which is made is that the effective volume of oxygen is small in comparison with that of the methyl group.

Bearing in mind the precedent of the absolute configuration of silicon [129], the good agreement suggests that the (+) antipode of the oxide can be ascribed to the R configuration with a high degree of probability:



Since there has been a correlation of the configuration of this compound with a tertiary phosphine and a phosphonium salt [38], their absolute configuration is also determined [142].

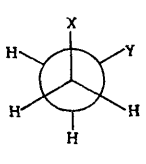


Fig. 4.

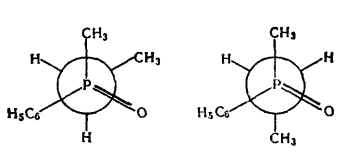


Fig. 5.

A comparison of the rotations of corresponding amine and phosphine oxides in various solvents, from Meisenheimer's data[9], is especially interesting (Table 3). Comparison of the values in Table 3 suggests that the essential role is played not by the nature of the central atom but by the character of its bond with oxygen (possibly, the degree of charge separation). The difference in $[M]_D$, very great in a non-polar solvent, disappears completely on passing to the hydrochloride, when the M–O bonds becomes of the same type as the others. It is significant that this takes place on account of a change in the rotation of the amine oxide, which increases regularly as the polarity of the N–O bond decreases, whereas the rotation of the phosphine oxide (bond not purely semipolar) is almost independent of the solvent. The calculation given above also describes the rotation of the amine oxide hydrochloride. The anomalously low rotation of the amine oxide in benzene may be explained by the formation of associates in the absence of reaction with the medium.

Meisenheimer's results with analogous compounds were not very definite, and are not always understood. Thus benzylmethylphenylphosphine has $[M]_D = +162°$ in HCl and $-17°$ in chloroform! Such a marked difference seems inexplicable. It is true that the experiment in this case, as in some others, is not completely reliable because the value of $[M]_D$ is often estimated from the difference in rotation of the diastereomers.

It is interesting that the molecule of ethylmethylphenyl--phosphine or -arsine is structurally similar to 2-phenylbutane. Calculation by Brewster's method for the two compounds gives a single value: $[M]_D = 40°$, which agrees well with that found experimentally for the hydrocarbon [143]. The results for phosphines and arsines[54-56] do not agree very well with one another but the simplest molecules have $[M]_D = 27.8°$. Here again there is the impression that the replacement of phosphorus by arsenic has no effect. The following discussion shows that this can be explained by distortion of the tetrahedron of the hetero-atom in the absence of a fourth substituent (compare Fig. 6).

The presence of a free electron pair instead of a fourth substituent necessitates the approach of the phosphorus atom to the plane of formation. If the Newman projection is constructed along the $R_2$–P bond, then the change in the angles of the pyramid also leads to a change in the angles between the substituents in the projections, the direction of which is easily understood. Evidently, in the limit the atom of phosphorus tends to take up a position in the plane $R_1R_2R_3$, and in the projection $R_1$ and $R_3$ would be situated on a single straight line. Actually at this moment the molecule acquires planar symmetry and loses its optical activity but as a matter of fact this state is not reached.

Further, $\Delta[M]_D$ is evidently, as Brewster once proposed, a sinusoidal[12] function of the angle formed by the bonds in the Newman projection; the tabulated values of $\Delta[M]_D$ are specially standardised by the direct multiplier $1/\sin 60° = 2/\sqrt{3}$ for the normal angle of 60°. Therefore if we wish to calculate the influence of a variable angle the multiplier should be $(2/\sqrt{3})\sin\varphi$. For the limiting point $\varphi = 30°$,

$$[M]'_D = \frac{2}{\sqrt{3}} \sin 30° [M]_D = \frac{1}{\sqrt{3}} \times 40° \simeq 23°.$$

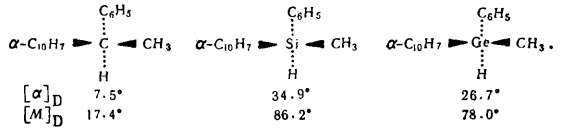
Consequently, in this way the lower limit for the angle of rotation can be roughly evaluated; as a result:

$$23° < [M]_D < 40°.$$

It is evident that the experimental value does not contradict this inequality.

Unfortunately there is no information on the rotation of phosphine salts; it seems that $[M]_D$ of the cation must be close to 40°.

The most valuable material for comparison relates to Group IV, for which Brook[144] constructed the first "isoconfigurational series" of enantiomers $R_1R_2R_3R_4M$ with identical structure and configuration, which differ only in the nature of the asymmetric atom M:



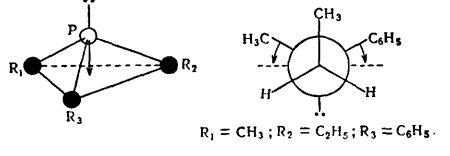

First of all it appeared that all (+) enantiomers have the absolute configuration R: the nature of the central atom does not affect the sign of the rotation. The optical rotatory dispersion curves are essentially similar and have a positive Cotton effect (Fig. 7).

The carbon analogue exhibits a much smaller angle of rotation: Brook finds that the rotation is a linear function of the electronegativity of the central atom.

It appears possible that the increase in $[M]_D$ on passing from carbon to silicon and germanium is due to the appearance of free *d* orbitals. It is known that there is an electronic displacement in the direction from aryl to silicon or

TABLE 3. $[M]_D$ of a phosphine oxide and amine oxide in various solvents.

| | $(CH_3)(C_6H_5)(C_2H_5)P \rightarrow O$ | $(CH_3)(C_6H_5)(C_2H_5)N \rightarrow O$ |
|---|---|---|
| Benzene (absolute) | +47° | +8—9° |
| Water | +38° | +24° |
| HCl | +40° | +40° |




$R_1 = CH_3$; $R_2 = C_2H_5$; $R_3 = C_6H_5$.

Fig. 6.

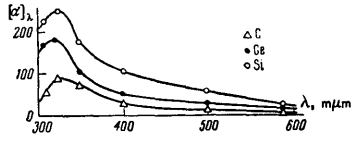
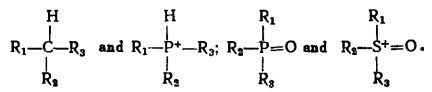



Fig. 7.

germanium [145]. There are several consequences, one of which may also affect the optical rotation: (1) increased electron density on the asymmetric atom; (2) shortening of the metalloid–aryl bonds on account of partial doubling of the bonds; (3) hindrance to free rotation about these bonds for the same reason.

Whereas in a carbon compound the rotation about C–aryl bonds, generally speaking, is free, then on account of the partial double bond character, some orientation of the ring can be preferred. In this sense it is interesting that passing from silicon to germanium has little effect on $[M]_D$. If the reason actually consists in the presence of the *d* orbital then a subsequent change, to an asymmetric tin atom, should slightly affect the rotation.

The relation of concentration of electron density at the asymmetric atom to the optical rotation is also of interest. This can most conveniently be traced by introducing various substituents in the aromatic ring adjacent to the asymmetric atom. In one instance [90] the replacement of hydrogen by a nitro-group significantly reduced the angle. Unfortunately investigations of this type have not been carried out in carbon stereochemistry, with a few exceptions [146-148]. Valuable information can be obtained by comparison of structurally analogous molecules containing asymmetric atoms which belong to different groups of the Periodic System (influence of charge), for example:



Such data are still absent. Naturally the study of each of these problems requires considerable experimental work.


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# ABILITY OF ELEMENTS TO FORM POLYMERS WITH INORGANIC CHAIN MOLECULES

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The chemistry of organoelemental compounds is being intensively developed as an independent branch of chemistry in the direction of studying the general regularities of the formation and transformation reactions of the organoelemental compounds, the investigation of the reactivitv of various compounds, and also in the field of the synthesis and study of the properties of high-molecular-weight compounds.

The development of the chemistry of high-molecular--weight organoelemental compounds is linked not only with the study of the transformation reactions of the monomeric compounds into polymers, but also with the investigation of the possible uses of various elements and their compounds for the synthesis of polymers. The synthesis of organoelemental polymers is complicated by the variety, not only of monomeric compounds, but also of elements whose monomeric compounds can be used for this purpose. Therefore we consider some aspects of the theory which characterise the ability of various elements to form homo- and hetero--chain polymers. Polymers which do not contain carbon atoms in the chain are known as polymers with inorganic main-chain molecules, framed‡ by various organic, inorganic, and organoelemental groups.

At present the general principles which determine the formation of inorganic chains of molecules of various elements have been insufficiently worked out, and the known reactions for the synthesis of polymers, for example, polyorganosiloxanes, are always accompanied by the formation of cyclic compounds, which serve as "monomers" for the synthesis of high-molecular-weight compounds.

The use of inorganic cyclic compounds framed by organic groups for the production of polymers is also linked with the fact that unsaturated compounds of the general formulae $R_nE{=}O$ and $R_nE{=}ER_n$, capable of polymerising through the double bonds, as in the synthesis of organic homo- and hetero-chain polymers[1-3], have not yet been obtained.

An attempt will be made here to establish the most important factors which determine the ability of elements to form inorganic rings and chain molecules, framed by organic and organoelemental groups. It is evident that the routes to the formation of inorganic rings and chain molecules are extremely varied, not only on account of the large number of elements which can be used to construct these chains, but also on account of the diverse types of chemical bonds which may be used in the formation of cyclic and chain polymeric compounds.

Two types of chemical bonds play an important part in the formation of polymers with inorganic chain molecules: covalent and coordination. They can be the basis for the formation of large molecules of various structures. Aggregates, consisting of a large number of ionic particles bound to one another by ionic bonds, for example, ionic crystals, cannot be considered as proper molecules, and such structures are not true polymers, although they consist of a large number of structural units. It is true that covalent bonds between elements with different electronegativities have polar character, or, in other words, are partly ionic, preventing the strict demarcation of polymers with inorganic chain molecules from ionic aggregates (crystals). Usually ionic aggregates have a three-dimensional structure, whereas for polymers there is greater interest in chains of linear, branched, or network type of molecular structure. The present review considers mainly polymers with chain molecules of such structure, for otherwise we would have to consider a large number of inorganic compounds going beyond the bounds of polymer

‡ Not considered in the text of the review.

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‡ The term "framed" presumably means having side-groups of the type mentioned (Ed. of Translation).

chemistry (for example, borides, silicides, silicates, and phosphides), although in broad conception they can be classified as high-molecular-weight compounds. Coordination polymers will also not be considered here. Polymers with inorganic chain molecules can also be formed using multicentric bonds, characteristic, in particular, of the boron hydrides [4-6]. However, such compounds have low stability, oxidise and hydrolyse readily, and also will not be considered here. Hence this article considers the ability of elements to form polymers with inorganic chain molecules framed by organic and organoelemental groups of the covalent and ionic type of chain structure.

General consideration of the experimental material both on homocyclic compounds and on compounds with chain molecules shows that unlike organic chemistry homo-rings play a lesser part and homo-chain molecules with a high degree of polymerisation are not formed. This is the result of the essential difference between the properties of carbon and those of other elements (and even of the non-metals of Periodic Group IV), in terms of ability to form stable chains or cyclic compounds consisting of the same atoms.

On the one hand, the energy of the C–C bond is greater than the E–E bond of other elements (Table 1), and on the other hand the C–C bond is chemically more inert than the E–E bond of other elements.

Carbon forms various types of chain molecules based on the C–C bond: linear, branch, network, cyclic. For other elements – either non-metals or metals – the formation of homo-chain molecules with a significant degree of polymerisation is not characteristic. Only compounds containing short E–E chains are known. For example, silicon forms long chains in the molecule $Si_{25}Cl_{52}$ where 25 atoms of silicon are directly linked [10], but this compound is unique and in other homologous series the highest terms are $Si_{10}F_{22}$,[11] $Si_4Br_{10}$,[12] $Si_6H_{14}$.[13] The longest Si–Si chain with organic side-groups is the molecule $Si_9(C_6H_5)_{16}(CH_3)_4$, where nine silicon atoms are directly linked [14]. Recently a series of polymeric compounds with P–P bonds has been described [15], but a very large degree of polymerisation was not attained.

On the contrary, the possibility of forming organoelemental hetero-chain molecules is much wider than in carbon chemistry, but the realisation of such possibilities is not always clear, since they are linked with the properties of various elements to form stable cyclic and chain molecules with one another. The tendency of various elements to form cyclic compounds and chain molecules depends on the chemical properties of the elements and, in particular, their electronic structure. We consider that an important factor determining the ability of an element to form hetero-chain polymeric molecules is its electronegativity and the electronic hybridisation of its atoms [16].

TABLE 1. E–E bond energies.

| Bond | Bond energies | | | Bond | Bond energies | | |
|---|---|---|---|---|---|---|---|
| | Ref. 7 | Ref. 8 | Ref. 9 | | Ref. 7 | Ref. 8 | Ref 9 |
| C–C | 83.1 | 66.2 | 64 | As–As | 32.1 | 35 | 38 |
| Si–Si | 42.2 | 45 | 50 | Sb–Sb | 30.2 | 29 | 34 |
| Ge–Ge | 37.6 | 45 | 40 | S–S | 50.9 | 54 | 50 |
| N–N | 38.4 | 21 | 32 | Se–Se | 44.0 | 41 | 42 |
| P–P | 51.3 | 48 | 50 | | | | |

TABLE 2. Electronegativities of the elements, after Pauling [7].

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li 1.0 | Be 1.5 | B 2.0 | | | | | | | | | | | C 2.5 | N 3.0 | O 3.5 | F 4.0 |
| Na 0.9 | Mg 1.2 | Al 1.5 | | | | | | | | | | | Si 1.8 | P 2.1 | S 2.5 | Cl 3.0 |
| K 0.8 | Ca 1.0 | Sc 1.3 | Ti 1.5 | V 1.6 | Cr 1.6 | Mn 1.5 | Fe 1.8 | Co 1.8 | Ni 1.8 | Cu 1.8 | Zn 1.9 | Ga 1.6 | Ge 1.8 | As 2.0 | Se 2.4 | Br 2.8 |
| Rb 0.8 | Sr 1.0 | Y 1.2 | Zr 1.4 | Nb 1.6 | Mo 1.8 | Tc 1.9 | Ru 2.2 | Rh 2.2 | Pd 2.2 | Ag 1.9 | Cd 1.7 | In 1.7 | Sn 1.8 | Sb 1.9 | Te 2.1 | I 2.5 |
| Cs 0.8 | Ba 0.9 | La–Lu 1.1–1.2 | Hf 1.3 | Ta 1.5 | W 1.7 | Re 1.9 | Os 2.2 | Ir 2.2 | Pt 2.2 | Au 2.4 | Hg 1.9 | Tl 1.8 | Pb 1.8 | Bi 1.9 | Po 2.0 | At 2.2 |
| Fr 0.8 | Ra 0.9 | Ac 1.1 | Th 1.3 | Pa 1.5 | U 1.7 | Np–Po 1.3 | | | | | | | | | | |

Consideration of the electronegativity of various elements (Table 2) shows that carbon occupies a central position between the most electronegative element, fluorine ($x_F = 4.0$) and the most electropositive element, caesium ($x_{Cs} = 0.8$).

Therefore carbon has the least tendency to donate or receive electrons, that is, to form positive or negative ions and less to submit to electrophilic or nucleophilic attack. This is one of the reasons for the stability of carbon chain molecules. Other elements possessing electronegativity close to carbon, for example, sulphur and selenium, are also characterised by an ability to form long chains of similar atoms, S–S or Se–Se. This explains also why other elements form less stable homo-chain structures.

If an element has an electronegativity greater than that of carbon, the homo-chain is of low stability on account of the tendency to produce electrons. Therefore long chains or rings consisting of N–N or O–O bonds are unstable. If the electronegativity of an element is less than that of carbon, the stability of the E–E bond is diminished, on account of the tendency to yield electrons. Hence B–B, Si–Si, P–P, As–As, and Ge–Ge bonds are readily oxidised and are less stable than the C–C bond.

The great stability of bonds between atoms of elements of different electronegativities (greater and less than for carbon) is probably linked with the compensations of opposite tendencies of the atoms which form the chain to give and receive electrons. Comparison of the mean electronegativities of the interconnected elements shows that for many pairs of elements the mean value is close to the electronegativity of carbon. Inorganic hetero-rings and polymers with organic side-groups, formed by alternation of two interconnected elements, have mean electronegativities differing from that of carbon by 0.35–0.40 units [17]. The following pairs of elements, for example, fall within this interval:

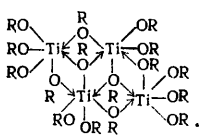
| | | | | | | |
|---|---|---|---|---|---|---|
| B–N | Al–N | Si–N | Ge–N | Ti–N | Sn–N | (Pb–N) |
| B–O | Al–O | Si–O | Ge–O | Ti–O | Sn–O | Pb–O |
| B–S | (Al–S) | Si–S | Ge–S | (Ti–S) | Sn–S | Pb–S |
| P–N | As–N | (Sb–N) | S–N | Se–N | — | — |
| P–O | As–O | Sb–O | — | Se–O | Mo–O | W–O |
| P–S | As–S | Sb–S | S–S | Se–S | — | — |

For all these pairs, except those in parentheses, inorganic rings [16,18] and some polymers [3,4,19] have been described. It should be noted that the concept of electronegativity relates to a simple bond of the interconnected elements and does not take into account that in molecules it

is possible for additional donor–acceptor bonds to be formed, unshared electron pairs to be delocalised, multicentric bonds to be formed, induction effects to operate, etc.[20]

An important factor, determining the ability of an element to form hetero-rings or hetero-chains, with organic side-groups, is the characteristic hybridisation of the electron cloud of the elements. It is determined by the number and direction of the chemical bonds, the presence or absence of unshared electron pairs and free orbitals, and also by the coordination number of the elements. Of course, the coordination number, that is, the number of atoms of one element with which the atoms of another element can be bound, is determined by steric factors (that is, the relation between the dimensions of the given atoms) as well as by electronic hybridisation.

Fundamentally, the coordination number (c.n.) of elements of the second period of the Periodic System is not greater than four. With elements of the third period the c.n. can reach 6, but the corresponding configuration is unstable. With elements of the fourth and fifth periods a higher c.n. is easily effected. The elements of these periods form octahedral structural units (at c.n. = 6), which readily unite to form monocyclic compounds and linear polymers and often form polymers with other types of structures, in particular, polycyclic coordination polymers. For example, the tetramer tetraethoxytitanium $[Ti(OC_2H_5)_4]_4$ is not a monocyclic coordination compound, as might be expected, and its molecule consists of four octahedra with Ti atoms at the centre, joined at the vertices[21], which can be represented by a structural formula containing four-membered Ti  Ti rings:



Inorganic rings and chain molecules are formed by alternation of two elements of different electronegativity, therefore it is important to consider, on the one hand, elements having an electronegativity greater than that of carbon (that is, oxygen and nitrogen) and, on the other, elements having an electronegativity less than that of carbon, in particular the non-transition elements: boron, aluminium, silicon, germanium, tin, lead, titanium, phosphorus, arsenic, and antimony. Sulphur and selenium, which have an electronegativity close to that of carbon, occupy an intermediate position.

The electronegative elements, oxygen and nitrogen, have the following structure of the valency electron shells:

$$\text{oxygen} - 2s^2\ 2p_x^2p_y^1p_z^1,$$

$$\text{nitrogen} - 2s^2\ 2p_x^1p_y^1p_z^1,$$

and form chemical bonds by virtue of the $p$ orbital. Covalent bonds, using $p$ orbitals, are separated by an angle of 90°. Both oxygen and nitrogen retain unshared electron pairs. They can form additional coordinate bonds or be delocalised intramolecularly into free orbitals of the element bonded with the oxygen or nitrogen. This means, in other words, the participation of the unshared pair of electrons in electronic hybridisation with the $p$ orbitals which leads to a change in the valence angle of oxygen or nitrogen from 90° to greater values. Therefore the angle of the N< or O< bonds can indicate the delocalisation of the unshared electron pairs or their partial participation in hybridisation with the $p$ orbitals. In inorganic hetero-rings there is the same phenomenon: the angles of the R–N< and O< bonds vary widely, depending on the elements with which they are connected.

Thus the valence angle of oxygen in a ring varies from 112° ± 4° in trimethylboroxole[22] to 142.5° in octamethylcyclotetrasiloxane[23]. The valence angle of nitrogen in a ring varies from 91.7° ± 2° in *N*-bis(trimethylsilyl)tetramethylcyclodisilazane[24] to 131° in octachlorocyclotetraphosphazene[25] and octamethylcyclotetraphosphazene[26].

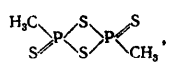
Since the valence angle can change over a wide range, oxygen, nitrogen, and sulphur have a great possibility of forming heterocyclic and hetero-chain polymeric compounds with many less electronegative elements.

Sulphur, as the electronegative element of a hetero-ring, is usually bivalent. The same can be said about selenium. The valence electrons of sulphur and selenium are disposed thus in the outer shell:

$$S^{II} \text{ and } Se^{II};\ s^2;\ p_x^1p_y^1p_z^1.$$

Evidently sulphur and selenium in the divalent state form $p^2$ bonds with a valence angle of 90°. This value is also observed in hydrogen sulphide, $SH_2$, but in the homo-ring $S_8$ it even acquires the value 107°.[27,28] The valence angles of sulphur in inorganic hetero-rings also vary over a wide range — from 75° in tetramethylcyclodisilthiane[29] to 138° in tribromoborosulphone[30].

However, sulphur has a tendency to form bonds of small angles: in the compound:



the valence angle of the sulphur in the ring is 84°,[31] but in hexamethylcyclotrisilthiane it is 110°.[29] In this connection the valence angle in tribromoborosulphone seems excessively large. Sulphur easily forms valence angles less than 90°, which facilitates the formation of four-membered rings with boron, silicon, and phosphorus, whereas not a single oxygen-containing four-membered ring is known (excepting coordination rings) and only one nitrogen-containing four-membered ring ($S_2N_2$). Hence the conclusion that the valence angles of nitrogen, sulphur, and oxygen are not the decisive influence on the formation of inorganic rings since they can be varied over a wide range of values and probably will not impede cyclisation with any less electronegative partner-element. However, they can determine the number of groups of interbonded elements in the hetero-ring and facilitate the formation of only one or two more sterically favourable hetero-rings from a whole series of possible ones. For example, 6-, 8-, 10-, and 12-membered hetero-rings, etc., with Si–O bonds are known, but $Si_2O_2$ hetero-rings are unknown. The hetero-rings $Si_2N_2$, $Si_3N_3$, $Si_4N_4$ are known, but the hetero-rings $Si_5N_5$ and $Si_6N_6$ are not known, although their oxygen analogues have been obtained[18].

There are now experimental data which show that combination of an element with oxygen leads to the formation of long E–O–E–O– chains more easily than combination of the element with nitrogen or with sulphur. In the case of

E–N and E–S alternations the tendency to ring formation is more sharply expressed and this probably explains why long E–N–E–N or E–S–E–S chains have not yet been obtained and why attempts to prepare them result only in derivatives of the corresponding rings. An exception is provided by the phosphazenes, but in such derivatives the valence angle of the nitrogen is greater and reaches values characteristic for oxygen. Evidently a small valence angle for an electronegative element facilitates cyclisation and hinders the formation of long chains. Hence the conclusion not only about the significance of steric factors but also that oxygen-containing inorganic polymeric chains are capable of reaching a high degree of polymerisation.

The value of the bond angle of an electronegative element is also determined by the number of atoms in an inorganic hetero-ring. For example, comparing the known hetero--rings of silicon formed by alternation of silicon with oxygen, nitrogen, and sulphur:

$$\underline{Si_2O_2}\ \underline{Si_4O_4}\ Si_6O_6\ Si_8O_8 \ldots Si_nO_n$$
$$Si_2N_2\ \underline{Si_3N_3}\ \underline{Si_4N_4}$$
$$\underline{Si_2S_2}\ \underline{Si_3S_3}\ Si_4S_4$$

(rings which are formed readily are underlined), we can conclude that on passing from oxygen-containing to nitrogen- and sulphur-containing cyclic compounds of silicon the tendency towards formation of lower-molecular-weight rings grows simultaneously with a decrease in the valence angle of the electronegative element.

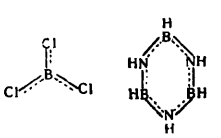
Let us now consider the hybridisation of elements more electropositive than carbon.

The atoms of Group III of the Periodic System (main subgroup): boron, aluminium, gallium, indium, thallium, are characterised in their compounds by $sp^2$ and $sp^3$ hybridisation: the latter is observed in the formation of an additional coordinate bond.

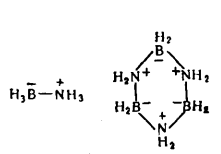
For boron $sp^2$ hybridisation is particularly characteristic. It determines the planar distribution of the bonds at an angle of 120°. This explain the planar structure of such molecules as $B(CH_3)_3$, $BF_3$, $BCl_3$, and the comparative ease of formation of $B_3N_3$ and $B_3O_3$ planar hetero-rings.

The elements of Group III have a free $p$ orbital which can be used by an unshared pair of electrons. With boron this can take place in two ways:

1. Intramolecular delocalisation of unshared electron pairs of an element bonded to boron (the formation of additional $\pi$ bonds between boron and the element bonded to it):



2. The formation of coordinated monomeric and cyclic compounds of boron (with $sp^3$ hybridisation of $\sigma$ bonds between boron and the element bonded to it):



In this case the bonds to boron are tetrahedrally directed, as in the carbon atom.

The advantageous valence angle of boron (120°) and the possibility of using its vacant $p$ orbital can evidently explain the fact that in all the reactions the formation of only 6-membered $B_3N_3$ and $B_3O_3$ rings is observed.

The formation of an 8-membered $B_4N_4$ ring [32] or the linear chain B–N–B–N– (with a low degree of polymerisation) [33] is observed only when the formation of a six-membered ring is sterically hindered.

With aluminium, gallium, indium, and thallium the tendency to use free $p$ orbitals is still greater than with boron, which leads to the formation of compounds with coordination number 4 or even 6 (since these elements can use the $d$ orbital). This leads, in particular, to the formation of coordinated rings and polymeric chains of aluminium, gallium, etc.

The elements of Group IV of the Periodic System have four electrons in the valency shell and with carbon three types of hybridisation are possible:

$sp^3$ four $\sigma$ bonds (tetrahedral direction);
$sp^3$ three $\sigma$ bonds (triangular direction) + one $\pi$ bond;
$sp$ two $\sigma$ bonds (linear direction) + two $\pi$ bonds.

Carbon does not possess $d$ orbitals. Hence in any hybrid state a carbon atom uses all its valency electrons and orbitals, that is, carbon has neither unshared electron pairs nor vacant orbitals.

The remaining elements of the principal subgroup of Group IV — silicon, germanium, tin, and lead (in the quadrivalent state) — possess empty $d$ orbitals. Usually four valency electrons participate in $sp^3$ hybridisation while the $d$ orbital remains vacant. Hence the structure of most of the compounds of these elements comprises a few united tetrahedra. The tendency to form $p_\pi$ bonds is quite insignificant for these elements and therefore the elements Si, Ge, Sn, and Pb do not form stable monomeric compounds with double bonds of the type Si=E, Ge=E, Sn=E, and Pb=E. The hybrid states $sp$ and $sp^2$ are uncharacteristic for these elements and they always change into the $sp^3$ hybrid state. This is important in the chemistry of inorganic rings and polymers with inorganic chain molecules, for thanks to the instability of the $sp$ and $sp^2$ hybrid states, the derivatives of silicon, germanium, tin, and lead, which from their composition should possess multiple bonds, polymerise to form rings or polymeric chains of various structures. For example, all compounds with the general formulae $R_2SiO_2$, $R_2SiNR'$, and $R_2SiS$ are polymerised with the formation of cyclic or polymeric structures [1-3,18].

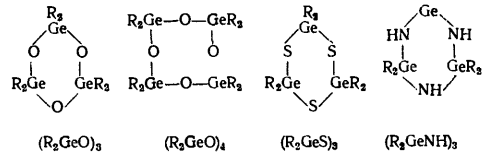
The existence of five vacant $d$ orbitals of silicon would in principle permit the formation of another five coordination bonds by filling them with unshared electron pairs of another element, but this is almost impossible sterically. The c.n. of silicon reaches six in the anion $[SiF_6]^{2-}$ and in certain complexes of $SiF_4$ with amines, which becomes possible owing to the small dimensions of the fluorine atom. With increase in the dimensions of the ligand the c.n. of silicon diminishes: the ion $[SiCl_6]^{2-}$ is unstable and the similar ion with bromine is generally not formed.

In relation to oxygen, silicon usually exhibits c.n. = 4, but some examples are known in which the silicon is linked with six oxygen atoms, for example, in an acetylacetonato--complex [34]. Silicon with c.n. = 5 is formed in an intermediate complex in several chemical reactions [35]. This is important in the chemistry of inorganic rings and polymers based on silicon, since such intermediate complexes appear

in the reactions of ring opening, telomerisation, and polymerisation by both electrophilic and nucleophilic reagents [3,18].

The presence of the empty *d* orbitals of the silicon atom brings about intramolecular delocalisation of the unshared electron pairs from atoms of oxygen, nitrogen, and chlorine bonded to the silicon. This leads to the appearance of double-bonding between such elements as Si–O, Si–N, and Si–Cl. In the chemistry of inorganic rings and polymeric chains this plays a determinative role and is probably one of the factors affecting the thermal stability of these compounds.

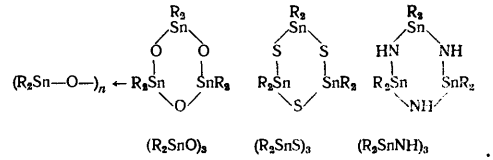
Similar conclusions can be drawn for germanium, tin, and lead. Germanium compounds of type $R_2GeO$, $R_2GeNR'$, and $R_2GeS$ are not monomeric. Cyclic and polymeric diorganogermoxanes [36] and trimeric organogermathianes $[R_2GeS]_3$ [37] have been described. It is interesting to note that the molecular weight of $R_2GeNH$ (R = $C_2H_5$) is close to that of a trimer [38] which indicates a cyclic structure:



$(R_2GeO)_3$ $(R_2GeO)_4$ $(R_2GeS)_3$ $(R_2GeNH)_3$

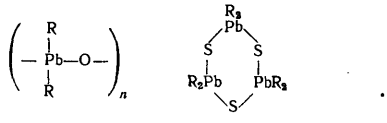
The molecular weight of the polymer $(R_2GeO)_n$ [36] is unknown.

Tin derivatives of the type $R_2SnO$, $R_2SnS$, and $R_2SnNR'$ are also polymeric. Oxygen derivatives of tin compounds are described as linear polymers [39] and as cyclic trimers [40]. Sulphur-containing derivatives [41] and nitrogenous derivatives [42] are cyclic trimers:

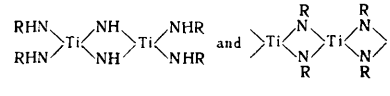


$(R_2SnO)_3$ $(R_2SnS)_3$ $(R_2SnNH)_3$

The lead derivatives of the types $R_2PbO$, $R_2PbS$, and $R_2PbNR'$ have been little studied. The oxygen derivatives are described as linear polymers [39] and the sulphur derivatives have a tripled molecular weight [43] indicating a cyclic structure:



Titanium, zirconium, and hafnium are transition elements of the fourth group and the *d* orbitals play an important part in their electronic structure. The value c.n. = 6 is characteristic for these elements and in the case of Zr and Hf even reaches c.n. = 8. Therefore the chemistry of polymeric compounds with inorganic chain molecules takes another form for these elements and the monocyclic compounds of these elements are not formed as a rule. Here, coordination polymers predominate. Titanium, for which c.n. = 4 and 6, exhibits great possibilities for the formation of rings and polymers. Compounds of the type:

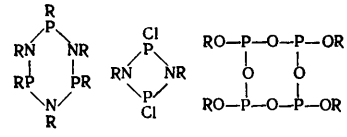


were recently described [44], reminiscent of silicon compounds with an analogous structure. When titanium has c.n. = 6, it forms polycyclic coordination compounds.

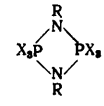
The elements of Group V have five valency electrons. Their valency is variable, and, depending on the distribution of the valency electrons in the orbitals, can be either three or five. In the case of phosphorus, arsenic, and antimony the following hybrid states are possible:

$$p^{III} - p^3;\ p^V - sp^3,\ sp^3d,\ \text{and}\ sp^3d^2.$$

The hybrid state $p^3$ plays a small part in the chemistry of inorganic rings and polymers. Only a few rings with tervalent phosphorus [43,45,46] are known:



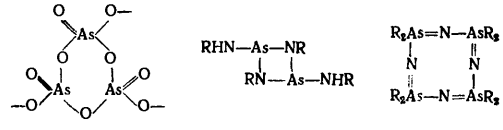
The hybrid state $sp^3d$ is also rarely encountered in the chemistry of phosphorus and only a few cyclic compounds of this type [47,48]:



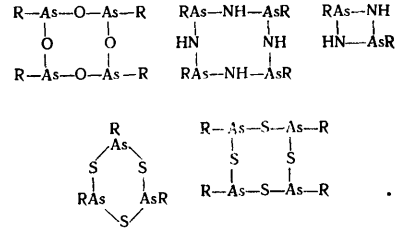
are known.

The most characteristic hybrid state of phosphorus is $sp^3$, which corresponds with the tetrahedral direction of the phosphorus bonds [49]. This hybrid state is encountered in all polymeric and cyclic compounds of phosphorus: in metaphosphates [49,50], phosphazene derivatives [51,52,53], and in phosphorus–sulphur compounds [54]. It is worth noting that phosphorus readily forms both cyclic and linear polymeric high-molecular chains.

In its compounds arsenic also usually displays the hybrid states $p^3$ (tervalent arsenic) and $sp^3$ (quinquevalent arsenic). A few cyclic arsenic compounds [55–57] and high-molecular-weight polyarsenates [4] have been described:



Compounds of the type RAsO, RAsNR', and RAsS are also known. Their molecular weights do not correspond to monomeric forms: RAsO [58] and RAsNH [59] are tetramers and RAsS trimers [58] and tetramers [60], which corresponds to the following cyclic compounds [61,62]:

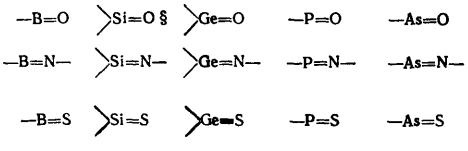


The elements of Group VI possess six valency electrons and exhibit the valencies 2, 4, and 6. Bivalent sulphur and selenium participate in inorganic rings and polymers as the electronegative element. As electronegative components sulphur and selenium enter inorganic rings and polymeric chains in the quadrivalent or sexivalent states respectively with $p^3$ (or $sp^2$) and $sp^3$ hybridisation. Cyclic compounds of sulphur with oxygen — for example $(SO_3)_x$ [63] — and nitrogen [64,65] are also now known. The non-transition elements under consideration can be divided into the following types: elements which after hybridisation have neither free orbitals nor unshared electron pairs (carbon); elements which after hybridisation have unshared pairs of electrons (nitrogen and oxygen); elements which after hybridisation have free orbitals [boron and aluminium ($p$ orbitals), silicon and germanium ($d$ orbitals)]; elements which after hybridisation have both unshared electron pairs and vacant orbitals (phosphorus, arsenic, antimony, sulphur, selenium, and tellurium).

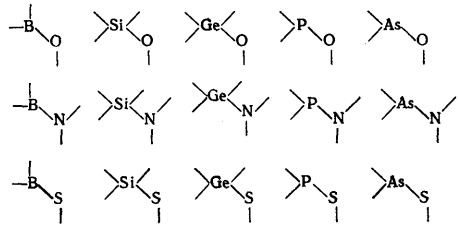
All transition elements have vacant orbitals, therefore they have a tendency to form mainly coordination rings and polymers.

As this classification indicates, carbon differs from all other elements (apart from hydrogen) in exhibiting neither free orbitals nor unshared electron pairs. In addition to its electronegativity, this property explains the especial stability of homo-chain structures with C–C bonds. Homo--rings and homo-chains of other elements, having an electronegativity close to that of carbon (for example, sulphur and selenium) enter into various reactions with electrophilic and nucleophilic reagents, on account of the existence of unshared electron pairs or vacant orbitals; therefore their reactivity is greater than for carbon chains.

As the examples given show, each element enters into the composition of an inorganic ring or polymeric chain in the hybrid state most stable and most characteristic for it. This explains the instability of the multiple bonds of some elements with oxygen, nitrogen, and sulphur. Not a single compound containing one of the following multiple bonds:

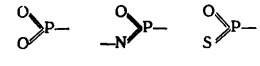


has yet been obtained. In such bonds boron, phosphorus(III), and arsenic(III) would have the hybrid state $sp$ or $p^2$, which are uncharacteristic for them. Silicon and germanium would also have the $sp^2$ hybrid state, which is uncharacteristic of them. Therefore such monomeric compounds with multiple bonds, if they are formed, would probably be labile and consequently difficult to isolate. In all the reactions in which the formation of monomers with such bonds could be expected, only cyclic or polymeric compounds with the following structural units are always obtained:

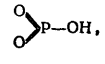


In such groups every element exhibits its stable hybridisation: boron $sp^2$, silicon $sp^3$, germanium $sp^3$, phosphorus(III) $p^3$, arsenic(III) $p^3$. Therefore, many compounds which in the initial period of development of organoelemental chemistry were considered monomers were shown by subsequent investigation to be cyclic or polymeric compounds. And now the literature contains descriptions of many compounds which are considered to be monomers with double bonds of the above type (in particular, in the chemistry of phosphorus, arsenic, and antimony), but the structure of these compounds was not studied and actually they are probably cyclic or polymeric compounds. The same can be expected of compounds of the types $R_nEO$, $R_nENR'$, and $R_nES$, where E = Al, Ga, In, Sn, or Pb.

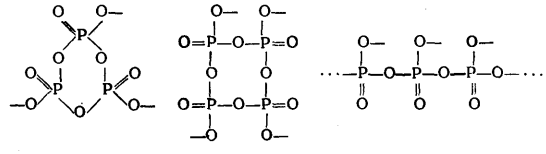
Electronic hybridisation also provides an explanation for the instability of the groupings:



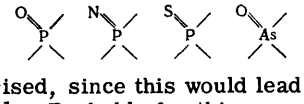
in which the phosphorus atoms have the $sp^2$ hybrid state, uncharacteristic of it. By polymerisation of such monomers phosphorus effects $sp^3$ hybridisation, which is more stable and characteristic of its quinquevalent state. Therefore, for example, metaphosphoric acid and its salts do not exist in the monomeric form:



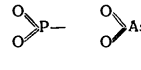
but only as cyclic or linear polymers:



On the basis of hybridisation it is possible to understand why other compounds which contain the same multiple bonds P=O, P=N, P=S (and also As=O, As=N–, and As=S–) are not polymerised. This occurs in those compounds in which the phosphorus(V) or arsenic(V) atom has a hybrid state most characteristic for it ($sp^3$). Compounds containing the grouping:



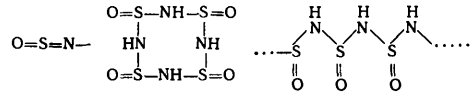
are not polymerised, since this would lead to the less stable hybrid state $sp^3d$. Probably for this reason compounds containing the groupings:



§ In mass-spectrographic investigations of polyorganosiloxane [66] the species $R_2Si{=}O$ were observed. They are formed in the depolymerisation of polyorganosiloxanes but cannot exist for any considerable time.

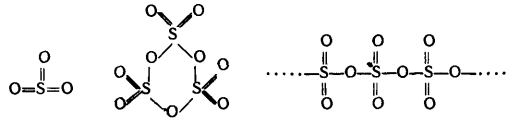
are polymerised only on account of one of the double bonds, which produces the hybrid state $sp^3$.

In the case of sulphur and selenium, the various hybridisations which are able to appear in a definite valency state, either monomeric compounds with multiple bonds or the corresponding cyclic and polymeric analogues can exist. For example, for quadrivalent sulphur the following compounds are known [65]:



although the hybrid states of sulphur in the monomer and in the polymers are different.

In the case of sexivalent sulphur the $sp^3$ hybrid state is more stable than the $sp^2$ hybrid state, therefore sulphur trioxide polymerises with formation of a cyclic trimer and a linear polymer [63]:



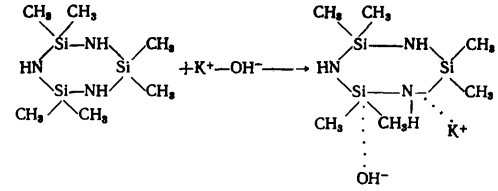
The stability of the $sp^3$ hybrid state of sexivalent sulphur explains why the sulphones $R_2SO_2$ do not polymerise, despite the presence of two double bonds in the molecule.

On the basis of the above review we can draw the following conclusions about the paths for obtaining inorganic rings and polymers with inorganic main-chain molecules with organic and organoelemental side-groups. In our opinion the most important direction of the synthesis of polymers with inorganic main-chain molecules is that which ensures the formation of chain molecules constructed from atoms of two or more elements alternating in the main chain. In choosing the elements for constructing the chains of large molecules it is necessary to take into account which type of hybridisation is most stable for these elements and also the electronegativity of the elements forming the chain. The alternation of elements in the chain of the molecule should be selected so that one element would be more electronegative and the other less electronegative than carbon. In this case the difference in the electronegativity of the elements leads to a polar type of bonds for the interlinked elements A–B (or to its partially ionic character), which increases the bond energy ($Dp_{AB}$) in comparison with the hypothetically pure covalent bond ($Dnp_A + Dnp_B$) in accordance with the formula:

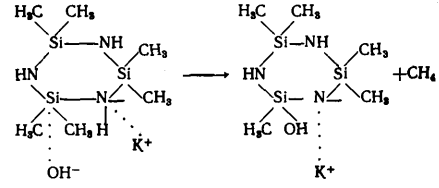
$$Dp_{AB} = Dnp_A + Dnp_B + 23.06\,(X_A - X_B)^2,$$

where $Dp_{AB}$ is the energy of the polar bond AB, $Dnp_A$ and $Dnp_B$ are the "non-polar contribution" of the corresponding elements A and B to the bond energy, and $X_A$, $X_B$ are the electronegativities of elements A and B on the Pauling scale.

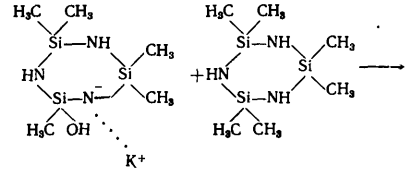
As examples illustrating this thesis we can quote the synthesis of polymers with silicon–nitrogen bonds obtained recently by catalytic polymerisation of dimethylcyclosilazanes [67]. The polymerisation of these rings with the aid of catalytic quantities of alkalis takes place not with cleavage of the ring, as occurs in the case of the alkaline polymerisation of dimethylcyclosiloxanes, but by detachment of a methyl group from the silicon atom and hydrogen from nitrogen, with formation of methane:

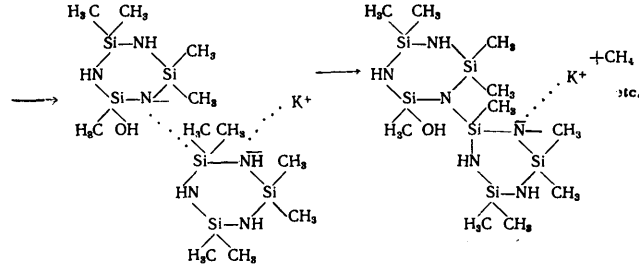


In the transitional complex formed as a result of redistribution of the electronic density one of the Si–C bonds is weakened and methane is detached with formation of a negatively charged ion:

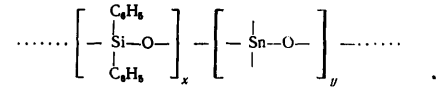


Subsequently the process proceeds through coordination of the ions of cyclosilazanes by the reaction:





Several polymers have been obtained with chain molecules, including both Si–O and Sn–O bonds. Such polymers are obtained from the disodium salt of diphenyldihydroxysilane and tin chloride [68]. These organostannosilicon polymers have the following structure:



Organostannosiloxane oligomers were obtained in an analogous way from difunctional organotin monomers and the sodium salts of dialkyl(aryl)dihydroxysilanes [69], and polyorganostannosiloxanes by the polycondensation of diethoxydimethylsilane with tin diacetate and with diacetoxydiisobutyltin [70].

The possibility of preparing polyorganostannosiloxanes of linear structure by the polycondensation of dialkoxy-derivatives of tin with organosilicon hydroxyl derivatives has been described [71].

In the formation of the main chains of large molecules steric hindrance can become an unsurmountable difficulty, for even when the hybrid state characteristic for the elements concerned is maintained and the electronegativity of the elements is correctly chosen the formation of the main chain of a large molecule is unsuccessful. This shows that in choosing the direction for the synthesis of polymers with inorganic chain molecules account should be taken of all the factors considered above.

In the present article an attempt has been made to evaluate the ability of various elements to form the chains of large molecules, and general consideration has been given to the trends for the preparation of polymers with inorganic chain molecules. The authors do not pretend to have given a complete exposition of these problems, but hope that the article will be of assistance to those who are working in the field of the synthesis and investigation of organoelemental compounds.


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# METHODS OF STEPWISE SYNTHESIS OF THE SPECIFIC $C_{3'}$–$C_{5'}$ INTERNUCLEOTIDE BOND

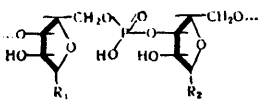
S. M. Zhenodarova

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## I. INTRODUCTION

The considerable advances in the elucidation of the role of nucleic acids in the biosynthesis of protein[1] have led to increasing interest in synthetic polynucleotides which serve as models in the investigation of the chemical, biochemical, and biological properties of nucleic acids. There is particular interest in the methods of preparation of nucleotides with a known sequence of nucleotide residues in the polynucleotide chain. One of such methods is the stepwise synthesis of the specific internucleotide bond which consists of a phosphodiester unit joined to the $C_{3'}$ atom† of one nucleotide and the $C_{5'}$ atom of another[2]:



In developing methods of synthesis of the specific $C_{3'}$–$C_{5'}$ internucleotide bond it is necessary to solve two principal problems: (1) to find ways of protecting the functional groups present in nucleoside and nucleotide molecules (the hydroxy-group of the sugar and the amino-groups of purine and pyrimidine bases) and thus obtain derivatives of the nucleosides and nucleotides with only one reactive group; (2) to achieve the condensation of these residues in such a way that only the $C_{3'}$–$C_{5'}$ phosphodiester linkage is formed. In both cases it is necessary to bear in mind the low stability of the $C_{3'}$–$C_{5'}$ linkage which is hydrolysed by acids[4] and alkalis[5] and isomerises to the $C_{2'}$–$C_{5'}$ linkage in an acid medium[6,7]. All these factors restrict the choice of protective groups, since their subsequent complete or selective removal often requires fairly severe conditions.

## II. METHODS OF SPECIFIC PROTECTION OF FUNCTIONAL GROUPS IN NUCLEOSIDES AND NUCLEOTIDES

The synthesis of the $C_{3'}$–$C_{5'}$ linkage may be achieved in two ways: (1) a nucleoside-3′ phosphate is condensed with a nucleoside having a free hydroxy-group in position $C_{5'}$ (5′-OH); (2) a nucleoside-5′ phosphate is condensed with a nucleoside having a free hydroxy-group in position $C_{3'}$ (3′-OH). Thus for the synthesis of the $C_{3'}$–$C_{5'}$ internucleotide bond it is necessary to have nucleosides with free 3′-OH and 5′-OH groups (nucleoside components) and nucleotides with a phosphate residue in position $C_{3'}$ or $C_{5'}$ with the remaining functional groups completely protected (nucleotide component).

### 1. Protection of Hydroxy-Groups in Deoxyribonucleosides and Deoxyribonucleotides

The preparation of protected deoxyribonucleosides and deoxyribonucleotides does not present great difficulties because there is no hydroxy-group in position $C_{2'}$ and the 3′-OH and 5′-OH groups are known to differ in their reactivity. The use of triphenylmethyl chloride (trityl chloride) for the protection of the 5′-OH group is based on this difference: trityl chloride reacts much more rapidly with the primary hydroxyl[8–12]. Although the trityl group is most often used for the protection of the 5′-OH group in deoxyribonucleosides[13] and deoxyribonucleotides[14], the acetyl group[15] and the di-(*p*-anisyl)phenylmethyl group (di-*p*-APM group) are employed for this purpose too[16,17]. The acetyl group has also been used for the protection of

† The numbering of the atoms in the base and sugar residues of nucleic acids is based on that given by Kochetkov *et al.*[3].

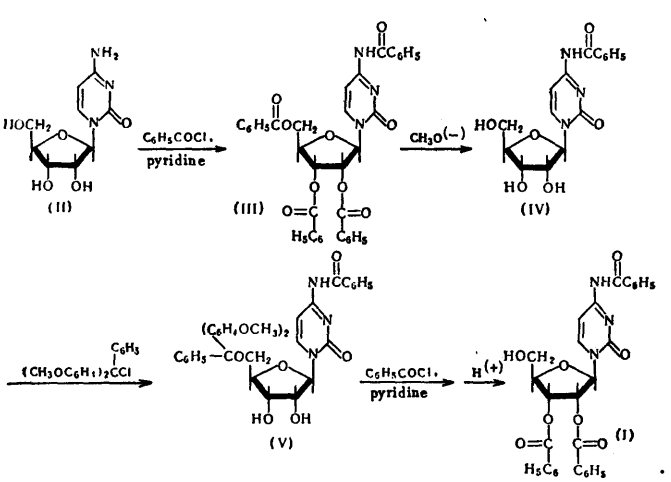
the 3'-OH group in deoxyribonucleosides[14] and deoxyribonucleotides[18], the mixture of 3'-*O*-acetyl and 5'-*O*-acetyl derivatives obtained in the first case being separated by countercurrent distribution[19].

The preparation of protected ribonucleoside and ribonucleotide derivatives is much more difficult since the hydroxy-groups in positions $C_{2'}$ and $C_{3'}$ do not differ in their properties.

## 2. Synthesis of Ribonucleosides with a Free Hydroxy-Group in Position $C_{5'}$

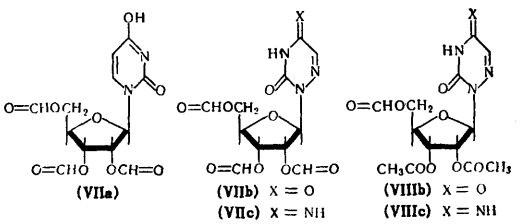
Ribonucleosides with a 5'-OH group may be obtained via the acetals of the *cis*-glycol group in the ribose residue: 2',3'-*O*-isopropylidene-[20,21], 2',3'-*O*-anisylidene-[22], 2',3'-*O*-cyclopentylidene-[22], 2',3'-*O*-cyclohexylidene-[22], or 2',3'-*O*-benzylidene-ribonucleosides[22,23]. However, the application of these ribonucleoside derivatives for the synthesis of oligonucleotides is limited, because the subsequent removal of the acetal group requires fairly severe conditions. For the same reason even the more labile *p*-methoxybenzylidene group[7] did not prove to be very suitable either. Nor was it possible to use on a preparative scale the method proposed by Todd and coworkers[24] for the synthesis of 2',3'-di-*O*-acetyluridine: by partial deacetylation of 2',3',5'-tri-*O*-acetyluridine with subsequent separation of the mixture of mono-, di-, and tri-acetyluridines by countercurrent distribution.

Usually ribonucleosides with a free 5'-OH group are obtained via the 5'-*O*-trityl derivatives: 2',3'-di-*O*-benzoyluridine was prepared from 5'-*O*-trityluridine[25] or from 5'-*O*-di-*p*-APM-uridine[26]. $N^6O^{2'}O^{3'}$-Tribenzoylcytidine (I) can be obtained by the reaction of cytidine (II) with benzoyl chloride in pyridine, the product being the fully benzoylated cytidine (III),[27] careful treatment of which with sodium methoxide gives crystalline $N^6$-benzoylcytidine (IV) in good yield. The 5'-OH group in (IV) is then protected with the di-*p*-AMP group and the 2'-OH and 3'-OH groups in the resulting $N^6$-benzoyl-5'-*O*-di-*p*-APM-cytidine (V) are rebenzoylated. The removal of the di-*p*-APM group in an acidic medium yields (I):



The simpler synthesis via 5'-*O*-di-*p*-APM-cytidine (VI), which is benzoylated with subsequent splitting of the di-*p*-APM group, cannot be used, since in the synthesis of (VI) some mono-$N^6$-di-*p*-APM-cytidine is also formed[26].

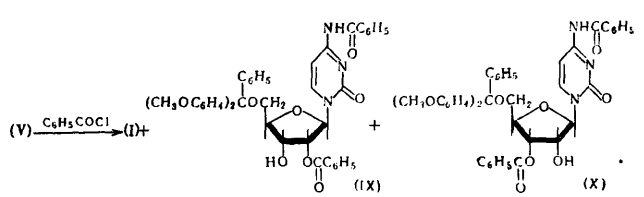
Šorm and coworkers[28] suggested the synthesis of specifically protected ribonucleosides via their *O*-formyl derivatives, which can be obtained by the usual formylation procedures[29-31]. *O*-Formyl groups are split off even on heating in methanol, i.e. under conditions in which other protecting groups, for example acetyl, are unaffected. Investigation of the methanolysis of 2',3',5'-tri-*O*-formyl derivatives of uridine (VIIa), 6-azauridine (VIIb), and 6-azacytidine (VIIc) showed that formyl groups in positions $C_{2'}$ and $C_{3'}$ are hydrolysed more rapidly than in position $C_{5'}$. The difference in the rate of methanolysis is almost independent of the structure of the heterocyclic base although the latter affects the rate of methanolysis of the formyl group in position $C_{5'}$: 5'-*O*-formyluridine hydrolyses to uridine in 1 h, while 5'-*O*-formylazauridine requires 16 h.



The 5'-*O*-formyl derivatives of (VIIIa) and (VIIIb) were prepared. The attempt at selective removal of the *O*-formyl group in the presence of an *O*-acetyl group was unsuccessful: on heating with methanol, 2',3'-*O*-diacetyl-5'-*O*-formylazauridine (VIIIb) and 2',3'-*O*-diacetyl-5'-*O*-formylazacytidine (VIIIc) were converted into (VIIb) and (VIIc).

## 3. Synthesis of Ribonucleosides with a Free Hydroxy-Group in Position $C_{3'}$

Numerous attempts to prepare ribonucleosides with a free 3'-OH group have been unsuccessful[26]. Partial benzoylation of (V) with a slight excess of benzoyl chloride yields a mixture of (I) and two mono-*O*-benzoylated substances, probably $N^6O^{2'}$-dibenzoyl-$O^{5'}$-di-*p*-APM-cytidine (IX) and $N^6O^{3'}$-dibenzoyl-$O^{5'}$-di-*p*-APM-cytidine (X), which could not be separated. Partial debenzoylation of (III) gives a mixture of $N^6O^{5'}$-dibenzoylcytidine (XI) and $N^6O^{3'}O^{5'}$-tribenzoylcytidine (XII) which can be separated on a silicic acid column. Treatment of (XI) with benzoyl chloride (somewhat more than one equivalent) gives both expected isomers: (XII) and $N^6O^{2'}O^{5'}$-tribenzoylcytidine (XIII).



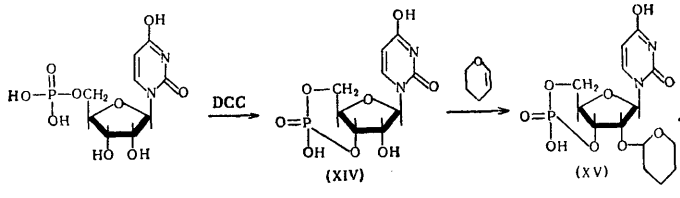
Phosphorylation of (XII) and (XIII) showed that some of the acyl groups migrate from 2'-OH to 3'-OH, in agreement with earlier data[32-34]. It is suggested that this migration may be acid-[35] or base-catalysed and that in an alkaline medium there is probably also rapid migration from 2'-OH to 3'-OH.[5] Taking all this into account, it may be assumed that direct use of ribonucleoside derivatives with a 3'-OH group and an acyl group in position $C_2$ is almost impossible.

4. Protection of Hydroxy-Groups in Ribonucleotides

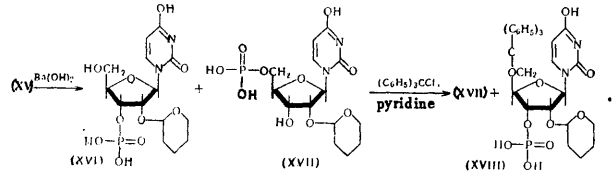
As already mentioned, the synthesis of oligonucleotides with the specific $C_{3'}-C_{5'}$ linkage requires that the nucleotides be fully converted into protected derivatives, so that the phosphate residue is the only reactive group, and that the groups protecting 5'-OH and 2'-OH or 3'-OH and 2'-OH should be removable independently of one another.

As in the case of deoxyribonucleotides, the use of trityl chloride was suggested for the protection of the 5'-OH group[36]. In order to protect the 2'-OH groups in mononucleotides, attempts were made to prepare the 2'-*O*-benzyl esters of nucleoside-3',5' cyclic phosphates using benzyl chloride and potassium t-butoxide[36,37]. However, the benzyl group migrates to the pyrimidine ring in the monobenzylated derivatives. According to the authors of these investigations, the discrepancy between their results and those of Todd and coworkers[38], who synthesised the *O*-benzyl ethers of nucleosides, is due to different reaction conditions being used.

The following method of protecting the 2'-OH group proved to be more successful[7,36]: uridine-5' phosphate in very dilute solution is converted in the presence of dicyclohexylcarbodiimide (DCC) into uridine-3',5' cyclic phosphate (XIV) which on treatment with dihydropyran in aqueous dioxan at about 20° is quantitatively converted into the 2'-*O*-tetrahydropyranyl (2'-*O*-THP) derivative (XV):




Hydrolysis of (XV) with barium hydroxide gives a mixture of 2'-*O*-THP-uridine-3' phosphate (XVI) and 2'-*O*-THP-uridine-5' phosphate (XVII) in 5 : 1 ratio, which could not be separated. Treatment of the mixture with trityl chloride in pyridine results in a quantitative yield of 2'-*O*-THP-5'-*O*-trityluridine-3' phosphate (XVIII), which can be readily separated from (XVII) (not participating in the reaction) by partition or ion-exchange chromatography:

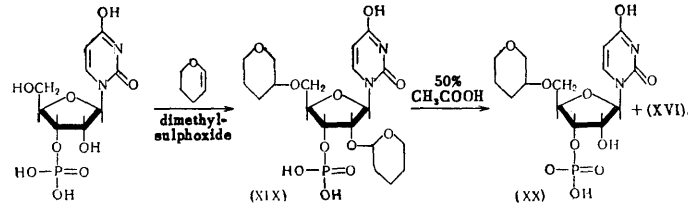



This pathway proved unsuitable for cytidine-5' phosphate, since opening of the phosphate ring with alkali is accompanied by rapid deamination of the cytosine moiety[39].

Both the trityl and the THP groups are removed on treatment of the derivative with aqueous acetic acid, the THP group being hydrolysed off at a higher rate than the trityl group[7]. Since stepwise synthesis of the $C_{3'}-C_{5'}$ linkage requires the selective removal of the 5'-*O*-trityl group, an attempt was made to use catalytic hydrogenation for this purpose, but the results were in many cases unsatisfactory[40,41]. In particular it was found that the cytosine ring may also be hydrogenated[42].

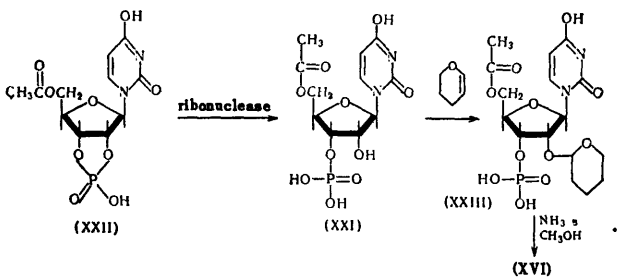
Bearing in mind that the ease of ionisation of *p*-methoxy-substituted triphenylmethanols increases greatly on introduction of each *p*-methoxy-group[43], Khorana and coworkers[7] suggested the use of a modified trityl group for the protection of the 5'-OH group. Investigation of the hydrolytic stability of 5'-*O*-*p*-anisyldiphenylmethyluridine, 5'-*O*-di-*p*-APM-uridine, and 5'-*O*-tri-*p*-anisylmethyluridine showed that the introduction of each *p*-methoxy-group increases the rate of hydrolysis in 80% acetic acid at 20° by a factor of about ten. Introduction of *p*-methoxy-groups into trityl chloride also increases the rate of its reaction with hydroxy-groups, including secondary hydroxy-groups, which may be a disadvantage in the preparation of nucleotide derivatives. It proved convenient to use di-*p*-APM chloride for the protection of the 5'-OH group, since the difference in the rate of removal of 2'-*O*-THP and 5'-*O*-*p*-anisyldiphenylmethyl groups is still insufficient for the selective elimination of the latter, while treatment of 2'-*O*-THP-5'-*O*-di-*p*-APM-uridine-3' phosphate with 80% acetic acid at 0° for 6 h gives a good yield of (XVI).

Todd[44] was the first to attempt the blocking of the 2'-OH group by treating uridine-3' phosphate with methyl iodide in the presence of silver oxide. He obtained a mixture of 2'- and 3'-phosphate derivatives. It is possible to obtain the protected ribonucleoside-3' phosphate by reacting the latter directly with dihydropyran in dimethylsulphoxide in the presence of trifluoroacetic acid[26]. In the case of uridine-3' phosphate the reaction is almost quantitative, the tetrahydropyranylation of the 2'-OH group being more rapid than the migration of the phosphate residue. Under the same conditions adenosine-3' phosphate gives 70% of 2',5'-di-*O*-THP-adenosine-3' phosphate and a small amount of *NO*$^{2'}$*O*$^{5'}$-tri-THP-adenosine-3' phosphate, which increases with the duration of tetrahydropyranylation. It was established that the rate of hydrolysis of the THP groups in positions $C_{2'}$ and $C_{5'}$ is different[45,46]: treatment of 2',5'-di-*O*-THP-uridine-3' phosphate (XIX) with 50% acetic acid at 0° for 3 h gives a mixture of (XVI) and 5'-*O*-THP-uridine-3' phosphate (XX), the latter predominating (75%). The mixture may be separated by treatment with di-*p*-APM chloride followed by chromatography on a DEAE-cellulose column:




Šorm and coworkers[47,48] suggested that the 2'-OH groups should be tetrahydropyranylated after preliminary acylation of the 5'-OH groups in ribonucleoside-3' phosphate, which makes possible subsequent selective removal of the protective groups, because the acetyl residue is more readily split off in an alkaline medium in which the THP group remains unaffected. The calcium salt of 5'-*O*-acetyluridine-3' phosphate (XXI) was obtained from 5'-*O*-acetyluridine-2',3' cyclic phosphate (XXII) by splitting the latter with pancreatic ribonuclease. Tetrahydropyranylation may be effected using the calcium salt and adding one equivalent of hydrochloric acid to form a homogeneous solution. It is also necessary to add a small excess of hydrochloric acid in order to catalyse the reaction, which

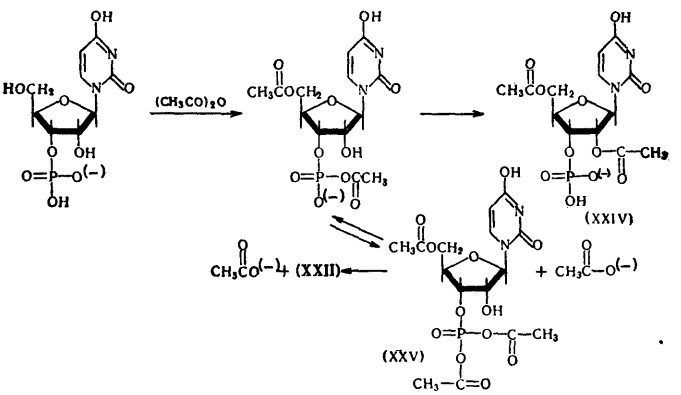
is quantitative under these conditions after 40–50 h at room temperature. There is no migration of the phosphate residue. The reacting resulting in the formation of 5′-*O*-acetyl-2′-*O*-THP-uridine-3′ phosphate (XXIII) is much more rapid (8 h) if it is carried out by adding two moles of hydrochloric acid per mole of phosphate to the ammonium or pyridinium salt of 5′-*O*-acetylnucleoside-3′ phosphate in a mixture of dimethylsulphoxide and dimethylformamide [49]. The acetyl group is split off by a mixture of methanol and ammonia at 50° (at 20° the yield of the deacetylated products is lower):



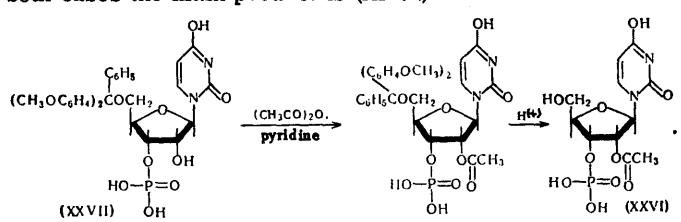

Apart from aqueous acetic acid, strongly acid ion-exchange resins, for example Dowex 50 in the pyridinium or ammonium form, can be used to remove the THP group. The rate of removal depends on the degree of cross-linking of the resin and the concentration of pyridine in solution: the THP group is readily removed if the degree of cross-linking is low, the rate of removal falling as the concentration of pyridine is increased. The most favourable conditions for the removal obtain when Dowex 50 × 8 in 30% pyridine is used.

The use of THP and di-*p*-APM nucleotide derivatives for the synthesis of dinucleoside phosphate showed that a disadvantage of these protective groups is their incomplete removal on brief treatment with acid [7] (longer treatment results in partial isomerisation of the $C_{3'}$–$C_{5'}$ linkage). Thus treatment of 2′-*O*-THP-5′-*O*-di-*p*-APM-uridylyl-(3′→5′)-uridine with 80% acetic acid for 4 h yields 50% of uridylyl-(3′→5′)-uridine. After treatment for 10 h, the yield rises to 69%, but the product contains about 1% of uridylyl-(2′→5′)-uridine. Similar results were obtained in the synthesis of uridylyl-(3′→5′)-adenosine: after a 4 h treatment with 80% acetic acid, 2′-*O*-THP-5′-*O*-di-*p*-APM-uridylyl-(3′→5′)-adenosine gave 54.5% of pure uridylyl-(3′→5′)-adenosine, while after 11 h the yield increased to 70%, but the product contained about 1.5% of uridylyl-(2′→5′)-adenosine. The low yield (28–40%) in the synthesis of uridylyl-(3′→5′)-uridine, uridylyl-(3′→5′)-cytidine, and uridylyl-(3′→5′)-adenosine from (XIX) and the corresponding derivatives of uridine, cytidine, and adenosine [26] is also due to the incomplete removal of the protecting groups, particularly the 5′-*O*-THP group.

Khorana and coworkers [45] suggested that these groups be replaced by acetyl groups. In contrast to the data of Šorm and coworkers [48] who state that acetylation of nucleoside-3′ phosphate always results in the formation of 2′,3′ cyclic phosphates, it was found that, depending on the conditions, the reaction of acetic anhydride with ribonucleoside-3′ phosphate can take place in different ways: in an acid medium uridine-3′ phosphate yields predominantly 2′,3′ cyclic phosphate, while in an alkaline medium (pyridine) an excess of acetic anhydride gives a mixture of (XXII) and 2′,5′-*O*-diacetyluridine-3′ phosphate (XXIV), which constitutes 35% of the mixture. If acetic anhydride is replaced by acetyl bromide, a 51% yield of (XXIV) is obtained. Acetylation of other ribonucleoside-3′ phosphates takes place similarly. Bearing in mind that the presence of water in the pyridine–acetic anhydride mixture reduces the yield of cyclic phosphate and assuming that the role of water reduces to the formation of acetate ions, Khorana and coworkers [45,46,50] suggested that the acetylation be carried out in an anhydrous medium using tetraethylammonium acetate as a source of acetate ions. (XXIV) was obtained in 92% yield from the pyridinium salt of uridine-3′ phosphate in dry pyridine with an excess (30-fold) of acetic anhydride at about 20° in 1 h. It is believed that (XXII) is formed via an intermediate diacylphosphate (XXV) and that acetate ions probably inhibit its formation:




The acetyl group has also been used to protect the 2′-OH group after preliminary blocking of the 5′-OH group in the ribonucleoside-3′ phosphate with a group which is stable in an alkaline medium and is removed in an acid medium [46]. Thus 2′-*O*-acetyluridine-3′ phosphate (XXVI) was obtained from (XX) and 5′-*O*-di-*p*-APM-uridine-3′ phosphate (XXVII) by treating them with an excess of acetic anhydride in pyridine with subsequent removal of the protecting group in the $C_{5'}$ position: the THP group is removed at pH 2.8 in the presence of Dowex 50 resin after 7.5 h at room temperature and the di-*p*-APM group after 7 min at pH 2.5. In both cases the main product is (XXVI).



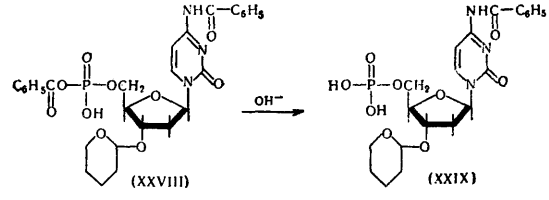

## 5. Protection of the Amino-Groups of the Purine and Pyrimidine Bases in Nucleosides and Nucleotides

The amino-groups in the purine and pyrimidine bases in nucleosides and nucleotides are extremely reactive [42,51–53]. Thus when 3′-*O*-acetylthymidine-5′ phosphate is condensed with 5′-*O*-trityldeoxycytidine in the presence of dicyclohexylcarbodiimide (DCC), the main reaction is phosphorylation of the amino-group of deoxycytidine by the activated nucleotide component [52]. Therefore in the synthesis of oligonucleotides with the $C_{3'}$–$C_{5'}$ linkage it is necessary to

protect the amino-groups as well as the hydroxy-groups of the nucleoside and nucleotide components. Acetyl[15,42,54], benzoyl[17,52,55], and anisyl[52,55] groups are usually employed for this purpose.

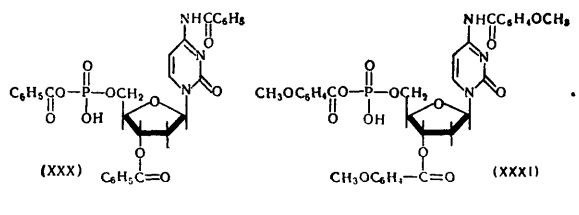
*N*-Acetyl derivatives of nucleosides and nucleotides are obtained from the *NO*-acetyl derivatives using the different rates of hydrolysis of the *O*-acetyl and *N*-acetyl groups[41,42]; in an alkaline medium the *O*-acetyl groups are removed much more rapidly than the *N*-acetyl groups. Nevertheless it was not possible to remove selectively the 3'-*O*-acetyl group from $N^6O^{3'}$-diacetyldeoxycytidine-5' phosphate[42]. The method of selective acetylation of the amino-group in cytidine-2',3' cyclic phosphate with a limited amount of the acetylating agent[54] proved to be unsuitable for the preparation of $N^6$-acetyldeoxycytidine-5' phosphate, since the acetic (or other) anhydride reacts with the mononucleotide, forming predominantly a mixed acylphosphate anhydride[56]. A disadvantage of *N*-acetyl protection is its instability in an acid medium[7,52,57]: partial removal of the *N*-acetyl group was noted after brief treatment with dilute acetic acid of $N^6$-acetyl-$O^{3'}$-THP-deoxycytidine-5' phosphate[52], $NO^{2'}O^{3'}$-triacetyl-$O^{5'}$-trityladenosine[57], and *N*-acetyl-$O^{5'}$--tri-*p*-anisylmethyladenosine[7]. Furthermore, *N*-acetyl derivatives of nucleosides and nucleotides are insufficiently soluble in pyridine.

*N*-Benzoyl derivatives[26,52,55] are more stable to acids and are more soluble. On prolonged treatment of 3'-*O*-THP--deoxycytidine-5' phosphate with benzoic anhydride in pyridine, compound (XXVIII) is probably formed, the anhydride bond in which is very stable to aqueous pyridine[58]. $N^6$-benzoyl-3'-*O*-THP-deoxycytidine-5' phosphate (XXIX) is obtained in high yield after brief treatment of (XXVIII) with alkali, followed by purification on DEAE-cellulose:




(XXVIII) (XXIX)

$N^6$-Benzoyldeoxycytidine-5' phosphate was obtained by the benzoylation of deoxycytidine-5' phosphate with an excess of benzoic anhydride or benzoyl chloride in pyridine with subsequent treatment of the product (XXX) with a mixture of pyridine and aqueous sodium hydroxide under rigorously controlled conditions[52]. *N*-Benzoyldeoxyadenosine-5' phosphate was obtained similarly[55]. The *N*-benzoyl group in the latter is more stable than in the corresponding derivative of deoxycytidine-5' phosphate. $N^6$-Benzoylcytidine is obtained by partial debenzoylation of $N^6O^{2'}O^{3'}O^{5'}$-tetrabenzoylcytidine with sodium methoxide[26]. Benzoylation of adenosine under mild conditions with an excess of benzoyl chloride gives a crystalline pentabenzoyl derivative[7]. At a high temperature two benzoyl groups can be added to the adenine ring[59,60]. It is suggested[7] that one of them is attached to $N^6$ and the other possibly to $N^2$.




(XXX) (XXXI)

*N*-Anisyl derivatives of nucleosides and nucleotides are very stable to alkali: treatment with alkali of a fully substituted derivative of deoxycytidine-5' phosphate (XXXI) gives a 90% yield of $N^6$-anisyldeoxycytidine-5' phosphate, no deoxycytidine-5' phosphate being detected in the product[52]. Study of the rate of hydrolysis of various *N*-acyldeoxycytidine-5' phosphates in 9 *N* ammonium and sodium hydroxides at room temperature showed that ammonium hydroxide is more effective in the hydrolysis and that the *N*-acyl residues can be arranged in the following sequence as regards their stability: *N*-anisyl > *N*-benzoyl > *N*-acetyl. After prolonged interaction of *N*-anisyl- and *N*-benzoyl--deoxycytidine-5' phosphate with alkali and with aqueous acetic acid, some deamination is observed[52]; it is even more extensive in the case of $N^6$-acylcytosines[27]. Ammonia does not cause deamination. When acetic acid is used, the degree of deamination varies, depending on the nature of the *N*-acyl group: the *N*-acetyl group is more readily deaminated than the *N*-benzoyl group.

## III. METHODS OF SYNTHESIS OF THE $C_{3'}$–$C_{5'}$ INTERNUCLEOTIDE BOND

### 1. Synthesis of Dinucleoside Phosphates with a Non--Specific Internucleotide Bond

The first attempts at the synthesis of dinucleotides led to the formation of dinucleoside phosphates in which the phosphate residue was linked to analogous carbon atoms of the respective sugar residues[61]. Thus uridylyl-(5'→5')--uridine was obtained from 2',3'-*O*-benzylideneuridine and phenyl phosphorodichloridate after the removal of the protecting groups[62]. When *p*-nitrophenyl phosphorodichloridate was used, thymidylyl-(5'→5')-thymidine was obtained from 3'-*O*-acetylthymidine[63,64]. Adenylyl-(5'→5')-uridine was prepared from the protected silver salt of adenosine-5' phosphate and 2',3'-isopropylideneuridine[65], and also by the method of mixed anhydrides[18,66]. Using the monoacyl chlorides of the activated nucleotide derivatives[19], adenylyl--(2'→5')-uridine, and also the first dinucleoside phosphate with the $C_{3'}$–$C_{5'}$ linkage, thymidylyl-(3'→5')-thymidine[19] were synthesised. Nevertheless this method did not find wide application, because the yield of the dinucleoside phosphate is small and the preparation and purification of the intermediate are difficult. Mixtures of substances with the $C_{2'}$–$C_{5'}$ and $C_{3'}$–$C_{5'}$ linkages were obtained in numerous experiments on the synthesis of dinucleoside phosphates and trinucleoside diphosphates from various derivatives of adenosine, guanosine, and cytidine using diphenyl phosphorochloridate[54]. The above methods of synthesis of dinucleoside phosphates leads to compounds with a non-specific internucleotide bond or requires starting materials which are not readily available.

### 2. The Carbodiimide Method of Synthesis of the $C_{3'}$–$C_{5'}$ Bond

The method providing for direct condensation of the nucleoside and nucleotide components in the presence of activating agents proved to be much more effective. The most widely used activating agent is DCC, the excess of which does not lead to side-reactions, and the dicyclohexylurea formed from it can be readily removed from the reaction mixture. Using in the reaction various nucleoside and nucleotide components (Table 1), Khorana and co-

TABLE 1. Preparation of dinucleotide phosphates by condensation in the presence of DCC.

| Nucleoside component | Nucleotide component | Yield of dinucleoside phosphate, % |
|---|---|---|
| 5′-*O*-di-*p*-APM-thymidine | 3′-*O*-acetylthymidine-5′ phosphate | TpT*, 75–76 |
| Ditto | *NO*$^{2'}$-diacetyldeoxyguanosine-5′ phosphate | TpdG, 68 |
| » | *NO*$^{2'}$-diacetyldeoxyadenosine-5′ phosphate | TpdA, 70 |
| *N*-Anisyl-*O*$^{2'}$-di-*p*-APM-deoxycytidine | 3′-*O*-acetylthymidine-5′ phosphate | dCpT, 75 |
| Ditto | *N*-anisyl-*O*$^{2'}$-acetyldeoxycytidine-5′ phosphate | dCpdC, 73 |
| *N*-Benzoyl-*O*$^{2'}$-di-*p*-APM-deoxycytidine | *NO*$^{2'}$-diacetyldeoxyguanosine-5′ phosphate | dCpdG, 97 |
| *NO*$^{2'}$-bis(di-*p*-APM)-deoxyguanosine | 3′-*O*-acetylthymidine-5′ phosphate | dGpT, 67 |
| Ditto | *N*-anisyl-*O*$^{2'}$-acetyldeoxycytidine-5′ phosphate | dGpdC, 64 |
| » | *NO*$^{2'}$-diacetyldeoxyguanosine-5′ phosphate | dGpdG, 60 |
| *N*-Benzoyl-*O*$^{2'}$-di-*p*-APM-deoxyadenosine | 3′-*O*-acetylthymidine-5′ phosphate | dApT, 70 |

* For the nomenclature and the abbreviations used in naming the polynucleotides, see Khorana[61].

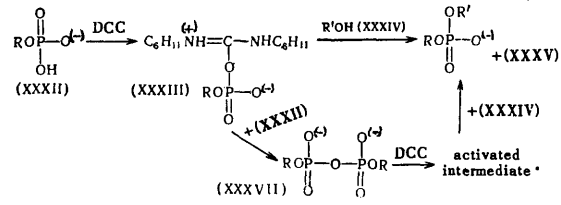
TABLE 2. Effect of the size of the protecting group in the nucleotide component on the yield of the dinucleoside phosphate.

| Nucleotide component | Nucleoside component | Yield of dinucleoside phosphate, % |
|---|---|---|
| 3′-*O*-Acetylthymidine-5′ phosphate | 5′-*O*-acetylthymidine or 5′-*O*-tritylthymidine | 60 |
| 5′-*O*-Tritylthymidine-3′ phosphate | 3′-*O*-acetylthymidine | 45 |
| 5′-*O*-Acetylthymidine-3′ phosphate | » | 81 |
| 5′-*O*-Trimethylacetylthymidine-3′ phosphate | » | 73 |
| 5′-*O*-Mesitylthymidine-3′ phosphate | » | 60 |
| *NO*$^{2}$-bis(di-*p*-APM)-deoxyguanosine-5′ phosphate | 5′-*O*-di-*p*-APM-thymidine | 12 |

workers[16] showed that, when equimolar amounts of both components and a fivefold excess of DCC are employed, the reaction rates are approximately the same, the yields varying from 60 to 76%. However, it should be noted that both the rate and the yield of the reaction greatly depend on the size of the protecting group in the nucleotide component[67,68] (Table 2)‡.

A 100% excess of one component raises the yield to 96–100% with respect to the second component[14]. Addition of a second mole of the nucleotide component at the end of the reaction does not increase the yield whilst addition of a second mole of the nucleoside component at the end of the reaction makes the yield almost quantitative. It is believed that the nucleoside component disappears as a result of a side-reaction[14,68]. In the reaction of deoxyribonucleotides the condensation proceeds in the same way regardless of the carbon atom in the carbohydrate residue to which the reacting groups are attached[14], but it is usual to condense nucleoside-5′ phosphates with nucleosides having a free 3′-OH group, since deoxyribonucleoside-5′ phosphates are more readily available than the 3′-phosphates and the derivatives of deoxyribonucleosides with a free 5′-OH group are in many cases unstable. On the other hand, for the specific synthesis of diribonucleoside phosphates, it is more convenient to use a procedure involving the condensation of protected ribonucleoside-3′ phosphate with a ribonucleotide having a free 5′-OH group, since ribonucleosides with a free 3′-OH group are virtually unavailable[26].

A study has been made of the mechanism of the formation of the phosphodiester linkage in the condensation of nucleotide and nucleoside derivatives in the presence of DCC.[15,42,67–71] It is believed that the first stage of the reaction is activation of the nucleotide component (XXXII) with formation of a protonated adduct (XXXIII), the alcoholysis of which with an excess of the nucleoside component (XXXIV) yields the dinucleoside phosphate (XXXV). (XXXIII), or its metaphosphate (XXXVI), forms the pyrophosphate (XXXVII) preferentially when stoichiometric amounts of (XXXII) and (XXXIV) are used. Actually in a study of the reaction of 5′-*O*-acetylthymidine (XXXVIII) with 3′-*O*-acetylthymidine-5′ phosphate (XXXIX) Khorana and coworkers[15] showed that in the first few minutes $P^1P^2$-di-(3′-*O*-acetylthymidine-5′) pyrophosphate (XL) is formed. Since pyrophosphates are not effective as phosphorylating agents, the next stage in the synthesis must be further activation of (XXXVII). This activation is inhibited by water or strong bases (such as tri-n-butylamine), addition of which results in pyrophosphates being the final reaction products[70], a fact which has been widely used for the synthesis of coenzymes and related compounds[72]:

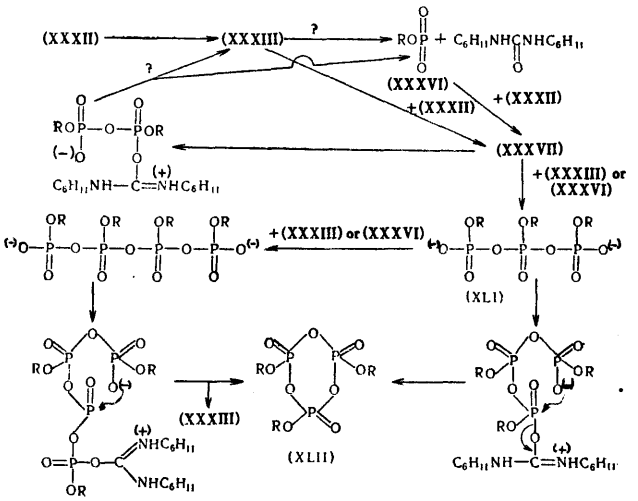



Study of substances obtained on treatment of (XXXIX) and (XL) with DCC in dry pyridine for 10–30 min established[68] that the main reaction product is $P^1P^2P^3$-tri-(3′-*O*-acetylthymidine-5′) triphosphate [(XLI), R = 3′-*O*-acetylthymidine-5′] in both cases. It is believed that the actual active phosphorylated intermediate is not (XLI) but the trimetaphosphate (XLII), which is readily converted into (XLI) in the presence of water[67,68]. Since trimetaphosphates are very labile[72,73], it was impossible to demonstrate directly the presence of (XLII) (R = 3′-*O*-acetylthymidine-5′) in the reaction mixture. However, model experiments with the more readily accessible ethyl phosphate confirmed the formation of (XLII) ($R = C_2H_5$), which is identical with the compound obtained in a preliminary experiment from silver trimetaphosphate and ethyl iodide[73]. The monomeric metaphosphate (XXXVI), which Todd regarded as an intermediate phosphorylating agent[74,75], can probably form as a short-lived intermediate, but according to Khorana[68] it is more likely to be attacked by the second phosphate anion (XXXII) than by the neutral hydroxy-group of (XXXIV). The possible reaction pathways of (XXXII) and (XLII) have been represented schematically by Weimann and Khorana[68] (see p. 27).

‡ More detailed information about the kinetics of the synthesis of the $C_3'-C_5'$ linkage in the presence of DCC is given in the paper of Khorana and coworkers[69] published after this review had been written.

### 3. The Use of Other Reagents for the Synthesis of the Specific $C_{3'}-C_{5'}$ Internucleotide Bond

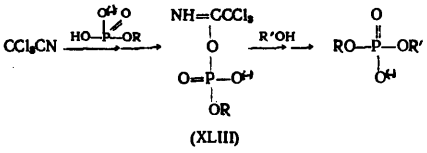
Apart from DCC, *p*-toluenesulphonyl chloride[13], mesitylenesulphonyl chloride[76], trichloroacetonitrile[77], carbonyldiimidazole[78,79], ethoxyacetylene[80-83], and *N*-alkyl-(methyl- or ethyl)-5-phenylisoxazolium salts have been proposed as activating agents for the synthesis of the $C_{3'}-C_{5'}$ linkage§[84,86].




Schematic representation of the formation of the trimetaphosphate (XLII) from the monoalkyl phosphate (XXXII).

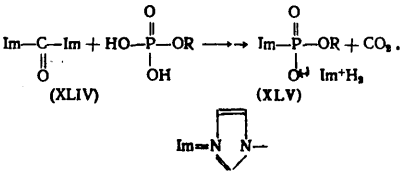
Condensation of the nucleoside and nucleotide components in the presence of *p*-toluenesulphonyl chloride also gives satisfactory yields of dinucleoside phosphates[15], but an excess of the reagent gives rise to the formation of side-products, in particular mixtures of polymers. The mechanism of the formation of the phosphodiester linkage in the presence of *p*-toluenesulphonyl chloride has not been studied in detail, but it has been suggested that the nature of the initial phosphorylating agent is the same as for the condensation in the presence of DCC¶.[68]

When a phosphomonoester is dissolved in a mixture of trichloroacetonitrile and pyridine, reactive intermediates — imidoylphosphates (XLIII)[92-95] — are formed and react with alcohols to give asymmetric phosphodiesters:




These observations were of interest for the development of methods of synthesis of the $C_{3'}-C_{5'}$ phosphodiester linkage. However, the first attempt to prepare thymidilyl-(3′→5′)-thymidine by the condensation of 5′-*O*-tritylthymidine-3′ phosphate with 3′-*O*-acetylthymidine in the presence of trichloroacetonitrile at room temperature over a period of 64 h was unsuccessful, the main product being $P^1P^2$-dithymidine-3′ pyrophosphate[14].

Carbonyldiimidazole (XLIV)[78,79] reacts with phosphomonoesters which are quantitatively converted into the imidazolides (XLV); these can be readily isolated as salts and possess phosphorylating properties[96]:

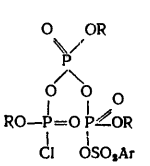



(XLV) forms phosphodiesters with alcohols but its application to the synthesis of the $C_{3'}-C_{5'}$ linkage is so far unknown†.

To compare the different activating agents, a study was made of the formation of thymidylyl-(3′→5′)-thymidine from (a) 5′-*O*-acetylthymidine-3′ phosphate and 3′-*O*-acetylthymidine or (b) from (XXXIX) and 5′-*O*-tritylthymidine, taken in stoichiometric amounts, at room temperature in pyridine in the presence of a 100% excess of *p*-toluenesulphonyl chloride or mesitylenesulphonyl chloride or a fourfold excess of DCC, ethoxyacetylene, or *N*-ethyl-5′-phenylisoxazolium fluoroborate[87,97]. It was found that the use of ethoxyacetylene in method (a) yields the symmetrical pyrophosphate after 96 h. The isoxazolium salt and DCC give approximately the same yield of the dinucleoside phosphate (68%). The sulphonyl chlorides proved to be the most effective in method (b): the yield of thymidylyl-(3′→5′)-thymidine in the presence of *p*-toluenesulphonyl chloride was 78% after 6 h, while in the presence of mesitylenesulphonyl chloride it was 71% after 1 h and 90% after 20 h. The use of activating agents such as mesitylenesulphonyl chloride permits the synthesis of the more soluble trialkylammonium salts of mononucleotides, which is impossible in the case of DCC and isoxazolium salts, since, as already mentioned, trialkylamines then lead to the formation of pyrophosphates[70].

§ The results of the use for this purpose of ethyl metaphosphate[88,89] and the product of the addition of phosgene to dimethylformamide[90,91] have also been published[87]. It was found that the first compound does not have any practical value for the synthesis of $C_{3'}-C_{5'}$ linkages, while the second gives a 30–40% yield of the dinucleoside phosphate, but side-reactions are possible.

¶ According to the latest data[87], the phosphorylating agent is in this case much more reactive than in the condensation in the presence of DCC and probably consists of the product of the addition of sulphonyl chloride to the trimetaphosphate:

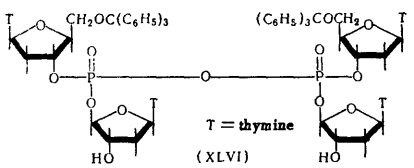


† The first attempt to obtain a dinucleoside phosphate was unsuccessful[87].

4. Synthesis of Oligonucleotides with the $C_{3'}-C_{5'}$ Bond

The methods of synthesis of oligonucleotides with a specific internucleotide bond must provide for the formation of such a bond when either the nucleoside or the nucleotide component or both simultaneously contain phosphodiester groups.

Khorana and coworkers[14,42] established that high-molecular-weight mixed oligonucleotides can be obtained by the usual methods of synthesis of dinucleoside phosphates. Three versions of the general procedure were examined. In the first version[42] the phosphodiester group was included in the nucleoside component: 5'-*O*-tritylthymidine-(3'→5')-thymidine was treated in pyridine with an excess of DCC for 1 h, to avoid the formation of an anhydride (XLVI), and then with two equivalents of 3'-*O*-acetylthymidine-5' phosphate for two days at room temperature. After treatment with alkali to remove the acetyl group, 5'-*O*-tritylthymidylyl-(3'→5')-thymidylyl-(3'→5')-thymidine was obtained in 68% yield, which after hydrogenation gave thymidylyl-(3'→5')-thymidylyl-(3'→5')-thymidine (83%). Thymidylyl-(3'→5')-deoxyadenylyl-(3'→5')-deoxycytidine[42] and thymidylyl-(3'→5')-deoxycytidylyl-(3'→5')-deoxycytidine[98] were obtained similarly.



(XLVI)

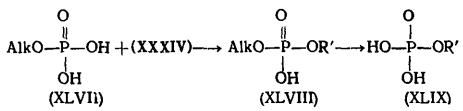
In the second version the phosphodiester group was included in the nucleotide component: 5'-*O*-tritylthymidylyl-(3'→5')-thymidylyl-(3'→5')-thymidine was obtained by the carbodiimide method in 49% yield from 5'-*O*-tritylthymidylyl-(3'→5')-thymidine-3' phosphate and 3'-*O*-acetylthymidine. Finally, the condensation was carried out with the phosphodiester group in both components: 5'-*O*-tritylthymidylyl-(3'→5')-thymidylyl-(3'→5')-thymidylyl-(3'→5')-thymidine was obtained from 5'-*O*-tritylthymidylyl-(3'→5')-thymidine-3' phosphate and thymidylyl-(3'→5')-3'-*O*-acetylthymidine in 23% yield[14]‡. The structure of the oligonucleotide was in all cases confirmed by enzymic hydrolysis. Thus it is possible to increase the chain length by stepwise synthesis of polynucleotides using components already containing internucleotide bonds. The optimum conditions for the stepwise synthesis of oligonucleotides with a specific internucleotide bond cannot be regarded as finally established. In particular, it should be borne in mind that the solubility of intermediate compounds diminishes with increase in chain length and this must complicate the requirements which have to be met by protecting groups.

‡ Recent communications have described the preparation of two triribonucleotides[99,100]: uridylyl-(3'→5')-uridylyl-(3'→5')-uridine (yield 80%) and adenylyl-(3'→5')-uridylyl-(3'→5')-uridine (yield 75%), two tetranucleotides: thymidylyl-(3'→5')-deoxycytidylyl-(3'→5')-deoxycytidylyl-(3'→5')-deoxycytidine[101] (yield 59%) and uridylyl-(3'→5')-adenylyl-(3'→5')-uridylyl-(3'→5')-uridine[100] (yield 75%), and two pentanucleotides: thymidylyl-(3'→5')-deoxyadenylyl-(3'→5')-thymidylyl-(3'→5')-thymidylyl-(3'→5')-thymidine[102] (yield 12%) and deoxycytidylyl-(3'→5')-deoxyguanylyl-(3'→5')-deoxycytidylyl-(3'→5')-deoxycytidylyl-(3'→5')-deoxycytidine[101] (yield 15–17%).

## IV. METHODS OF SYNTHESIS OF OLIGONUCLEOTIDES WITH A FREE PHOSPHOMONOESTER GROUP

True oligonucleotides, i.e. oligonucleotides with a free phosphate residue at the end of the polynucleotide chain, are obtained in two ways: either by introducing the phosphate residue into the oligonucleotide itself or by synthesising the phosphodiester linkage from the nucleoside component in which the phosphate group is protected.

The phosphate residue is nowadays introduced into the oligonucleotide by a method based on the condensation of the alcohol (XXXIV) and the monoalkyl phosphate (XLVII) in the presence of DCC:



(XLVII) (XLVIII) (XLIX)

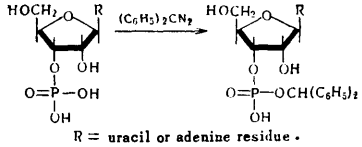
(XLVII) is chosen in such a way that the alkyl group is selectively removed after the formation of the phosphodiester (XLVIII), the final result of the reaction being the conversion of (XXXIV) into its phosphate (XLIX).[103] The phosphorylating agents investigated were monobenzyl phosphate[68,70], β-cyanoethyl phosphate[104], and tetra-*p*-nitrophenyl pyrophosphate[105]. β-Cyanoethyl phosphate, which in contrast to other phosphorylating agents is stable and becomes active only in the presence of DCC, proved to be the most convenient for the phosphorylation of oligonucleotides[106]. Since DCC is always used in a large excess, the reaction does not require absolutely anhydrous conditions. Usually a 1.5–2-fold excess of β-cyanoethyl phosphate is employed for phosphorylation. The excess of the reagent is completely decomposed after 5 min in 1 *N* sodium hydroxide at 100° and after 30 min in 0.1 *N* sodium hydroxide at 100°. The β-cyanoethyl group is removed from the nucleotide after 2 min at 100° in 1 *N* sodium hydroxide while at 50° in 0.1 *N* sodium hydroxide the rate of removal is much lower than in the reagent itself. 2 *N* sodium hydroxide removes the β-cyanoethyl group from the dinucleotide derivative in about 1 min at 0°,[14] i.e. the group can probably be selectively eliminated in the presence of certain other protecting groups, such as *N*-benzyl groups, in purine and pyrimidine bases. Free amino-groups are phosphorylated by β-cyanoethyl phosphate but the resulting phosphoramidate bonds can be readily broken: in the case of guanosine and adenosine in a weakly acid or even neutral medium and in the case of cytidine in a weakly alkaline or neutral medium on heating to 100°. Glycoside bonds are not broken under these conditions. This method was used to phosphorylate 5'-*O*-tritylthymidylyl-(3'→5')-thymidine[14], which was treated with an excess of a mixture of β-cyanoethyl phosphate and DCC, the mixture containing three times more DCC than β-cyanoethyl phosphate. When the above reagents are present in an equimolar ratio, the yield of the phosphorylated product does not exceed 23% even if the mixture were taken in a fivefold excess with respect to the dinucleoside phosphate. After treatment of the phosphorylation product with alkali, the pure dinucleotide was isolated in 68% yield. 5'-*O*-Phosphorylthymidylyl-(3'→5')-thymidine-3' phosphate and the tetranucleotide thymidylyl-(3'→5')-thymidylyl-(3'→5')-thymidylyl-(3'→5')-thymidine-3' phosphate[14] were obtained similarly from thymidylyl-(3'→5')-thymidine[52]. Thymidylyl-(3'→5')-thymidine-3' phosphate was also obtained using tetra-*p*-nitrophenyl pyrophosphate[15].

Another phosphorylating agent which has been used is dibenzyl phosphorochloridate[15]: thymidylyl-(5′→3′)-thymidine-5′ phosphate was obtained as the sodium salt in 50% yield. Phosphorylation of 5′-*O*-tritylthymidylyl-(3′→5′)--thymidine gives thymidylyl-(3′→5′)-thymidine-3′ phosphate in low yield, probably because of the relatively low activity of the secondary 3′-OH group.

The second method of preparing oligonucleotides with a terminal phosphomonoester group, based on a nucleoside with a protected phosphate group as one of the starting materials, has been used in several versions, differing in the nature of the protecting groups in the phosphate residue being "introduced" and in the condensation conditions. Thymidylyl-(5′→3′)-thymidine-5′ phosphate was obtained from 3′-*O*-acetylthymidine-5′ phosphate and thymidine-5′ dibenzyl phosphate using DCC.[15,18] The benzyl groups were removed by hydrogenation in 10% acetic acid in the presence of palladium oxide on barium sulphate[107] and the acetyl group by mild alkaline treatment. The crystalline trisodium salt of the dinucleotide was isolated in a yield not exceeding 40%. The relatively low yield is probably due to complications which arise as a result of the monodebenzylation of the dibenzyl phosphate group. Lowering of the temperature to 0° hardly increases the yield: condensation of *NO*$^{3'}$-diacetyldeoxyadenosine-5′ phosphate with thymidine-5′ dibenzyl phosphate followed by removal of the protecting groups gave 40% of deoxyadenylyl-(5′→3′)--thymidine-5′ phosphate[15].

The use of β-cyanoethyl derivatives of nucleoside phosphates as the nucleoside components was more successful[14]: 5′-*O*-tritylthymidine-3′ phosphate and thymidine-3′ β-cyanoethyl phosphate were condensed in the presence of DCC, using 1 : 1, 2 : 1, and 1 : 2 ratios of the initial components. The yield of the dinucleotide was approximately the same in all the experiments (55–60%). It is interesting that with the 1 : 1 ratio the condensation proceeds better if the nucleoside component contains the phosphate group: when 3′-*O*-acetylthymidine was used instead of thymidine-3′ β-cyanoethyl phosphate, the yield of the dinucleoside phosphate was 45% instead of 55–60% in the case of the dinucleotide. Condensation of 5′-*O*-tritylthymidylyl-(3′→5′)-thymidine-3′ phosphate with 1.5 moles of thymidine-3′ β-cyanoethyl phosphate gave thymidylyl-(3′→5′)-thymidylyl-(3′→5′)--thymidine-3′ phosphate in 44% yield.

It has also been suggested that the hydroxy-group in the phosphate residue could be protected with a t-butyl group[86] which is introduced by the trichloroacetonitrile method[108] and is removed with 20% acetic acid. In addition, the reaction with diphenyldiazomethane may be used for this purpose[86]:




R = uracil or adenine residue.

Because of the large size of the diphenylmethyl residue, the 2′-OH group becomes "inaccessible" and does not participate in condensation. This method has been used to prepare the first synthetic diribonucleotide, uridylyl--(3′→5′)-uridine-3′ phosphate[108]: the pyridinium salt of 5′-*O*-acetyl-2′-*O*-THP-uridine-3′ phosphate[48] was reacted with the ammonium salt of uridine-3′ diphenylmethyl phosphate in the presence of a sevenfold excess of DCC in pyridine. After four days the protecting groups were removed and uridylyl-(3′→5′)-uridine-3′ phosphate was isolated in 30% yield. Uridylyl-(3′→5′)-adenosine-3′ phosphate (yield 39%) was synthesised similarly.

In one of the latest papers on stepwise synthesis of oligonucleotides with the $C_{3'}$–$C_{5'}$ linkage[98] it is suggested that the introduction of the phosphomonoester group be carried out by transphosphorylation, using phenyl phosphate and the appropriate enzyme[109].

All the oligonucleotides synthesised, starting with dinucleoside phosphates, are listed in Table 3.

TABLE 3. Synthetic oligonucleotides with the $C_{3'}$–$C_{5'}$ linkage.

| Substance | References | Substance | References |
|---|---|---|---|
| Thymidylyl-(3′→5′)-thymidine | 13–16, 69 | Thymidylyl-(3′→5′)-thymidine-3′ phosphate | 15 |
| Thymidylyl-(3′→5′)-deoxyguanosine | 16,69 | Uridylyl-(3′→5′)-uridine-3′ phosphate | 108 |
| Thymidylyl-(3′→5′)-deoxyadenosine | 15,16,42, 69 | Uridylyl-(3′→5′)-adenosine-3′ phosphate | 108 |
| Thymidylyl-(3′→5′)-deoxycytidine | 15 | Thymidylyl-(3′→5′)-thymidylyl--(3′→5′)-thymidine | 14,42 |
| Deoxycytidylyl-(3′→5′)-thymidine | 15,16,69 | Thymidylyl-(3′→5′)-deoxyadenylyl--(3′→5′)-deoxycytidine | 42 |
| Deoxycytidylyl-(3′→5′)-deoxycytidine | 16,69 | Uridylyl-(3′→5′)-uridylyl-(3′→5′)--uridine | 99,100 |
| Deoxycytidylyl-(3′→5′)-deoxyguanosine | 16,69 | Adenylyl-(3′→5′)-uridylyl-(3′→5′)--uridine | 99,100 |
| Deoxyguanylyl-(3′→5′)-deoxycytidine | 16,69 | (5′-Phosphoryl)thymidylyl--(3′→5′)-deoxycytidylyl-(3′→5′)--deoxycytidine | 98 |
| Deoxyguanylyl-(3′→5′)-thymidine | 16,69 | Thymidylyl-(3′→5′)-thymidylyl--(3′→5′)-thymidylyl-(3′→5′)--thymidine | 14 |
| Deoxyguanylyl-(3′→5′)-deoxyguanosine | 15,16,69 | Thymidylyl-(3′→5′)-deoxycytidylyl--(3′→5′)-deoxycytidylyl-(3′→5′)--deoxycytidine | 101 |
| Deoxyadenylyl-(3′→5′)-thymidine | 15,16,69 | Uridylyl-(3′→5′)-adenylyl-(3′→5′)--uridylyl-(3′→5′)-uridine | 100 |
| Uridylyl-(3′→5′)-uridine | 7,36 | Thymidylyl-(3′→5′)-deoxyadenylyl--(3′→5′)-thymidylyl-(3′→5′)-thymidylyl-(3′→5′)-thymidine | 102 |
| Adenylyl-(3′→5′)-adenosine | 26 | Deoxycytidylyl-(3′→5′)-deoxyguanylyl-(3′→5′)-deoxycytidylyl--(3′→5′)-deoxycytidylyl-(3′→5′)--deoxycytidine | 101 |
| Uridylyl-(3′→5′)-cytidine | 26 | | |
| Uridylyl-(3′→5′)-adenosine | 7,26 | | |
| Cytidylyl-(3′→5′)-uridine | 49 | | |
| Uridylyl-(3′→5′)-azauridine | 48 | | |
| Cytidylyl-(3′→5′)-azauridine | 49 | | |
| (5′-Phosphoryl)thymidylyl--(3′→5′)-thymidine | 15,18 | | |
| (5′-Phosphoryl)thymidylyl--(3′→5′)-deoxyadenosine | 15,18 | | |


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# RECENT DEVELOPMENTS IN METAL CHEMISTRY

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## 1. HISTORICAL

Metals and alloys have played an important role in the development of human civilisation since the earliest times. However, they have only been the object of scientific investigation since the 17th–18th centuries. The development of the chemical approach to the formation of alloys is discussed in a number of papers [1-6].

Mendeleev's Periodic Law[7] of the chemical elements was by far the most important single contribution to the understanding of the regularities of chemical interactions between metals. The application of this law to the study of interactions between metals is due to Kurnakov[8]. It was he who proposed the term "metallic compounds or metallides", now widely used in the chemistry and physics of metals and in metal science, for the compounds formed by the combination of metals. The term will be used in the present article [but is hereafter translated "intermetallic compounds" (Ed. of Translation)].

The thermodynamic works of Gibbs[9] were of the utmost relevance to the development of equilibrium studies in chemical systems, including metallic systems. His papers on heterogeneous equilibria, as interpreted by Kurnakov, led to the creation of an international language based on the geometrical representation of the equilibrium diagrams of systems. Since the beginning of the 20th century, the work of Tammann[10], Roberts-Austen[11], Le Châtelier[12], and Howe[13] has contributed to progress in this direction. Systematic studies of metal interactions and of equilibrium and phase transformation diagrams received further impetus from the general advances in physicochemical analysis[14,15], metallography[16-19], and physical metallurgy[20-23].

## 2. DEFINITION OF THE SCIENCE OF METAL CHEMISTRY

The chemical approach to the science of alloys, which began with Kurnakov's application of the Periodic Law and with his equilibrium studies, has been called the chemistry of alloys[24,25], but is now unified under the general heading of metal chemistry[26-28]. This science straddles the boundary between inorganic and physical chemistry, and is also related to crystal chemistry, solid state physics, and metallography.

The general problems with which metal chemistry is concerned, identified during its development, were formulated as follows in a paper[28] presented to the Plenary Session of the Division of Chemical Sciences of the Academy of Sciences of the USSR in 1956: "the study of chemical interactions involving the metallic elements of the Periodic Table, with each other or with metalloids, with formation of solutions and compounds showing metallic and covalent bond character, and the establishment of the general principles underlying the formation, structure, and properties of this broad range of solutions and compounds of metals as a function of their composition".

Metal chemistry is a subdivision of inorganic chemistry, dealing with the formation (as a result of the interaction between atoms of metals and metalloids) of solid solutions or of intermetallic compounds of variable or fixed composition. These compounds do not, as a rule, obey the theory of valency thus: the chemistry of metallic solutions and intermetallic compounds is richer and more comprehensive than the chemistry of compounds of non-metals.

There is no class of inorganic (or, indeed, of organic) compounds, in which the tendency towards isomorphic substitution or introduction of foreign atoms into the crystal lattice is developed as strongly as in the formation of various metallic solid solutions. In this respect, only the very large number of naturally occurring inorganic materials is at all comparable with metallic solid solutions and intermetallic compounds: these are the minerals, which can show a strong tendency towards isomorphic substitution of compounds within a series (for example, oxides, sulphides, silicates, etc.), and iron meteorites, which consist mainly of solid solutions of iron, nickel, and cobalt.

Metal chemistry encompasses the chemical reactivity problems of more than 80 metals of the Periodic Table. Many products of the reaction of metals with non-metals (boron, carbon, silicon, and to a lesser extent oxygen, nitrogen, etc.) also show metallic or covalent bond character. Solutions and compounds of metals with these non-metals are also studied in metal chemistry, and in many respects these compounds can be visualised as cross-links between purely metallic compounds and compounds having a covalent or ionic bond character.

It is the purpose of metal chemistry to study: (1) the principal factors which determine the interaction between metals; (2) the formation of solid solutions between metals; (3) the formation of intermetallic compounds; (4) the crystal chemistry of reactions in metallic systems; (5) interactions between intermetallic compounds.

These problems continue to be the object of extensive investigations by chemists, physicists, and metallurgists. Very many papers in this field have been published in the past 50 years. A number of contemporary problems in metal chemistry were discussed at a special symposium on the physical chemistry of metallic solutions held in London[29].

## 3. PRINCIPAL FACTORS WHICH DETERMINE THE INTERACTION BETWEEN METALS

The conditions leading to the formation of complex substances with metallic bond character have not yet been definitely established. Problems concerning the electron distribution and the chemical bond character in complex metallic solutions and intermetallic compounds are particularly difficult. However, there are a few generally accepted physicochemical factors[18-29] which appear to determine, largely if not completely, the conditions of formation of metallic solid solutions and intermetallic compounds.

The most important condition for characterising the reactions between metals is their relative position in the Periodic Table, which determines similarities and differences in the electronic structure of the atoms and in the physicochemical properties of the elements.

Generalising the opinions expressed by various authors, we can accept the view that the nature of the interaction of metals with each other and with metalloids is very largely determined by the following factors: (1) the atomic radii; (2) the position in the electronegativity series of the elements; (3) the valency and ionisation potential.

None of these factors, taken in isolation, can explain the nature of the reactivity of metals. Correct conclusions can only be reached by considering them as interrelated factors.

### Atomic Radii

Many reactions between metals differ from normal chemical reactions (such as ionic, molecular, etc.) by having an atomic mechanism and by forming solutions and compounds in which the bond between the atoms is typically metallic. From this point of view, interatomic distances (which are determined by the atomic radii of the elements) acquire a special significance.

Atomic radii, like many other properties of the elements, exhibit a strong periodicity when plotted against atomic number. Atomic radii are shown in Fig. 1. In contrast to earlier methods of presentation by periods, the atomic radii are arranged by groups of the Periodic Table. In this scheme, the elements beryllium, boron, and aluminium are assigned to the B subgroups of second and third Groups II and III, because this provides greater continuity of the atomic radii than the alternative assignment to the A subgroups.

Nekrasov's "Course of General Chemistry"[30] mentions further examples of the similarity in chemical properties between beryllium and the metals of the zinc subgroup and aluminium. Also in the electronegativity series of the elements, beryllium is adjacent to the metals of subgroup IIB (see below).

As regards atomic radii, all the elements can be classified into three families: one includes the elements of moderately high atomic radius, the other two families include the elements at either extreme of the range of atomic radii.

Inspection of Fig. 1 shows the following characteristic features: the largest atomic radii are found with the metals of low atomic number of subgroups IA and IIA, that is, the most typically metallic elements; the smallest radii apply to the typical metalloids — B, C, N, O, H — found in the B subgroups of Groups III–VII. Within this series of elements the atomic radius decreases continuously from B to H. Heavy metals (of high atomic number) in those groups, such as In, Tl, Sn, Pb, Sb, Bi, Te, and Po, also show an increase in atomic radius with increasing atomic number. Metals belonging to transition groups (from III to VIII) and having unfilled *d*-electron shells, and also metals of Groups I and II (subgroup B) have intermediate values of the atomic radius, and most of them belong to the first family.

Within any one group, the atomic radius of the elements changes in the sense of continuous decrease with decrease in atomic number. Very closely similar elements, such as Ti, Zr, Hf; V, Nb, Ta; Mo, W; Fe, Co, Ni; Ag, Cu; and others, have very similar atomic radii.

The similarity (or the difference) in atomic radii of the elements, in conjunction with other properties of the reacting atoms, exerts a decisive influence on the interaction between metals, particularly as regards the formation of solid solutions.

### Position in the Electronegativity Series of the Elements

The second factor which determines whether a reaction of metallic character is possible is the position of the metals in the electronegativity series of the elements. In spite of the great importance of this factor in chemical reactions[31-37], its application to metal chemistry has attracted little attention. The concept of electronegativity[31,34,36]

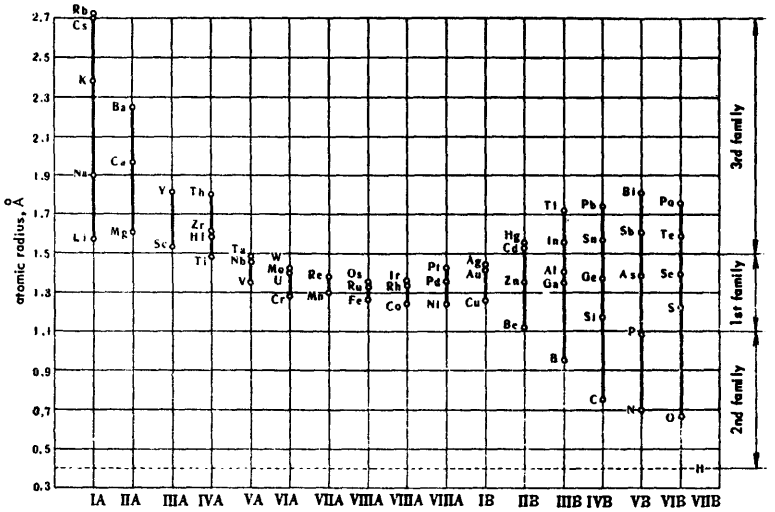



Fig.1. Variation of the atomic radii of the elements with their position in the groups of the Periodic Table.

embraces all the properties of an element stemming from the behaviour of the outer electrons of the atom. As a rule an element is electropositive if it shows a predominant tendency to give up electrons, and it is electronegative if its electron affinity is greater. The electronegativity difference between atoms A and B during formation of a chemical bond can be identified with the extent of electron transfer from atom A to atom B. The theory of this process is discussed in a number of monographs and reviews[31-35]: the conclusion is that metals are the most electropositive elements, and non-metals the most electronegative.

The electronegativity of the elements is arranged in an arbitrary series such that each element is electropositive with respect to the following element and electronegative with respect to the preceding element. In accordance with the project on the nomenclature of inorganic compounds set up by the Commission on the Nomenclature of Chemical Compounds, of the Division of Chemical Sciences of the Academy of Sciences of the USSR[36], the arbitrary electronegativity series for metals and non-metals is reproduced in Table 1.

It can be seen from Table 1 that the most electropositive metals are those of the alkali and alkaline earth series (with the exception of beryllium), whilst the metals of the B subgroups and beryllium are the most electronegative. These groups of metals are separated by braces in the table. Thus, as we have already pointed out, beryllium is situated close to aluminium from the standpoint of this important chemical property, and its behaviour towards other metals resembles that of aluminium rather than that of magnesium.

The transition group metals are situated between these two extreme poles corresponding to the electropositive and the electronegative metals. This series begins with actinium and ends with nickel, the most electronegative element of this group. In Table 1, the transition group is also separated from the other groups by a brace.

With very few exceptions, the electronegativity of metals within a group increases from bottom to top (see Table 1) with decreasing atomic number: for example U–W–Mo–Cr, etc. The exceptions are lithium, magnesium, beryllium, and tin, which occupy more electronegative positions than their analogues. The non-metals, bracketed together at the bottom of the table, show large deviations from electronegativity sequence within a group.

TABLE 1. Electronegativity series of the elements.

| | |
|---|---|
| Fr—Cs—Rb—K—Na<br>Ra—Ba—Sr—Ca—Li—Mg | electropositive metals |
| Ac—La—lanthanides—Y<br>Sc—Th—Hf—Zr—Ti<br>Pa—Ta—Nb—V<br>U—W—Mo—Cr<br>Re—Os—Ir—Pt<br>Tc—Ru—Rh—Pd<br>Mn—Fe—Co—Ni | transition group metals |
| Au—Ag—Cu—Hg—Cd—Zn<br>Tl—Pb—In—Ga—Al—Be<br>Bi—Sn—Sb—Ge | electronegative metals |
| Si—B—Te—As—P—C—H—At →<br>← Se—S—N—Br—Cl—O—F | non-metals |

The position of an element in the electronegativity series plays two important roles: it establishes the cause of the formation of solid solutions and intermetallic compounds and it explains the gradual transition from metallic compounds through covalent compounds to ionic compounds. The arbitrary electronegativity series of the elements helps to systematise the designation of intermetallic compounds.

In naming inorganic compounds, the most electropositive metal should be taken to be the electropositive part of the compound, and all the other elements present should be taken to be the electronegative part according to their position in the electronegativity series. As proposed by the above-mentioned Commission[36], the electropositive metal is written first in the formula of the compound. This basis of classification can also be used for naming intermetallic compounds†.

† The order in Table 1 is not that given in the 1957 IUPAC rules (Ed. of Translation).

The order in which the elements of ternary and more complex intermetallic compounds are written is the following: the most electropositive metal is written first in the formula, followed by the other elements in order of decreasing electropositivity. By analogy with Kurnakov's terms "metallic compounds" or "metallides", we may use the terms aluminides, beryllides, borides, carbides, nitrides, etc. All such generic names for intermetallic compounds are derived from the name of the electronegative elements present in the compounds.

## Valency and Ionisation Potential

The main factor which controls chemical reactions between elements is, of course, their valency.

The number of valency or outer electrons frequently ensures that the atoms in the resulting chemical compounds are present in stoichiometric ratios.

The number of valency electrons in interacting metals, and their quantum state, play an important part in determining the limiting concentrations of solid solutions and the composition of intermetallic compounds. The valency of the elements, like the properties discussed above, depends on their position in the Periodic Table. The most electropositive metals (Group I) have one outer electron; the number of these electrons increases as the number of the group increases, to six for metals and to seven for non-metals.

The increase in the number of outer electrons and in the interatomic binding force is reflected by a decrease in interatomic distance and in other properties of the metals, which show a gradual increase in density, in melting point, in hardness, in yield point, in elastic modulus, and a decrease in compressibility coefficient.

The binding force of electrons within the atom is determined by the ionisation potential, which is measured by the energy required to remove the outer (valency) electrons from the atom[31-34].

The first ionisation potentials of the elements of the Periodic Table are reproduced in Fig. 2 (after Vedeneev *et al.*[34]). Again, they are arranged in groups rather than by atomic number. From these data we can say that the most electropositive metals (Group I) have the lowest ionisation potentials, and that the ionisation potential increases with increasing group number: this is evident from Fig. 2. Another characteristic feature is that the transition group metals show very small differences in electronegativity irrespective of the number of outer electrons. This is a very significant factor in the formation of a wide class of solid solutions based on these metals.

With certain exceptions, the ionisation potential decreases within a group as the atomic number of the element increases. Metallic elements differ from non-metals in having lower ionisation potentials: this is particularly striking with elements of one and the same group. Thus, the ionisation potential of Group IVB elements, with the same number of outer electrons, drops sharply on going from C to Si, and more gradually on going from Si towards the more metallic elements Ge, Sn, and Pb (see Fig. 2). The ionisation potentials of the Group VB elements cover a wider range, that of nitrogen being highest, those of phosphorus and arsenic also quite high, and similar, and those of antimony and bismuth not far from the values

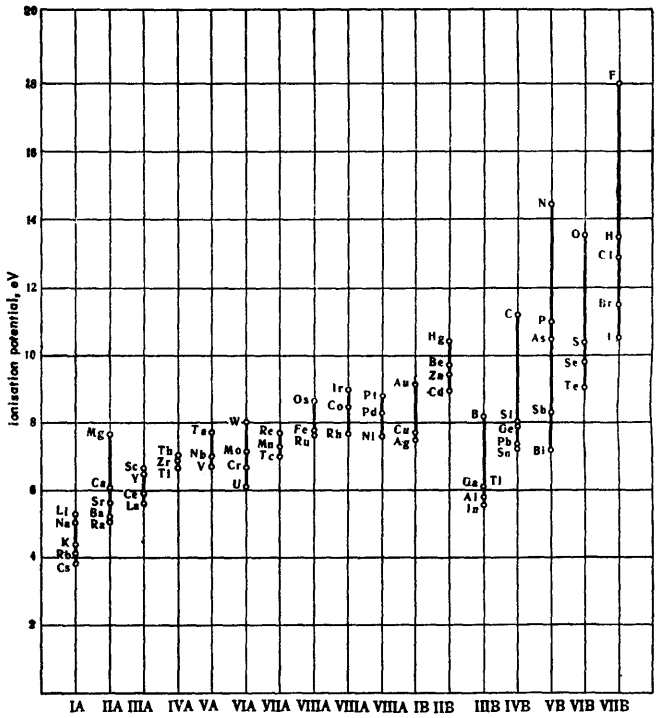



Fig. 2. Ionisation potential (first) of the elements arranged in groups of the Periodic Table.

typical of metals. Hence we can say that metals of low ionisation potential tend to give up their outer electrons during ordinary chemical reactions, whereas non-metals (large ionisation potential) readily accept electrons. Accordingly, reactions between metals and non-metals will produce compounds of ionic bond type.

Metal chemical reactions, in contrast to ordinary chemical reactions, show a characteristic tendency to form crystalline phases in which the electrons reside in the interionic regions, and can move with relative ease. This peculiarity of the collective distribution of valency electrons in the crystal lattice of complex metallic substances, without directional bonds, is highly typical of many metallic solutions and compounds. As a consequence, many products of metal chemical reactions have the metallic type of chemical bond.

By studying the physicochemical nature of metallic solid solutions, and the transition from solid solutions to compounds, it is easy to demonstrate a gradual change in chemical bond type and to relate it to the respective positions of the constituent elements in the Periodic Table. The wide spectrum of bond types observed in the products of reactions between metals, varying from purely metallic to ionic, demonstrates the fundamental status of the Periodic Law in the theory of metallic alloys.

## 4. FORMATION OF SOLID SOLUTIONS OF METALS

The term solid solutions (literally, "solidified solutions") first appeared in the literature in a report by Matthiessen[6], who studied the electrical conductivity of alloys as a function of composition, and was able to distinguish chemical

compounds, "solidified solutions", and mechanical mixtures of two metals from the shape of the "composition–property" curves. Following the development of the theory of phase equilibria, the concept of solid solutions achieved a wider significance, and was extended to include all solid phases of variable composition: isomorphous mixtures of metals, silicates, and other inorganic and organic systems. Thus, its influence has spread to all the fundamental types of equilibrium diagram for chemical systems[9,14,15,38,39].

The discovery of X-rays and their application to the study of the crystal structure of matter has made possible further developments in the theory of the formation of metal solid solutions. The conditions leading to the formation of solid solutions could be explained on the basis of ideas regarding the crystal lattice, the way in which atoms are located at crystal lattice sites, and data on interatomic distances in crystals. Metallic solid solutions (phases of variable composition) are formed either by replacing solvent atoms by solute atoms in the crystal lattice or by introducing solute atoms into the interstices of the solvent lattice. Thus, we now refer to two types of solid solution: 1) substitutional solid solutions, 2) interstitial solid solutions.

The fullest review of the historical developments in the science of solid solutions, of the theory of their formation, and of problems of chemical binding in metallic solid solutions is contained in the papers presented to the All-Union Conference on Solid Solutions, organised by the Division of Chemical Sciences and by the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR [39,40] in 1944.

Many theoretical approaches to the nature and properties of metallic solid solutions were considered at that conference. Substitutional solutions are treated as solutions or as the chemical replacement of metal atoms in the solvent metal lattice by foreign atoms (S. T. Konobeevskii), and it is shown that the formation of all metallic solid solutions is accompanied by a positive thermal effect, arising from the formation of chemical bonds between solvent and solute atoms. Dorfman concludes[40], from a study of various nickel solid solutions, that a rudimentary form of valence bond between atoms of the solvent and of the alloying element is present.

Thus, solid solutions are described as phases of variable composition with a single type of chemical bond. Under certain conditions, chemical reactions can occur in a uniform medium of these solutions: they take the form of ordered distributions of atoms and of singularities and extrema in the physicochemical properties on the composition–property diagrams.

Many theoretical problems in the chemistry of metallic solutions and of reactions occurring in such media (for example, heterogeneities in solid solutions and the formation of various compounds with a special type of bond between the electrons of the different atoms) have great scientific interest. These problems are discussed in a special monograph by Grum-Grzhimailo[41].

From the chemical point of view, problems such as the electronic structure of solid solutions, the theoretical model of the structure of solid solutions (Friedel *et al.*), atomic radii and distortions of the crystal lattice, lattice structure and lattice defects in solid solutions, are equally important. These problems are of immediate relevance to the departures of real solid solution systems from the ideal conditions of homogeneity and stability. Departures of this type are symptomatic of chemical reactions between the dissolved atoms.

Modern researches on the physicochemical nature of solid solutions confirm that the theory of metallic solid solutions is based on the electronic theory of metals[43]. The basic postulate of this theory is that the atoms of solid solutions are randomly distributed in the lattice, and that the electrons are distributed (as in the case of pure metals) in the interstices between lattice ions, without any directional bonds. This model of the atoms and electrons of the solvent and solute metals presupposes the existence in the lattice of solid solutions of ionised atoms, with a collective distribution of quasi-free electrons. However, the possibility of interactions between the electrons of different atoms cannot be excluded, since atoms of different kinds are present in such a lattice[41,42].

The presence of chemical binding of this type in solid solutions manifests itself in changes in the thermochemical, physical, and other properties of systems consisting of solid solutions. These changes cannot be easily explained by simple geometrical considerations of substitutional or interstitial foreign atoms in the lattice of the solvent metal, without allowance for the chemical interaction between the electrons of the different atoms in solid solution lattices.

The number of valency electrons involved, and the extent to which they interact, control the conditions of formation of solid solutions, the degree of distortion of the crystal lattice, and the degree of disorder in the distribution of the atoms over the solid solution lattice. As we shall show below, these same factors determine the change from solid solutions to intermetallic compounds.

We shall now discuss the basic factors which control the conditions of formation of metallic solid solutions.

The most general and most important factor, as Ageev correctly points out[43], is the position of the elements in the Periodic Table, since this determines the electronic structure of the interacting atoms. From this fundamental factor stem derived criteria, which determine the conditions most favourable to the formation of a continuous series of solid solutions. These are: (1) not too large a difference in atomic radii and in electronegativity and ionisation potential — as was pointed out in the previous Sections, this criterion is met mainly by metals which are analogues or which occupy neighbouring positions in the Periodic Table; (2) if all these parameters have reasonably similar values, a continuous series of solid solutions is formed provided that the atomic radii do not differ by more than 8–10%. The conditions most conducive to the formation of a continuous series of solid solutions are that the metals should belong to the same group and have the same number of valency electrons, and that they should be capable of crystallising in isomorphous lattices.

If the difference between the atomic radii of the metals is increased from 10 to 16%, if their position in the electronegativity series is changed, or if the number of valency electrons is varied, the tendency to form solid solutions decreases. When the difference between the atomic radii exceeds 16%, and the difference in electronegativity and ionisation potential is large, there is a sharp drop in the tendency to form solid solutions, and when the difference exceeds 20% not only are solid solutions not formed, but the metals are immiscible even in the molten state.

This relation between atomic radii and the ability to form solid solutions can be explained by assuming that the

crystal lattice of the solvent metal can accommodate a certain amount of distortion when solvent atoms are replaced by solute atoms. Evidently, there is a maximum degree of lattice distortion beyond which the lattice has no stable existence. The writer has discussed these problems in the particular case of iron solid solutions[44]. Fig. 3 shows the distribution of atoms in the $\alpha$-Fe body-centred cubic lattice, both without lattice distortion (Fig. 3*a*) and with lattice distortion due to a 15% difference in atomic radius between a solute atom and iron (Fig. 3*b*). It is easy to see, by comparing Figs. 3*a* and 3*b*, that the solvent lattice becomes deformed when this difference ($dr$) increases: as long as the atomic radius difference is no more than 8–10%, atoms can be replaced indefinitely without destroying the stability of the lattice, but for larger radius differences (15% and over), and larger degrees of lattice distortion, solvent atoms can be replaced only up to a definite concentration at which the solubility limit is reached and a new phase of different crystal lattice type is formed. Analogous effects have also been reported by other workers[20,41] in the formation of solid solutions with various interatomic radii.

This treatment of the conditions under which solid solutions will form, being primarily based on the size-factor, is not comprehensive and should be coupled with the behaviour of the valency electrons and their interactions in the lattice of solid solutions.

The criteria for the formation of a continuous series of solid solutions listed above are most nearly satisfied by transition group metals with an unfilled *d*-electron shell, showing the greatest similarity in atomic radii and chemical properties (see Figs. 1 and 2). Many metals of these groups will give continuous solid solutions both within their group of the Periodic Table (same number of outer electrons) and with metals of adjacent groups (small difference in the number of valency electrons). Examples of this are the interactions between metals of the following groups: Group IV Ti, Zr, Hf; Group V V, Nb, Ta; Group VI Cr, Mo, W; Group VIII Fe, Co, Ni (iron subgroup) and Pd, Pt, Ir (platinum subgroup), and others. Metals crystallising in different lattice types are the only exceptions.

All the analogue-metals of the above triads form continuous series of solid solutions with one another. Continuous solid solubility for many of these systems was predicted by the writer[44] and confirmed by later work[45]. The formation of continuous series of solid solutions by metals of the transition groups also shows some regularity along horizontal rows, as evidenced by the systems Ti–V, Ti–Cr, Zr–Nb, Nb–Mo, Nb–W, etc.

The maximal number of systems of this type was calculated, according to the crystal lattice type, for three

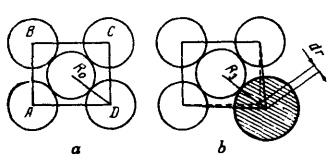



Fig. 3. Arrangement of atoms in the $\alpha$-Fe lattice (body-centred cubic) and in derived solid solutions:
*a*) in the $\alpha$-Fe lattice;
*b*) after substitution of an atom with 15% difference in radius.

classes of continuous solid solutions: (1) face-centred cubic lattice ($\gamma$-Fe); (2) body-centred cubic lattice ($\alpha$-Fe); (3) hexagonal lattice ($\alpha$-Ti).

Systems with continuous solid solutions between transition group metals of these three classes are listed in Table 2, which shows that metals which are nearest analogues can give continuous solid solutions even when the difference in atomic radii is as high as 10–11% (Ni–Rh, Ni–Ir, and some others). This is an example of the position of the elements in the Periodic Table and the similarity in chemical properties having a decisive effect on the nature of the interaction.

These metallic systems had not been investigated prior to the writer's publication[44], and the continuity of the solid solutions was then only tentatively predicted. Many of the systems have now been experimentally investigated, and it has been shown that the solid solutions are indeed continuous[45].

The systems with continuous solid solubility listed in Table 2 include the most refractory metals. Some typical fusion diagrams for these systems are shown in Fig. 4. As an example, we have reproduced the diagrams for systems with the $\gamma$-Fe lattice (Fe–Ni, Pt–Ir), the $\alpha$-Fe lattice (Fe–Cr, Cr–Mo, Cr–W, etc.), and the $\alpha$-Ti lattice (Ti–Zr, Zr–Hr, Ru–Os).

The tendency to form continuous solid solutions within a group of elements is also shown by groups other than the transition metals within which the difference in atomic radii is small and the electronic structure of the atoms is similar. This rule applies equally to highly electropositive and highly electronegative metals, including also some metalloids.

For example, among the electropositive metals, pairs such as K and Rb, Rb and Cs, Ca and Sr, Ca and Ba, and Ba and Sr, and among the electronegative elements Ge and Si, Bi and Sb, and Sb and As, have closely similar atomic radii and other properties (see Figs. 1 and 2), and

TABLE 2.

| Binary metal systems | Atomic diameters of the metals (Å) and difference in diameter, % | | | Binary metal systems | Atomic diameters of the metals (Å) and difference in diameter, % | | |
|---|---|---|---|---|---|---|---|
| | I | II | difference | | I | II | difference |
| **Continuous solid solutions of metals with the $\gamma$-Fe lattice in the systems:** | | | | **Continuous solid solutions of metals with the $\alpha$-Fe lattice in the systems:** | | | |
| $\gamma$-Fe—Ni | 2.52 | 2.49 | 1.2 | $\alpha$-Fe—Cr | 2.54 | 2.57 | 1.2 |
| $\gamma$-Fe—$\beta$-Co | 2.52 | 2.50 | 0.8 | $\alpha$-Fe—V | 2.54 | 2.69 | 5.9 |
| $\gamma$-Fe—Rh | 2.52 | 2.68 | 6.3 | Cr—Mo | 2.57 | 2.80 | 8.9 |
| $\gamma$-Fe—Pd | 2.52 | 2.74 | 8.7 | Cr—W | 2.57 | 2.82 | 9.7 |
| $\gamma$-Fe—Ir | 2.52 | 2.71 | 7.6 | Cr—V | 2.57 | 2.69 | 4.7 |
| $\gamma$-Fe—Pt | 2.52 | 2.77 | 9.9 | Mo—W | 2.80 | 2.82 | 0.7 |
| $\beta$-Co—Ni | 2.50 | 2.49 | 0.4 | Mo—V | 2.80 | 2.69 | 4.1 |
| $\beta$-Co—Rh | 2.50 | 2.68 | 7.2 | Mo—Nb | 2.80 | 2.94 | 5.0 |
| $\beta$-Co—Pd | 2.50 | 2.74 | 9.6 | Mo—Ta | 2.80 | 7.94 | 5.0 |
| $\beta$-Co—Ir | 2.50 | 2.71 | 8.4 | W—V | 2.82 | 2.69 | 4.8 |
| $\beta$-Co—Pt | 2.50 | 2.77 | 10.8 | W—Nb | 2.82 | 2.94 | 4.3 |
| Ni—Rh | 2.49 | 2.68 | 7.6 | W—Ta | 2.82 | 2.94 | 4.3 |
| Ni—Pd | 2.49 | 2.74 | 10.0 | V—Nb | 2.69 | 2.94 | 9.3 |
| Ni—Ir | 2.49 | 2.71 | 8.8 | V—Ta | 2.69 | 2.94 | 9.3 |
| Ni—Pt | 2.49 | 2.77 | 11.2 | Nb—Ta | 2.94 | 2.94 | 0.0 |
| Rh—Pd | 2.68 | 2.74 | 2.2 | **Continuous solid solutions of metals with the $\alpha$-Ti lattice in the systems:** | | | |
| Rh—Ir | 2.68 | 2.71 | 1.1 | | | | |
| Rh—Pt | 2.68 | 2.77 | 3.3 | $\beta$-Ti—$\beta$-Sc | 2.93 | 3.28 | 9.3 |
| Pd—Ir | 2.74 | 2.71 | 1.1 | $\alpha$- and $\beta$-Ti—$\alpha$- and $\beta$-Zr | 2.93 | 3.19 | 8.9 |
| Pd—Pt | 2.74 | 2.77 | 1.1 | $\alpha$- and $\beta$-Ti—$\alpha$- and $\beta$-Hf | 2.93 | 3.17 | 8.2 |
| Ir—Pt | 2.71 | 2.77 | 2.2 | $\alpha$- and $\beta$-Zr—$\alpha$- and $\beta$-Hf | 3.19 | 3.28 | 0.6 |
| | | | | $\beta$-Zr—$\beta$-Sc | 3.19 | 3.28 | 5.6 |
| | | | | $\beta$-Hf—$\beta$-Sc | 3.17 | 3.02 | 5.0 |
| | | | | Os—Ru | 2.68 | 2.70 | 0.8 |
| | | | | Os—Re | 2.68 | 2.75 | 2.6 |
| | | | | Ru—Re | 2.70 | 2.75 | 1.9 |

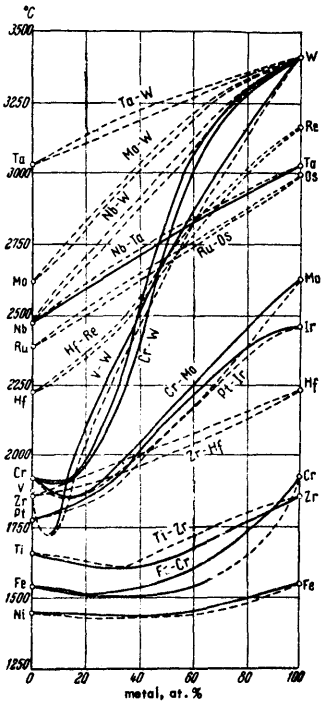



Fig.4. Fusion diagrams of systems of transition group metals forming continuous solid solutions.

form continuous solid solutions[45]. The mutual replacement of germanium and silicon, or antimony and arsenic atoms in the crystal lattice of these substances depends on the closeness of the atomic radii, on the equality of the number of valency electrons, and on the identity of crystal types. It is characteristic of these systems that germanium and silicon, being nearest analogues, can form continuous solid solutions in spite of the fact that one of them is a metal and the other a typical non-metal.

However, if the difference in atomic radii and in ionisation potential and electronegativity is large for elements of a given group (for example, C and Si, Bi and As), solid solutions cannot be formed, even though the number of valency electrons is the same[45].

The tendency towards restricted solid solubility in systems increases as we go from metal analogues to metals belonging to different groups, with different metal chemical properties (atomic radii, electronegativities, and number of valency electrons).

Thus, the tendency of a given metal (from Group VIII, say) to form solid solutions with metals of the Fourth Period decreases from right to left, whilst the opposite is true for a Group IV metal, the tendency decreasing from left to right. This can be illustrated by taking Ni (Group VIII) and Ti (Group IV) as examples.

The solubility of metals in nickel decreases in the following sequence:

| | Ni → Co → Fe → Mn → Cr → V → Ti → Sc → Ca → K | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Solubility, at. % | 100 | 100 | 100 | 50 | 43 | 15 | unknown—insoluble. | |

Nickel forms continuous solid solutions with the series from Co to Mn; from Cr to Sc only restricted solid solutions are formed, the solubility decreasing from Cr toward Ti and Sc, and with Ca and K there is practically no interaction. This is exactly what would be expected from the similarities and the differences in metal chemical properties between these metals and nickel. With titanium — a Group IV metal — the situation is reversed. The solubility of elements in β-titanium decreases in the sequence

| | V → Cr → Mn → Fe → Co → Ni | | | | | |
|---|---|---|---|---|---|---|
| Solubility, in Ti, at. % | 100 | 100 | 28 | 20 | 13 | 10 |

The β modification of titanium forms continuous solid solutions with V and Cr, but it forms only restricted solid solutions with Mn, Fe, Co, and Ni. It is clear from the solubility series that the maximum concentration of metals having a restricted solubility in β-titanium also decreases progressively from manganese towards nickel, that is, as the difference in metal chemical properties between these metals and titanium increases.

The systems formed by the β modification of titanium with the series of elements from Cr to Ni are illustrated in Fig. 5. Whereas Cr has an unrestricted solubility in β-titanium, the solubility of the other metals at their eutectic temperature decreases continuously in the sequence Mn → Fe → Co → Ni. The crystallisation temperature of the eutectic also decreases accordingly in these systems. The strictly sequential decrease in solubility in β-titanium of the series Mn → Fe → Co → Ni corresponds to the increasing separation of these elements of the Fourth Period from the position occupied by titanium, to a gradual increase in the number of electrons in the unfilled *d* shell, and to an increasing difference in atomic radii between titanium and these elements. These regular changes in limiting solubility can be demonstrated with many other metals.

Thus, starting from the fundamental physicochemical factors which determine the type of interaction between metals, the formation of solid solutions can be similarly classified for a number of metals of the Periodic Table. This has been done for silver and copper[20], magnesium and aluminium[46,47], iron and nickel[46,48], and chromium and

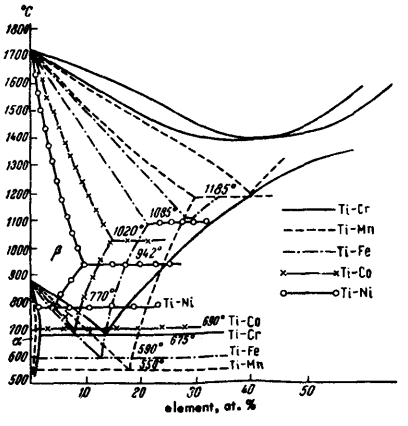



Fig.5. Fusion and solubility diagrams for the systems formed by β-Ti with Cr, Mn, Fe, Co, and Ni.

titanium[49,50]. The solubility of various elements in manganese[51] has been discussed recently, as well as more general aspects of the metal chemistry of niobium and vanadium, including the problem of the solubility of elements in these metals[52,53].

A knowledge of the mutual solubility of metals in binary systems is valuable in studies of the equilibria in multicomponent metallic systems with solid solutions. The limiting concentrations of alloys in multicomponent systems can be calculated from data on the behaviour of metals in binary systems, and complex solid solution compositions can be made. Calculations of this type were made by the writer for the production of 4-, 6-, 15-, and 16-component solid solutions based on nickel[54] and of 5-, 9-, and 10-component solid solutions based on $\alpha$-titanium.[55] These complicated solid solutions have many properties which are superior to those of pure metals and binary solid solutions. The preparation of these multicomponent solid solutions and the study of their properties are therefore of great theoretical and practical interest.

## 5. FORMATION OF INTERMETALLIC COMPOUNDS

The formation of various types of compound by metals with other metals or with non-metals is one of the characteristic reactions of metal chemistry. The products of such reactions have been termed intermetallic compounds or metallides[8]. This term applies to all the compounds formed between metals, whether their bond type is metallic or covalent. In addition to the reviews already mentioned[24-29], many investigations have been concerned with the formation, classification, and structure of intermetallic compounds, and have surveyed work in progress[56-61].

On the basis of the general principles for the classification of chemical compounds put forward by Kurnakov[8,14,15], intermetallic compounds can be subdivided into two main types: (1) compounds of variable composition (or berthollides), and (2) compounds of fixed composition (or daltonides).

These two types of intermetallic compounds are now generally accepted, and the terms are widely used in inorganic chemistry, metallography, and metal physics. They include not only the intermetallic compounds formed by crystallisation from molten alloys but also the compounds formed by transformations from solid solutions (see below). Among the berthollides and daltonides are included the many compounds formed by metals with non-metals of small atomic radius, such as carbon, nitrogen, oxygen, and hydrogen, and also the compounds with covalent bond type and semiconductor properties. Many compounds called carbides, nitrides, and sometimes suboxides and hydrides are in fact interstitial phases and have typically metallic properties.

The classification of high-melting compounds has been critically discussed[62] for a wide variety of compounds (mostly intermetallic compounds of the transition metals). The compounds were assigned to the following three classes: (1) compounds of two metals (true intermetallic compounds); (2) metal-like compounds (carbides, nitrides, phosphides, etc.); (3) compounds of two non-metals (non-metallic compounds between boron and carbon, carbon and silicon, etc.).

There is also a classification based on the regular changes in chemical bond character associated with the position of the elements in the Periodic Table. The first class includes the compounds formed by metals with other metals, that is, the true intermetallic compounds, such as beryllides, aluminides, stannides, antimonides, and many others. In the second class we find once again compounds with metallic bond type. The compounds of the first and the second class usually have a relatively simple crystal structure and belong to the cubic, the hexagonal, or the tetragonal system (close-packed atoms). All these compounds are studied in metal chemistry. Some of the compounds in the second class, composed predominantly of non-metal atoms, and the compounds formed by two non-metals, are non-metallic. Their chemical bond type is covalent or even ionic. Many have a complex crystalline structure and show semiconductor properties (high electrical resistance).

These compounds behave as independent components in equilibrium systems, and show distinctive singular points on composition–property diagrams (with the exception of the berthollides).

The singularity of properties is a characteristic criterion of compounds of fixed composition, whether formed by crystallisation from the melt or by transformations from solid solutions.

We will consider the metallic compounds formed as a result of decomposition of solid solutions. These compounds were first discovered (in 1914) by Kurnakov, during slow cooling of continuous solid solutions[56] in the Au–Cu system. The two compounds $AuCu_3$ and AuCu were identified in this way. Subsequently, compounds of this type were reported in many solid solutions, and called Kurnakov compounds in honour of their discoverer[26]. In contrast to solid solutions, all these compounds are characterised by an ordered distribution of atoms in their lattice.

At the present time, the systems giving continuous series of solid solutions without compound formation can be considered exceptional. Textbooks of physicochemical analysis[14,15], and many of the papers mentioned above[29], assign separate phases — corresponding to compounds on the equilibrium diagrams (see Fig. 6*a*) — to these metallic formations. These possess regions of homogeneity and the compositions of the compounds are distinguished by singular points. Compounds of this type are formed not only from continuous solid solutions, but also in systems with restricted solid solubility regions. Typical of these compounds are $VNi_3$, $VCo_3$, $MnAu_3$, $MgAg_3$, $Au_3Zn$, $Cu_3Zn$, $Fe_3Al$, and many others.

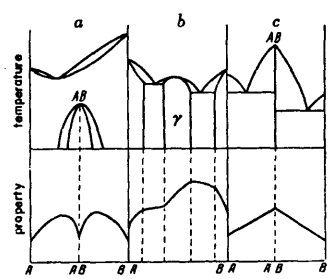



Fig. 6. Schematic equilibrium diagrams for metallic systems with three types of compound:
*a*) Kurnakov compound;
*b*) compound of the berthollide type;
*c*) compound of the daltonide type.

Among the recently discovered compounds are $Ti_6Al$ and $Ti_3Al$, formed from the restricted $\alpha$ solid solutions of aluminium in titanium[62]. Fig. 7, prepared from results obtained in the writer's laboratory, gives the equilibrium diagram of the system (above) and the variation of the Hall effect with alloy composition after long annealing (below). The compound $Ti_6Al$ is characterised by a break in the curve, whereas $Ti_3Al$ corresponds to the maximum at the intersection of two curves. The formation of this type of compound in the Ti–Al system causes marked changes in alloy properties; this has helped to clarify several anomalies in the mechanical and other properties of these alloys.

We have further developed Kurnakov's ideas regarding the importance of solid solutions in the formation of various types of compound, and have suggested that lower oxides of titanium can exist in the wide $\alpha$ solid solution region of the titanium–oxygen system. A detailed study of the alloys of the Ti–O system (up to 35 at.% oxygen) has recently provided experimental proof of the formation of the two previously unknown compounds $Ti_6O$ and $Ti_3O$ from titanium $\alpha$ solid solutions[63]. Both these compounds have metallic properties and crystallise with a hexagonal lattice, but $Ti_3O$ gives an X-ray pattern with superlattice lines which are characteristic of an ordered structure. The compounds $Ti_2O_3$ and $TiO_2$, which were previously known, belong to the valency type. The recently discovered compounds $Ti_6O$ and $Ti_3O$ can be classified as interstitial phases: they are still the only known examples of oxygen-containing compounds formed from restricted solid solutions. Because of these results, instead of the existing equilibrium diagram (Fig. 8) of the Ti–O system, showing a wide region of titanium $\alpha$ solid solutions, a new diagram was proposed[63], including the new compounds $Ti_6O$ and $Ti_3O$ (see Fig. 9). Analogous compounds of the suboxide type can be expected in other systems of chemically reactive metals with restricted oxygen solubility, for example, Zr–O, Hf–O, V–O, Nb–O, etc. A study of these systems would therefore be of interest.

The discovery of these compounds is very relevant to the understanding of the structure and physicochemical

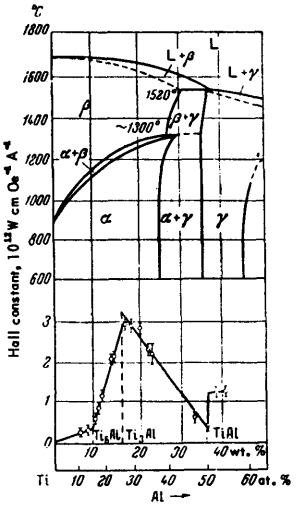



Fig. 7. Equilibrium diagram of the Al–Ti system and variation of Hall constant with composition.

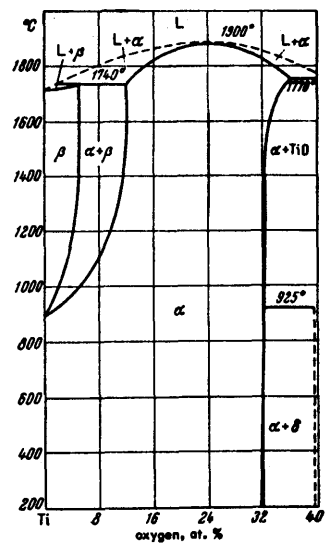



Fig. 8. Equilibrium diagram of the Ti–O system, showing wide field of titanium $\alpha$ solid solutions (from published data).

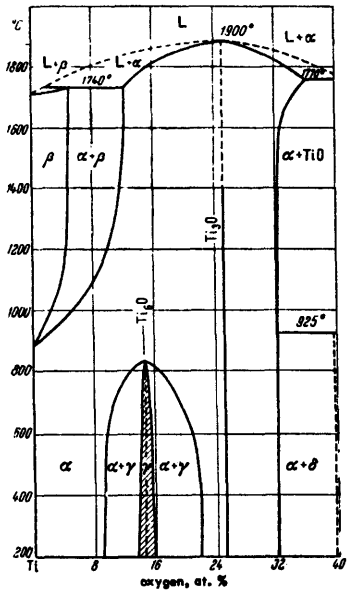



Fig. 9. Equilibrium diagram of the Ti–O system, showing the formation of the compounds $Ti_6O$ and $Ti_3O$ (from recent results).

properties of the alloys of titanium, zirconium, etc. which contain a high proportion of oxygen, and should help to throw light on the influence of oxygen on the mechanical and other properties of these metals.

The formation of intermetallic compounds and their relative stability depends on the difference in chemical properties (electronegativity, ionisation potential) of the interacting elements. The stability of intermetallic compounds

and the strength of their chemical bonds can be judged, as with any other chemical compound, by their heats of formation[64-66].

The available data show that the compounds between metal analogues, in which the difference in chemical properties between the two kinds of atom taking part in compound formation is smallest, are the least stable. In this sense, the least stable compounds are the Kurnakov compounds with an ordered structure, formed from solid solutions of analogue-metals. For example, the compound AuCu, mentioned above, has a heat of formation of 0.37 kcal × × mole$^{-1}$, whilst the compound FeCr, also formed from solid solutions, in the Fe–Cr system, has a heat of formation of 0.78 kcal mole$^{-1}$.

The author has made a study of the regularities displayed by the heats of formation of the intermetallic compounds of nickel of composition $MNi_3$, showing a gradual increase in the electronegativity difference between nickel and the metal M.

Fig. 10, prepared from the results of this work[67], shows the heats and temperatures of formation of the compounds of nickel with the following metals: Fe, Mn, Cr, V, and Ti, belonging to Groups VIII, VII, VI, V, and IV within the same period of the Periodic Table. As the difference in properties between nickel (electronegative) and the metals Fe, Mn, Cr, V, and Ti (electropositive) increases (see Table 1), the stability of the nickel compounds of composition $MNi_3$, involving these metals, increases in the sequence $FeNi_3 \rightarrow MnNi_3 \rightarrow CrNi_3 \rightarrow VNi_3 \rightarrow TiNi_3$.

The partly anomalous behaviour of the compound $CrNi_3$ in the above series calls for further examination. The first four compounds are formed from solid solutions and are therefore typical Kurnakov compounds, whereas $TiNi_3$, the most stable of the five, has the highest heat and temperature of formation and crystallises from the liquid phase. It should be noted that the difference in formation conditions (from the solid or the liquid phase respectively) has no effect on the gradual change in properties. This is proof of the generality of our proposition that the stability and the gradual changes in chemical bond strength of intermetallic compounds are a function of the position of the reacting elements in the Periodic Table.

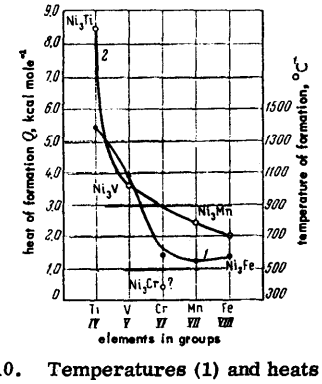



**Fig. 10.** Temperatures (1) and heats (2) of formation of compounds of nickel with iron, manganese, chromium, vanadium, and titanium of composition $MNi_3$.

We will now discuss some features of the formation of compounds of variable composition (the berthollides). They are characterised by the presence of a homogeneity region, and by the absence from the composition–property diagrams of well-defined singularities at the ordinates drawn through the composition of these compounds (see Fig. 6*b*). In the general classification of intermetallic compounds, berthollides are intermediate in stability between Kurnakov compounds and the compounds of the daltonide type. There are known examples of the formation of Kurnakov compounds from berthollide compounds stable at high temperatures when the temperature is lowered. A striking example of this is the transformation on cooling, in the Cu–Zn system, of the high-temperature $\beta$ phase of CuZn (berthollide) into the $\beta'$ phase (Kurnakov compound). The composition and crystal structure of these compounds is often determined by the ratio of the number of outer electrons to the number of atoms in the lattice of the compound. These compounds have been termed electron compounds; their quantum-mechanical theory is discussed in a number of papers[19,20,68]. Phases of this type are most readily formed by interaction between those metals of the B subgroups which are near neighbours in the Periodic Table and have a small electronegativity difference.

Isolated examples of the formation of such phases can be recognised in systems based on metals of Group I (Cu, Ag, Au) and metals of Groups II (Zn, Cd, Hg), III (Tl, In, Ga), V (Bi, Sb), and others. In some cases, the compounds under discussion are formed when these metals react with metals of the transition groups[46]. In the homogeneity region of these compounds, the properties change smoothly with composition, as shown in Fig. 6*b*.

With increasing difference in chemical properties between the reacting elements, associated with an increase in electronegativity difference, in the difference in ionisation potential, and in the difference in the number of valency electrons between the metals, the tendency to form intermetallic compounds of the second type (daltonides) increases. As shown in Fig. 6*c*, these are characterised by singularities in the composition–property diagrams.

This is particularly true of the interaction between the most electropositive metals of Groups I and II and the most electronegative metals of the B subgroups of Groups II–VI. This confirms Kurnakov's prediction[8] that the alkali and alkaline earth metals, being the main carriers of basic or metallic properties, should most readily form a variety of compounds with the heavy (and most electronegative) metals such as Hg, Zn, Cd, Pb, Sn, and Bi.

The gradual transition from metallic solutions through systems with berthollide compounds to intermetallic systems in which daltonides are formed can be demonstrated by selecting binary systems composed of analogue-metals and of metals differing in their chemical properties. Fig. 11, taken from Hansen and Anderko[45], shows three types of binary system: systems with continuous solid solutions of two nearest-analogue electropositive metals of Group I (K and Rb), restricted solid solutions based on metals and the berthollide $\omega$ phase in a system of two electronegative metals (Hg and Cd), and lastly a system in which no solid solutions are formed, but giving rise to six compounds of fixed composition (K, the most electropositive metal, and Hg, the most electronegative metal). All these compounds ($KHg_{11}$, $KHg_8$, $KHg_4$, $KHg_3$, $KHg_2$, and KHg) have higher melting points than their constituent metals: they are characterised by bonds of the metallic type and are typical intermetallic compounds.

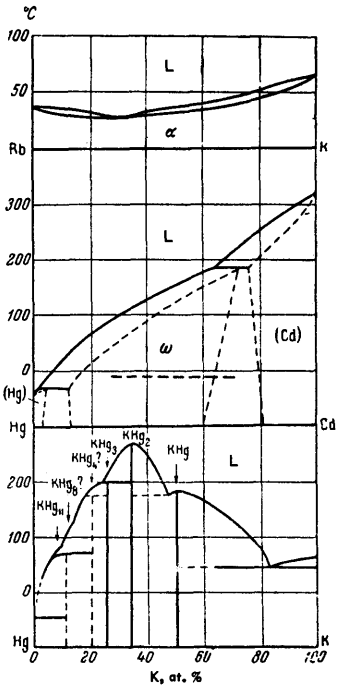



Fig. 11. Equilibrium diagrams of systems of two analogue-metals (K–Rb and Hg–Cd) and of metals from different subgroups (K–Hg).

On the other hand, compounds with different types of chemical bond are formed[31,65,66] in some metal–non-metal systems according to the concentration of the electronegative element. For example, in the series of compounds $Ti_6O$, $Ti_3O$, TiO, $Ti_2O_3$, and $TiO_2$ of the Ti–O system, the first two have metallic bonds, TiO has covalent bonds, and $Ti_2O_3$ and $TiO_2$ have predominantly ionic bonds.

Many compounds, for example, those formed by the electropositive metal magnesium with electronegative elements, show a characteristic transition from metallic to covalent and ionic bond character as the difference in chemical properties between the second component and magnesium is increased. This can be observed in the series of compounds formed by magnesium with the elements of Group IV (Pb, Sn, Ge, and Si). It should first be noted that all the compounds of magnesium with these elements correspond to the normal valency relationships: their composition is described in every case by the formula $Mg_2X$. As the electronegativity of the elements increases from Pb towards Si, transition from a purely metallic bond ($Mg_2Pb$) to a covalent bond takes place ($Mg_2Sn$, $Mg_2Ge$, $Mg_2Si$).

This same transition and gradual change in bond type is observed also in the series of compounds formed by magnesium with the elements of the Third Period: $Mg_3Al_2$, $Mg_2Si$, $Mg_3P_2$, MgS, and $MgCl_2$. These compounds also obey the valency rules, as their composition shows. The elements Al, Si, P, S, and Cl, present as a constituent, show increasing electronegativity and ionisation potential (see Table 1 and Fig. 2). Of these, only Al is a true metal, the remainder being non-metals. Although Al is situated in the Third Period close to Mg, it is quite unlike the electropositive element magnesium in its electronegativity (see Table 1). Hence, aluminium and magnesium form a series of compounds, including $Mg_3Al_2$, all of which are typically metallic. The next three compounds, $Mg_2Si$, $Mg_3P_2$, and MgS have covalent bonds and are semiconductors, possibly with partial ionic bond character. The last compound of this series, $MgCl_2$, is a typical compound with ionic bond character.

As the difference in chemical properties between magnesium and the above elements increases, whether along a group or along a period, the strength of the chemical bond of the magnesium compounds increases. This is reflected in an increase in the heat of formation and melting point of compounds of a given stoichiometric composition, as shown in Table 3.

The table lists the change in heat of formation ($Q$, kcal × × mole$^{-1}$) of compounds of magnesium with elements showing gradually increasing electronegativity difference with respect to magnesium.

A general survey of the heats of formation of compounds is sufficient to show that intermetallic compounds have much lower heats of formation than compounds of a covalent or ionic bond type. In all three columns of Table 3 the heat of formation increases from top to bottom, in the same sense as the electronegativity of the reacting elements: from Pb to Si for Group IV (B subgroup), from Te to O for Group VI (B subgroup), and from Si to Cl for the Third Period.

The stability of intermetallic compounds is also related to their melting point. The highest chemical bond strength corresponds, as a rule, to the highest melting point. This is illustrated by the linear plots of Fig. 12, which join the melting points of the compounds of Mg with Pb, Sn, Ge, and Si.

The melting points of the compounds $Mg_2Pb$, $Mg_2Sn$, $Mg_2Ge$, and $Mg_2Si$ show a gradual increase, corresponding to the tabulated heats of formation. For comparison, Fig. 12 also shows published values[45] of the melting point of compounds of lithium with lead and tin. These also show an increase in melting point on going from $Li_4Pb$ to $Li_4Sn$.

Linear extrapolation to the hypothetical compounds $Li_4Ge$ and $Li_4Si$, for which there are no published data, affords an estimate of their melting points (~870° for $Li_4Ge$ and ~980° for $Li_4Si$).

These regularities in the heats of formation and the melting points of intermetallic compounds, depending on the relative positions of the reactants in the Periodic Table, are expected to apply to many intermetallic and metal-like compounds. This can be demonstrated by inspection of a series of compounds between metals and metals or between metals and non-metals. Regularities of this type have been found in the gradual change in chemical bond type and heat of formation of borides[69], carbides[70], silicides[71],

TABLE 3. Heats of formation of compounds of magnesium with various elements.

| Compounds with Group IVB elements | $Q$, kcal mole$^{-1}$ | Compounds with Group VIB elements | $Q$, kcal mole$^{-1}$ | Compounds with elements of the Third Period | $Q$, kcal mole$^{-1}$ |
|---|---|---|---|---|---|
| $Mg_2Pb$ | 4.2 | MgTe | 25.0 | $Mg_2Si$ | 6.3 |
| $Mg_2Sn$ | 6.1 | MgSe | 30.0 | $Mg_3P_2$ | 25.6 |
| $Mg_2Ge$ | 6.1 | MgS | 42.2 | MgS | 42.2 |
| $Mg_2Si$ | 6.3 | MgO | 73.0 | $MgCl_2$ | 51.1 |

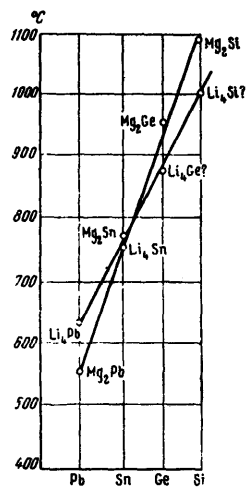



Fig. 12. Melting points of compounds of magnesium and lithium with Group IVB elements.

phosphides[72], and other compounds between metals and non-metals.

Tentative heats of formation[69-71] ($Q$, kcal mole$^{-1}$) of some borides and carbides of transition metals of Groups IV and V, of identical stoichiometry, are reproduced in Table 4. Although the data available for the borides of these metals are incomplete, we may conclude that the heats of formation increase in the same order as the electropositivity of the metal. The compounds formed between phosphorus and various metals are perhaps the most interesting from this point of view.

Starting from the fundamental properties of the phosphorus atom — larger atomic radius and lower electronegativity than its analogue, nitrogen — Samsonov and Vereikina point out[72] that the compounds of phosphorus with the transition metals cannot be regarded as interstitial phases except for the lanthanide phosphides. From electronegativity considerations, metal phosphidès should have a much lower ionic bond character than nitrides, and their properties should be less metallic than those of arsenides, antimonides, and bismuthides. Phosphorus also gives intermetallic compounds more readily than does sulphur.

As the number of phosphorus atoms in transition metal phosphides decreases, the role of the M–P and P–P bonds becomes less important and the M–M bond becomes predominant. The properties of the phosphides, like those of the carbides and nitrides, become more metallic under these conditions.

TABLE 4. Heats of formation of some metal borides and carbides.

| Group | Borides | | Carbides | | Group | Borides | | Carbides | |
|---|---|---|---|---|---|---|---|---|---|
| | composition | $Q$, kcal × mole$^{-1}$ | composition | $Q$, kcal × mole$^{-1}$ | | composition | $Q$, kcal × mole$^{-1}$ | composition | $Q$, kcal × mole$^{-1}$ |
| IV | $TiB_2$ | 70.2 | TiC | 43.8 | V | $VB_2$ | — | VC | 30.2 |
| | $ZrB_2$ | 78.0 | ZrC | 44.4 | | $NbB_2$ | 36.0 | NbC | 33.6 |
| | $HfB_2$ | – | HfC | 81 | | $TaB_2$ | > 52 | TaC | 36.0 |

TABLE 5. Heats of formation of phosphides of the iron group.

| Compound | $Q$, kcal mole$^{-1}$ | Compound | $Q$, kcal mole$^{-1}$ | Compound | $Q$, kcal mole$^{-1}$ |
|---|---|---|---|---|---|
| $Fe_3P$ | 13.1 | $Co_2P$ | 28.45 | $Ni_5P_2$ | 17.4 |
| $Fe_2P$ | 19.25 | CoP | 34.0 | $Ni_2P$ | 19.2 |
| FeP | 29.0 | $CoP_3$ | 64.0 | $NiP_2$ | 38.0 |
| $FeP_2$ | 42.0 | | | $NiP_3$ | 45.2 |

In keeping with their greater percentage of metallic bond character, phosphides should have a lower heat of formation than nitrides. This is because the ionisation potential and electronegativity of the phosphorus atom are lower than those of the nitrogen atom. The transition from phosphides containing relatively few phosphorus atoms to phosphides containing more phosphorus atoms is accompanied by an increase in heat of formation ($Q$, kcal mole$^{-1}$), as shown[72] by the phosphides of iron, cobalt, and nickel listed in Table 5.

These data indicate that, as the number of phosphorus atoms in the compounds increases, so does the number of P–P and P–M bonds; as a result, covalent and ionic bonds begin to predominate. These raise the bond strength and bring about an increase in the heat of formation of the compounds.

Samsonov and Rodzinskaya[73] have demonstrated some measure of regularity in the chemical bond character of sulphides, related to the electronic structure of rare-earth elements and sulphur. They point out that "metallisation" of the bond occurs to a greater extent in sulphides than in the nitrides of the same metals, and ascribe this to the ionisation potential of sulphur, which, like that of phosphorus, arsenic, and carbon, is lower than the ionisation potential of nitrogen (see Fig. 2). Consequently, the sulphides of these metals (of given stoichiometric composition) can be expected to show greater collectivisation of the electrons from the metal and from the sulphur, and greater metallisation of the bond, than the corresponding nitrides. However, even the sulphides retain some covalent and ionic bond character: as in the phosphides, this increases with the number of sulphur atoms in the compound. For example thorium monosulphide ThS is a typical intermetallic compound[74], whereas $Th_2S_3$, $Th_4S_7$, and $ThS_2$ are classified among the compounds with a covalent and partially ionic bond.

This discussion of the influence of the physicochemical nature of the constituent atoms upon the nature of the chemical bond in intermetallic compounds demonstrates the importance of the metal chemical properties of the elements from the point of view of the formation of various types of compound. Many of the physical, mechanical, and other properties of these compounds are determined by the strength of the chemical bond.

## 6. CRYSTAL CHEMICAL REACTIONS IN METALLIC SYSTEMS

The study of crystal chemical reactions in metallic systems[28,74] is one of the main aspects of current work in the field of metal chemistry. The term includes a wide variety of reactions involved in phase transformations in

metallic systems and in surface reactions in the solid (crystalline) state. In contrast to the familiar chemical reactions in liquid and gaseous media, which usually occur by a homogeneous mechanism, these reactions are essentially heterogeneous and occur in a crystalline medium. We shall therefore call them crystal chemical reactions. Many of the problems involved are part of the general development of solid state chemistry.

Crystal chemical reactions include: (1) reactions leading to the formation of Kurnakov compounds from solid solutions; (2) reactions leading to the formation of compounds or other phases from supersaturated solid solutions; (3) eutectoid and peritectoid reactions; (4) surface reactions (oxidation, reduction, and other reactions in the solid state); (5) solid-phase reactions between powders of metals and non-metals.

Crystal chemical reactions are atomic rather than molecular in character[75]. They relate to the rearrangement and mutual replacement of atoms in a crystalline medium, and their rates are controlled by diffusion processes. The range of reaction times presented by these reactions is unusually wide: they vary from instantaneous reaction (in the case of martensitic transformations) to hundreds, thousands, or millions of hours, up to geological times (low-temperature decomposition of supersaturated solid solutions, etc.).

The rates of reactions in the solid state depend on a number of equilibrium considerations. Firstly, they depend on the chemical composition and crystal structure of the reaction medium, on the temperature, and on the pressure. These factors can accelerate or suppress the reaction rate. For example, it has been shown that individual chemical species involved in these processes correspond to singularities in the "composition–reaction time" diagrams. Hence, the author[76] has proposed a method of physicochemical analysis based on the effect of composition on the reaction time or the reaction rate in metallic systems. Studies of the reactivity of alloys (solid solutions, intermetallic compounds, heterogeneous alloys) are concerned with metal chemical reaction problems. Solid solutions and compounds can exhibit chemical passivation (the loss of reactivity at normal or elevated temperatures). Many corrosion-resistant and heat-resisting metallic materials have been developed on the basis of these properties. These are frequently homogeneous metallic solid solutions or intermetallic compounds. The chemical stability of these materials is hundreds of times greater than that of the starting components.

Crystal chemical reactions have one special feature in common: since they take place in the solid state, the intermediate states of reactions in progress may be "frozen" under various conditions, giving rise to a metastable structure of the resulting compounds or phases. Phases of this kind, being still in their formation stage, are dispersed in varying degrees: their atoms are not in their equilibrium crystal lattice sites. Due to their non-equilibrium state, these atoms are more reactive than the atoms of solid solutions and compounds in a state of equilibrium. This is strikingly confirmed by the high catalytic activity of many metastable states of metallic solid solutions and compounds[77].

A detailed characterisation of crystal chemical reactions and a substantially complete survey of the literature would go beyond the scope of the present review: there will be only a brief discussion of some types of crystal chemical reaction.

As was stated above, many solid solutions (both continuous and restricted) can undergo reactions with formation of Kurnakov compounds having, as a rule, a different type of crystal structure as compared with the solid solutions from which they are formed. The atoms have an ordered distribution in the lattice of these compounds, in contrast to the disordered structure of solid solutions. The compositions of these compounds can be recognised by singularities in the composition–property diagrams, and they extend over definite regions. The classical example of this type of equilibrium diagram arose from the experimental study[45,46] of the copper–gold system (see Fig. 13), showing the compounds $Cu_3Au$ and CuAu. Both these compounds, formed from solid solutions, are characterised by singular points on the plots of electrical resistivity and hardness against composition (Fig. 13).

Examples of the formation of Kurnakov compounds are very numerous[45]. At the moment, systems of solid solutions in which compounds of this type cannot be detected under suitable conditions are definitely exceptional.

Many restricted solid solutions in metallic systems show varying solubility in the solid state. As a rule, the solubility is highest at temperatures of transition from the solid to the liquid state (that is, at the solidus point), and decreases with decrease in temperature, as shown schematically by curves $SQ$ of Fig. 14*a*.

Because of this change in solubility, heat treatment — quenching the alloys from temperatures close to the solidus point — can be used to fix the solid solutions in a state of supersaturation for concentrations extending almost to the limiting solubility of the component at point $S$. The linear variation of lattice parameter with composition can be used to confirm that the solution is in a supersaturated condition, as shown in Fig. 14*b*. Under favourable conditions, decomposition of the supersaturated solid solution and precipitation of the phase in excess can occur in these metastable systems. This follows from thermodynamic considerations of the free energies of the phases in the

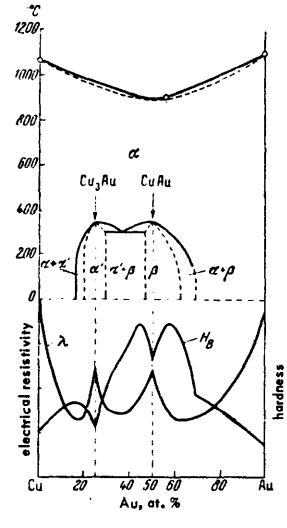



Fig. 13. Equilibrium diagram of the Au–Cu system, and change in electrical resistivity and hardness with alloy composition.

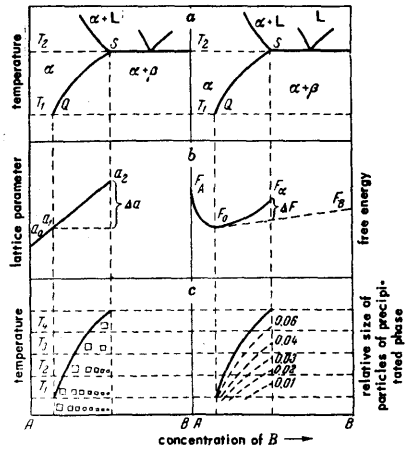



Fig. 14. Diagram showing changes in solubility (*a*), lattice parameter and free energy (*b*), and particle size of the precipitated phase formed by decomposition of supersaturated solid solutions (*c*).

equilibrium and the metastable states. The right-hand side of Fig. 14*b* shows the change in the free energy $F_A$ of the phase in equilibrium at temperature $T_1$. The minimum of the curve ($F_0$) corresponds to the equilibrium solubility limit, and its maximum ($F_\alpha$) to the non-equilibrium state of the $\alpha$ supersaturated solid solution. It follows that the supersaturated $\alpha$ solid solution must necessarily undergo transformation with formation of a precipitated phase in supersaturated (quenched) alloys lying to the right of the equilibrium solubility curve *SQ*. These decomposition reactions involve atomic rearrangements, the formation of intermediate, highly disperse phases, and the approach to and achievement of equilibrium phase structures. The grain size of the precipitated phases formed in these crystal chemical reactions depends on the composition, temperature, and time of the reaction.

The particles of the precipitated phase obtained in a fixed time at temperatures $T_1$, $T_2$, $T_3$, and $T_4$ are shown schematically in Fig. 14*c* as small squares (on the left) and as plots of their relative size (on the right). The size of the particles depends on the temperature and on the composition of the supersaturated solid solutions; it is determined by the conditions of formation of crystal nuclei and by the rate of growth of these nuclei.

This type of decomposition reaction in supersaturated solid solutions of metallic systems has been studied in a large number of alloys based on aluminium, iron, nickel, titanium, and other metals. They are of the utmost importance in raising the strength, heat-resistance, and changing other physicochemical properties as a function of conditions, and of the structure of the solid solutions undergoing decomposition and of the phases which are precipitated from them.

We can also suggest general mechanisms for the crystal chemical reactions occurring during eutectoid and peritectoid transformations in metallic systems.

Since a detailed discussion of these reactions is out of the question, we will merely state that eutectoid reactions proceed according to the scheme

$$\text{solid solution } \gamma \rightleftarrows \alpha + \text{AB (or } \beta \text{ phase)},$$

whereas peritectoid reactions involve the scheme

$$\gamma + \alpha \rightarrow \text{AB (or } \beta \text{ phase)}.$$

These reactions have their own individual peculiarities, depending also on composition and temperature, and the resulting phases can pass through a succession of intermediate states and exhibit different crystal structures. These reactions are particularly significant when the metals can exist in polymorphic modifications (Fe, Ti, Zr, etc.). These problems are dealt with in general textbooks on solid state chemistry[75] and metallography[18-23].

Surface reactions in alloys, occurring when these materials are heated in air or in special media[75,78-80], are a separate class of crystal chemical reactions. The branch of crystal chemistry concerned with reactions between metals and non-metal powders and with the formation of solid solutions, compounds, and heterogeneous alloy structures[75,81,82] has also attracted a great deal of work.

## 7. INTERACTION BETWEEN INTERMETALLIC COMPOUNDS

The reactions between intermetallic compounds, like reactions between metals, are determined by a number of physicochemical factors, which the writer has previously formulated[83]. The different types of interactions between intermetallic compounds in binary systems of these compounds can be described by means of the three main types of equilibrium diagram (see Fig. 15):

1. System AB–AC (continuous series of solid solutions),
2. System AB–AX (restricted series of solid solutions),
3. System AB–AY (eutectic mixtures without solid solutions).

The following factors are conducive[84] to the formation of continuous solid solutions (Fig. 15*a*) in intermetallic systems: (1) isomorphous crystal lattices of the two compounds; (2) identical chemical bond type; (3) compounds including elements with similar metal chemical properties; (4) compounds of identical stoichiometric composition.

Unless these conditions are met, the intermetallic compounds form only restricted solid solutions (Fig. 15*b*), and in the limit, for very large differences in chemical properties between the components, only mechanical mixtures are

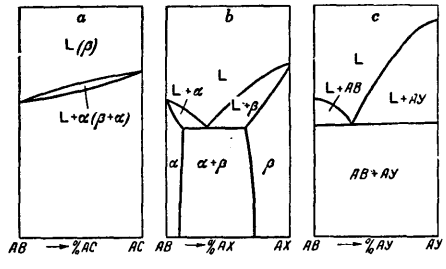



Fig. 15. Types of equilibrium diagram for intermetallic systems:
*a*) continuous solid solutions;
*b*) restricted solid solutions;
*c*) eutectic mixtures without solid solutions.

formed (Fig. 15*c*). All these problems of interactions between intermetallic compounds of different types have attracted a great deal of attention in recent times, and would justify a separate review article.

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Thus, our review of the development and present status of the science of metal chemistry leads us to conclude that metal chemistry, as a scientific discipline, can unify the study of the interactions of over 80 metals of the Periodic Table, both with each other and with non-metals. By suitable application of Mendeleev's Periodic Law, metal chemistry establishes the principles which control the formation of the different classes of metallic solutions and compounds.

Metallic solid solutions, as phases of variable composition, have on the whole a single type of chemical bond: the metallic bond. On the other hand, there is a large number of intermetallic compounds showing very different bond types, from metallic to ionic. The study of solid solutions and metal compounds is highly relevant to an understanding of the mode of interaction of many metals, and it makes possible the prediction of equilibrium diagrams for as yet unknown simple and multicomponent metallic systems.


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# PYROGRAPHITE (PREPARATION, STRUCTURE, PROPERTIES)

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## I. INTRODUCTION

Pyrolytic graphite is the product of the pyrolysis of hydrocarbons on surfaces heated to 1000–2500°C. In recent years this material has attracted very considerable attention from research scientists, technologists, and engineers working in various fields of science and technology. This is because of the many quite unique properties of pyrolytic graphite. Its strength at temperatures

above 2500° exceeds that of any other known material. It has the highest ratio of strength to density (Fig. 1); its thermal and electrical properties show a very characteristic and highly developed anisotropy, the thermal conductivity being very low in the direction normal to the plane of deposition.

The particular method of preparation used ensures that pyrolytic graphite is practically a non-porous material.

Pyrolytic graphite (or pyrographite) also has great practical interest as one of the starting elements used in the production of other pyrolytic materials (pyrometals, pyrocarbides, pyrocarbonitrocompounds, etc.). The results of investigations on the production, structure, and properties of pyrographite can evidently be used to a great extent in the characterisation of these other pyrolytic materials. This is particularly true of the various pyrocarbides and pyrocarbonitrides, which can be expected to play an increasing part in the immediate future.

The study of the effect of formation conditions upon the structure and properties of pyrographite is very interesting also from a purely scientific point of view. Single crystals of graphite large enough to permit measurements of its physical and chemical properties have not yet been prepared. The properties of graphite are commonly studied using polycrystalline two-component or multicomponent materials, prepared by a kind of ceramic technique from graphitised carbon particles and a binding medium. The properties of specimens of these materials depend on many extraneous factors, such as the degree of dispersion of the particles, complex contact phenomena, uncontrolled porosity, etc.

The properties of pyrographite, which is prepared without the use of a binder, depend only on purely structural arrangements. Therefore, pyrographite is very attractive as a subject for investigation, especially in studies of the electrophysical properties of graphitised carbons.

## II. SHORT DESCRIPTION OF THE METHODS FOR THE PREPARATION OF PYROGRAPHITE

Pyrolytic carbon can be prepared by two paths:

1. Carbonisation, i.e. pyrolytic decomposition of carbon-containing materials in a condensed phase.

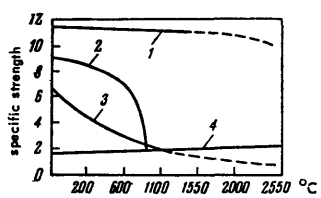



Fig. 1. Effect of temperature on the specific strength (ratio of strength to specific gravity) of pyrographite and of some other materials:
1) pyrographite, along the *a* axis;
2) stainless steel;
3) tungsten;
4) graphite.
[The units of specific strength are not given; it is often given as strength/density (Ed. of Translation).]

2. Deposition of carbon, i.e. homogeneous or heterogeneous decomposition of hydrocarbon gases and vapours.

In addition, pyrographites can be classified according to their preparation temperature into low-temperature (produced at 800–1100°) and high-temperature materials (produced at temperatures above 2000°). Low-temperature pyrographite can be prepared by deposition and by carbonisation methods, whereas the high-temperature form is usually prepared exclusively by deposition.

In the deposition method[1,2], hydrocarbons are made to impinge on a heated surface either in a stream of carrier gas at atmospheric pressure or by diffusion of gaseous hydrocarbons or the vapours of liquid hydrocarbons in an evacuated reactor. The carrier is usually an inert gas (nitrogen, argon, or helium).

There are many reports[3-14] of the use of various amounts of hydrogen in the reaction mixture, added to decrease the rate of pyrolysis.

The solid deposition substrate, usually made of graphitised carbon, is heated either by induction or by a direct or an indirect resistance heater. Maintaining a constant temperature during the deposition seems to be very important. Many vacuum processes for making pyrographite have been described[6-8,15]. They differ mainly in the degree of vacuum used (from $10^{-1}$ mmHg[6-8] to $10^{-7}$ mmHg[15]).

## III. PHYSICOCHEMICAL PROCESSES OCCURRING DURING THE PREPARATION OF PYROGRAPHITE

The extreme thermal decomposition of hydrocarbons has been investigated by many workers[1,2,7,8,11-61]. One of the earliest papers on the mechanism of the thermal decomposition of hydrocarbons was published by Berthelot[41] as long ago as in 1866.

There are a number of opinions regarding the mechanism of the high-temperature pyrolysis of hydrocarbons.

According to Tesner and his coworkers[20,22-35], and also some non-Soviet authors[12-14,21], the decomposition of hydrocarbons on surfaces heated to high temperatures involves the direct dissociation of hydrocarbon molecules into carbon and hydrogen. However, Wheeler considers[13] that the decomposition proceeds through the adsorption of a hydrocarbon molecule on the surface, followed by dehydrogenation of the adsorbed molecule.

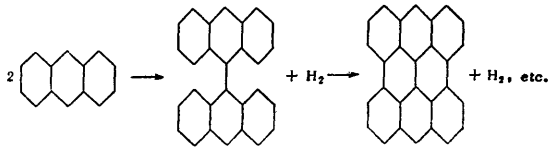
At low concentrations, the formation of pyrolytic graphite can only occur heterogeneously, since gaseous reactions are precluded. According to Tesner and Rafal'kes[25,29], the rate of formation of a pyrolytic film at 800–1000° is directly proportional to the hydrocarbon concentration, i.e. the reaction is of the first order with respect to the hydrocarbon. As the concentration is raised, the probability of gaseous reactions increases, and at a well-defined critical concentration (which Tesner calls[29] the "threshold" concentration) the reactions in the gas phase begin to produce carbon in a very fine state of subdivision (soot). However, the formation of carbon at the heated surface continues even when soot begins to precipitate in the reaction volume.

Tesner and his coworkers believe[20,22-26,29] that the inhibition by hydrogen of the pyrolysis reaction results from activated adsorption of hydrogen on the surface or from Stefan flow of hydrogen from the surface[31]. According to other workers[12-14,21], the effect of hydrogen can be

explained by a shift of the equilibrium towards the reactants.

An alternative mechanism suggested for the formation of pyrocarbon states that hydrocarbons are dehydrogenated during pyrolysis to give complex polymeric aromatic compounds, which are ultimately converted into solid particles. According to this hypothesis, pyrocarbon is an aggregate of extremely high-melting polymeric hydrocarbons[1,8,9,17,38,39,51]. This provides a fairly simple description of the pyrolysis of aromatic compounds. Kinney *et al.*[1,38,39] studied the pyrolysis of benzene and some of its derivatives and found that the yield of pyrocarbon increases with the molecular weight of the aromatic compound, and that under these conditions fission of the aromatic rings does not occur, since low-molecular-weight acetylene hydrocarbons are not detected in the effluent gases even when hydrogen is used as the carrier gas — hydrogen should favour the formation of these compounds. Gases which usually accompany acetylene (e.g. ethylene) are also absent[1].

These features of the pyrolysis of aromatic compounds were confirmed by the work of Rudenko[2], who demonstrated the absence of products from the decomposition of the benzene ring in the gases obtained from the pyrolysis of benzene. In a study of the pyrolysis of anthracene, Kinney *et al.*[39] obtained resinous products as well as solid carbon. Chromatographic analysis of the resin revealed the presence of the anthracene condensation products 9,10-diphenylanthracene and 1,2,5,6-dibenzanthracene. A fraction having an ultraviolet adsorption spectrum identical to that of 9,9′-bianthryl was isolated. Multiple dehydrocondensation, analogous to the process observed during coking of petroleum products[52], obviously occurs:




The presence of diphenylanthracene is due to the excess hydrogen, which causes partial rupture of the aromatic rings. The reaction occurs on the surface as a result of sorption and dehydrogenation of the hydrocarbons, with formation of highly condensed products unlikely to diffuse into the gas phase. On this model, hydrogen lowers the yield of carbon by causing hydrogenation.

The fact that hydrogen has a more pronounced effect in the pyrolysis of non-aromatic hydrocarbons[22] lends support to these views, since these compounds evolve more hydrogen.

Grisdale and coworkers[17,50] have suggested a similar mechanism, but they believe that condensation of aromatic rings occurs in the gas phase, with subsequent deposition of high polymers on the surface. The main evidence in favour of their mechanism is the frequent appearance of spherical drop-like formations on the pyrographite surface. However, the authors do not advance any really serious arguments in support of their views. The attempt by Conroy *et al.*[38] to detect highly condensed aromatic hydrocarbons in the gas phase was unsuccessful.

Other workers[15,40-49,51,53,58,60] point out that the pyrolysis of hydrocarbons involves a free-radical mechanism. Thus, the pyrolysis is characterised by the so-called "wall effect", i.e. the recombination of radicals at the walls of the reaction chamber or at other surfaces within the reaction zone.

In addition to wall recombinations (chain breaking), reactions between radicals occur also in the reaction volume: these lead to a whole spectrum of more complex hydrocarbons.

Hague and Wheeler[44] consider that the initial act in the decomposition of methane is the formation of hydrogen and a methyl radical.

Bone and Coward[11], and also Fischer[36,45], are of the opinion that the first stage in the decomposition of methane involves the formation of the radicals $CH_3$, $CH_2$, and CH.

Rice *et al.*[46] have shown that gaseous hydrocarbons, in particular butane and propane, when passed through a quartz tube heated to 800–1000° at a pressure of 10 mmHg, can destroy Pb, Zn, and Sn mirrors at a distance of 30–40 mm from the reaction zone. This is evidence for the presence of free radicals.

Rice and Dooley[47] showed that the main reaction occurring during the pyrolysis of ethane is dissociation into free radicals rather than splitting off of molecular hydrogen, as had been assumed by many other workers.

Poltorak and Voevodskii[58] used deuteration to prove that the pyrolysis of propane occurs by a radical mechanism; this relies on the ready exchange between deuterium and the hydrogen of free radicals. Propane was pyrolysed in the presence of deuterium, and deuterium was detected in the hydrocarbons produced by the reaction in amounts which were not a function of reaction time.

Shantarovich and Pavlov[60] studied the kinetics of the thermal cracking of methane on porcelain and carbon black surfaces. The shape of the kinetic curves given by the cracking reaction on carbon black is indicative of autocatalysis, the acceleration being due to the development of a chain process. The authors conclude that the decomposition of methane occurs by the following scheme:

$$CH_4 \rightarrow CH_3 + H,$$
$$H + CH_4 \rightarrow CH_3 + H_2,$$
$$CH_3 \rightarrow CH_2 + H,$$
$$CH_3 + CH_4 \rightarrow C_2H_6 \text{ or } CH_2 + CH_4 \rightarrow 2CH_3.$$

Retardation by hydrogen is probably associated with chain breaking by hydrogen, and with displacement of the equilibrium towards the reactants. A critical inspection of the suggested mechanisms prompts the following remarks.

The direct decomposition mechanism lacks adequate experimental proof. The authors quote only activation energy values, which are found to be of the same order as the energy of the C–H bond. The formation of carbon from aromatic hydrocarbons is inexplicable on the basis of this mechanism.

The multiple dehydrogenation mechanism is more realistic, and can claim sounder experimental confirmation. The retarding effect of hydrogen on the rate of formation of pyrolytic graphite is an additional indirect proof of the dehydrogenation scheme for the formation of carbon films. However, in view of the work of Stehling and others[40,42], a purely condensation type of mechanism is unacceptable. It is clear that this mechanism occurs in conjunction with radical polymerisation.

The radical mechanism for the formation of pyrolytic graphite appears to us to be the most probable, since it has quite unambiguous experimental confirmation. We may therefore describe the formation of pyrolytic graphite as follows.

When the hydrocarbon molecules enter the high-temperature region, they are split into free radicals. With aromatic hydrocarbons, fissure occurs at C–H bonds, whereas with aliphatic hydrocarbons the C–C bond is mainly affected[61]. The hydrogen atoms produced by the cleavage of the molecules react with the incandescent carbon surface to give lower hydrocarbons and their radicals: $CH_4$, $CH_3^{\cdot}$, $C_2H_5^{\cdot}$, $C_2H_6$, $C_2H_2$, $C_2H^{\cdot}$, and $^{\cdot}C\equiv C^{\cdot}$. These produce active centres on the carbon surface, able to react with newly formed radicals. Extensive dehydrogenation and consolidation of the radicals occurs before these can enter into the reaction from the gas phase.

Thus, a large number of local interactions occurs simultaneously at many sites. The resulting film of pyrolytic graphite is a true replica of the outline of the substrate surface, showing that the carbon atoms cannot move over the surface at high temperatures.

The hydrocarbon residues, being on a hot surface whose energy is higher than that of the surrounding gas phase, can split off hydrogen and react with neighbouring residues, thus forming a crystal lattice.

Since aromatic structures are thermodynamically the most stable at high temperatures, cyclisation takes place on the surface, with formation of a graphitic network. The distance between graphitic planes, and the development of three-dimensional order, depend on the deposition temperature. At low hydrocarbon concentrations (whether under atmospheric pressure or in a vacuum) and at temperatures of the order of 2000° the fundamental processes take place on the surface. At temperatures above 2800° in a vacuum the vapour pressure above the carbon surface is so high[62] that the radicals cannot reach the surface, and decomposition of the hydrocarbons occurs in the gas phase.

At relatively low temperatures (~ 1100°) the energy of the surface is much lower, and the radicals can penetrate inside the pores of the carbonaceous material and decompose there. This is the basis of the bulk densification of graphitised carbon articles, designed to impart greater strength and hardness and lower permeability to gases[19,20]. The process should be carried out at low concentrations, for otherwise the orifices of the pores may become rapidly covered over, and prevent the penetration of the hydrocarbon into the material.

Simultaneously with the surface decomposition, reactions leading to the formation of biphenyl, acetylene, hydrogen, etc. take place in the bulk[43]. The rate of these reactions is determined by the concentration of the vapours undergoing pyrolysis and also by the temperatures and duration of the process and by the physicochemical properties of the surface.

The influence of temperature and of partial pressure of the gas on the rate of growth of the carbon film was investigated by Murphy *et al.*[54], who used the logarithmic equation of Chen *et al.*[63] to describe the effect of these factors:

$$\log\left(\frac{m}{pT}\right)=\log\left[\frac{\pi D}{\rho L}\delta K\frac{k}{h}\left(\exp\frac{\Delta S^*}{R}\right)\right]-0.4343\,\frac{\Delta H^*}{RT},$$

where $m$ is the rate at which the electrical conductance increases, $p$ the partial pressure of the hydrocarbon, $D$ the diameter of the film of pyrographite, $\rho$ the electrical resistivity of the film, $L$ the length of the film of pyrographite, $\delta$ the thickness of a monatomic layer of carbon in the film of pyrographite, $K$ the rate constant for the growth of a monatomic layer, $k$ Boltzmann's constant, $h$ Planck's constant, $\Delta S^*$ the entropy of activation under standard conditions, $\Delta H^*$ the activation energy standard conditions, $R$ the gas constant, and $T$ the absolute temperature.

The rate constants measured experimentally for the pyrolysis of benzene, toluene, and methane are plotted against $1/T$ in Fig. 2. The linear plot shows that the reaction rate is quite low at temperatures below 860°, but becomes very large above 940°.

Similar kinetic curves were reported by Mar'yasin and Tesner[23,24], who studied the kinetics of the deposition of pyrographite films by the pyrolysis of methane in the temperature range 1400–1700°. This indicates that the temperature coefficient of the pyrolysis reaction rate is high. Between 1600° and 1800° this coefficient can apparently exceed the temperature coefficient which determines the lowering of the activation energy attending the ordering of the structure of the pyrographite film. This results in the phenomenon of structure disordering described below, and causes a decrease in the density of pyrographite in this temperature range.

The influence of the surface on the production of pyrolytic graphite needs special consideration.

Kobozev[56], in his study of the cracking of methane to acetylene, investigated the possible catalytic effect of the surface in the pyrolysis of methane to carbon. He found that the yield of carbon on the walls of the reactor was increased 50- to 100-fold when quartz or porcelain vessels were used. The reaction was typically catalytic, as shown also by the very specific action of various materials, depending on the type of surface, which was observed during a search for catalytic poisons to suppress the pyrolysis of methane to carbon.

Benevolenskaya and Kel'tsev[59] state that active alumina surfaces produce the most extensive decomposition of hydrocarbons undergoing cracking. At 1300° the hydrogen content of the effluent gases was as high as 96–97%.

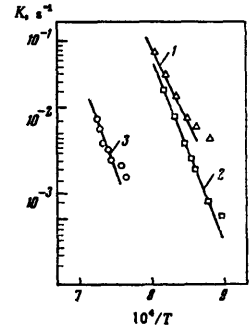



Fig. 2. Temperature variation (after Murphy *et al.*[54]) of the rate constant ($K$) for the pyrolysis of: *i*:
1) toluene;
2) benzene;
3) methane.

Kinney and Del Bel[1] studied the pyrolysis of aromatic hydrocarbons from benzene to chrysene on different surfaces. They found, in particular, that the rate of pyrolysis (e.g. of anthracene to carbon) increases with the amount of coke present in the reactor, which suggests a heterogeneous catalytic reaction. The rate of reaction is increased also by silicon, mullite, and quartz, the quartz being by far the least effective.

According to Holdeman and Botty[55], heavy metals are the most active catalysts for the formation of pyrolytic carbon. They believe that the cracking of methane to carbon at temperatures up to 1000–1200° is a purely surface catalytic process. The actual catalyst in this case is either adsorbed carbon or the substrate surface, modified by the reducing action of hydrocarbon radicals and hydrogen at these temperatures.



Fig.3. Electron diffraction pattern of pyrographite.

## IV. STRUCTURE OF PYROGRAPHITE

The remarkable properties of pyrographite are very much bound up with the structure of the material. This is particularly true of its highly developed anisotropy.

We know[64] that the various kinds of graphitic carbon material have in common a highly polymeric arrangement of the carbon atoms, which exist in hexagonal planes of different sizes and differently oriented in space.

In the most highly ordered state (graphite single crystals) the hexagonal planes of carbon atoms are stacked in the sequence ABAB. The interatomic distance in the six-membered rings is 1.42 Å, and between the symmetrically disposed planes it is 6.71 Å. In the hexagonal graphite lattice, three $\sigma$ electrons form strong covalent bonds with three neighbouring atoms in the plane, and the fourth electron forms a weak $\pi$ bond with a carbon atom from a neighbouring plane. The highly anisotropic properties in two mutually perpendicular directions is a direct consequence of this arrangement.

The opposite limiting case, a completely disordered state, corresponds to a statistically indeterminate distribution of the separate carbon planes over the volume of the material, the binding between the planes involving hetero-atoms, functional groups, or linearly polymerised carbon atoms.

However, this is an extreme case. In practice, even the most disordered carbonaceous materials consist of stacks of hexagonal planes which are mutually parallel, oriented with respect to the normal, and have dimensions of the order of 25 Å in thickness and 35 Å in diameter. These crystallites are bound together by the uncompensated valencies of the corner atoms, and also by the linearly polymerised carbon, hetero-atoms, etc. already mentioned.

Between these two extremes we find a whole range of intermediate structures[65]. Their distinguishing feature is the fact that the size of the crystallites in the direction of *a* axis varies from 50 to a few hundred Ångstrom units, and that only two-dimensional order persists. This means that orientation is complete only with respect to the normal to the crystallites.

Pyrographite is typical of the class of polycrystalline intermediate structures. However, it is distinguished by a high degree of preferential crystal orientation, observed in the aggregates of crystallites. The evidence for this is the electron diffraction pattern shown in Fig. 3 and the clearly developed hexagonal symmetry of the reflection patterns. X-Ray diffraction studies[66,67] have shown that the individual crystallites have a well-developed texture of (002) planes parallel to the deposition surface (Table 1).

This crystallographic picture is in good agreement with the results obtained by Fialkov *et al.*[68] in an X-ray structural investigation of natural graphites which had been made amorphous.

Other diffraction work has shown[8,67,69] that the degree of orientation of the hexagonal planes with respect to the deposition surface increases at higher deposition temperatures. The preferential orientation of pyrographite as a function of deposition temperature is assessed by X-ray diffraction[67] from the intensity of the (002) reflections obtained when the deposition surface is aligned at various angles to the incident beam. The degree of preferential orientation was evaluated[67] as the ratio of $n_{max}$ to $n_{min}$, the relative intensities obtained with the deposition surface perpendicular and parallel to the incident X-ray beam.

Bragg and Packer[70], from measurements of the integral intensity of the (002) line, constructed a plot of this parameter (expressed in arbitrary units) against the inclination of the specimen ($\alpha$) to the incident beam. They showed (Fig. 4) that the intensity of the (002) line varies linearly with $\alpha$ [Fig. 4 shows that the logarithm of the intensity varies linearly with $\alpha^2$ (Ed. of Translation)] for specimens deposited at 1950° (*1*) and 2100° (*2*). Heating at 3000° for various times (curves *3* and *4*) introduced some departures

TABLE 1. X-Ray diffraction analysis of pyrographite.

| Specimen | Interplanar spacing, $d_{002}$, Å | Crystallite size along a axis, $L_a$, Å | Degree of graphitisation (Ref. 71) |
|---|---|---|---|
| Prepared[66] in induction-heated vacuum furnace at 2300° | 3.38 | 300 | 0.57 |
| Prepared[66] in induction-heated vacuum furnace at 2400° | 3.35 | 600 | 1.0 |
| Prepared[66] in a vacuum resistance furnace at 2100° | 3.42 | 235 | 0.07 |
| Prepared[66] in a vacuum resistance furnace at 2500° | 3.37 | — | 0.78 |

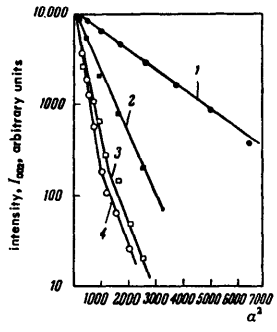



Fig. 4. Variation of the intensity $I_{002}$ with the angle of incidence of the X-ray beam (after Bragg and Packer [70]) for different specimens of pyrographite, deposited: 1) at 1950°; 2) at 2100°; 3) at 2100°, followed by heat treatment for 5 min at 3000°; 4) treated for 25 min at 3000°.

TABLE 2. Influence of temperature and method of heating of the deposition surface upon the degree of preferential orientation.

| Deposition temperature, °C | Method of heating | Subsequent heat treatment | Preferential orientation | | Literature references |
|---|---|---|---|---|---|
| | | | $n_{max}/n_{min}$ | $\chi_\perp/\chi_\parallel$ | |
| 1 | 2 | 3 | 4 | 5 | 6 |
| 2100 | in resistance furnace (at atmospheric pressure) | none | — | 8 | 10 |
| 2100 | in resistance furnace (at atmospheric pressure) | none | — | 11 | 10 |
| 2100 | in resistance furnace (at atmospheric pressure) | heated to 2900° | — | 16 | 10 |
| 2300 | in resistance furnace (at atmospheric pressure) | heated to 2900° | — | 17 | 10 |
| 2100 | in resistance furnace (at atmospheric pressure) | heated to 3400° | — | 24 | 10 |
| 2300 | in resistance furnace (at atmospheric pressure) | heated to 3400° | — | 40 | 10 |
| 1700 | induction (*in vacuo*) | none | 5 | — | 88 |
| 1700 | induction (*in vacuo*) | 3 h at 2500° | 5 | — | 88 |
| 2400 | induction (*in vacuo*) | none | 2000 | — | 88 |
| 2100 | in resistance furnace (*in vacuo*) | none | 2000 | — | 88 |
| 2500 | in resistance furnace (*in vacuo*) | none | 4000 | — | 88 |

from linearity. However, Fig. 4 justifies the general conclusion that the (002) planes of the crystallites in pyrographite show a gaussian distribution, which can be expressed in the form:

$$I(\alpha) = I_0 \exp(\alpha^2/2\sigma^2),$$

where $\sigma$ is the variance of the distribution.

At higher preparation temperatures, and after high-temperature treatment, $\sigma$ decreases. Measurements of the diamagnetic susceptibility of a pyrographite film in the above-mentioned directions are a good method for evaluating structural anisotropy [10].

Data on the degree of preferential orientation as a function of deposition temperature and method of heating are reproduced in Table 2. It can be seen that the value of $n_{max}/n_{min}$ varies from 5 at 1700° to approximately 4000 at 2500°.

The magnetic measurements reveal quite substantial changes in anisotropy after heat treatment (up to 3400°) of specimens prepared at 2100–2300°.

At temperatures of 2200–2300° and above, the pyrographite begins to develop three-dimensional order. This transition is preceded by a steady increase in crystallite size with temperature (both the height $L_c$ and the diameter $L_a$), and by a decrease in interplanar spacing (Table 1). The transition manifests itself by the appearance and development of a (112) X-ray structural reflection, detected by the increase in the ratio of line intensities $I_{112}/I_{110}$.

Another quantitative test of the incipient three-dimensional ordering is provided by the sharp increase in electrical and thermal anisotropy. Taking a value of approximately 3.42 Å for the interlayer distance in the disordered state, and 3.355 Å in the single crystal, Kasatochkin and Kaverov [71] proposed the parameter $\gamma$ for estimating the degree of graphitisation:

$$\gamma = \frac{3.425 - C_0/2}{3.425 - 3.355} = \frac{3.425 - C_0/2}{0.065},$$

where $C_0/2$ is the measured interlayer distance of the specimen.

Fig. 5 shows the variation of the three-dimensional ordering parameter of pyrographite with deposition temperature. By using induction heating (curve *1*), values varying between 0 and 1 can be obtained in the temperature range 1700–2400°.

These changes are characteristic of all types of graphitic carbon showing good graphitisation (homogeneous graphitisation, in Franklin's terminology [72]). When heating is by passage of an electric current through the specimen on which deposition is taking place (*cf.* curve *2* of Fig. 5), the graphitisation parameter is much lower. The difference between the two methods of heating is most probably due to an increasing thermal isolation of the pyrographite layer on the heater, causing a decrease in deposition temperature with increasing distance from the original surface of the heater.

Blackman and Ubbelohde [69] have published photometric curves obtained in an X-ray diffraction study of individual specimens of pyrographite of different thickness. Fig. 6 shows that the (*h*0*l*), (*hkl*), and (00*l*) lines decrease in intensity and increase in width as the thickness of the deposit increases, indicating a decrease in the degree of three-dimensional order with increasing separation from the original deposition surface.

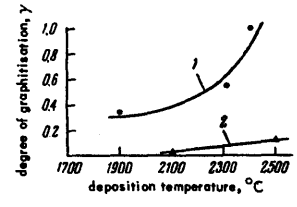



Fig. 5. Effect of deposition temperature and method of heating on the parameter for three-dimensional structural ordering in pyrographite:
1) heating in induction furnace;
2) heating in resistance furnace.

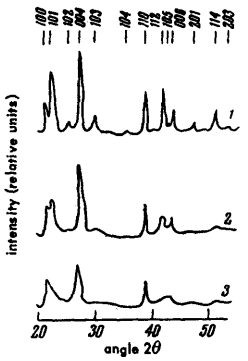



Fig. 6. Photometric traces from an X-ray diffraction study[69] of pyrographite, taken at various distances from the basal deposition plane:
1) 0.33 mm; 2) 0.49 mm; 3) 0.59 mm.

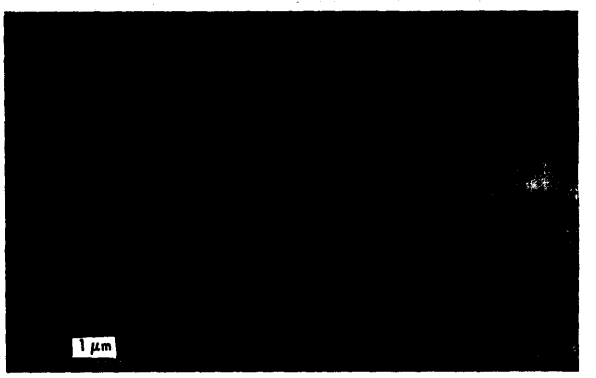



Fig. 8. Structure of pyrographite, observed in an electron microscope (× 8400).

Quite sharp differences in character between the resulting structures are revealed by the X-ray diffraction data for deposits of pyrographite obtained by Collingan and Galasso[37]. These authors showed that the structure of pyrographite is not a function of temperature only. Thus, they report that the (*hkl*) lines of specimens prepared at 1900° in an induction-heated furnace are sharper than those of specimens produced in a resistance furnace at 2200° and 2300°. It is right to point out, in this connection, that the deposition temperature is not a unique and sufficient criterion for the formation of the pyrographite structure. In addition to the temperature and to the method of heating, the composition and pressure of the gas phase, the gas flow rate, etc., can be expected to have a definite effect on the structure.

Fig. 7 shows a typical pyrographite microstructure, consisting of columnar formations of conical shape. As shown by X-ray diffraction, the hexagonal carbon planes are preferentially oriented normally to the conical formations, whose dimensions are typically a few microns. At higher deposition temperatures the columnar formations become dispersed[9,73,120].

High-temperature plastic deformation at 2750° tends to convert (10) lines into (100) and (101) lines. Thus, the degree of three-dimensional order — assessed by the increase in intensity of (101) lines — increases with the amount of plastic deformation[74]. Examination of pyrographite[75] in the electron microscope has revealed polygonal formations with a very fine internal structure.

The present authors have been able to detect[120] subgrains of less than 0.1 μm diameter in pyrographite preparations in the electron microscope (Fig. 8), thus confirming earlier reports[75,76].

## V. PROPERTIES OF PYROGRAPHITE

### 1. Density

The specific gravity of polycrystalline graphitised carbon materials is one of their most important characteristics. This criterion is also very informative with pyrolytic graphite.

The variation of density with deposition temperature has been described by Brown and his coworkers[7,8,73,77].

On the curve of density against deposition temperature (Fig. 9) we may distinguish the following sections: (1) 1000–1400°; (2) 1400–1700°; (3) 1700–2000°; (4) 2000–2500°.

It can be assumed that the density of a pyrolytic graphite deposit is controlled by two main factors: (1) the mobility of carbon atoms on the deposition surface (the rate of

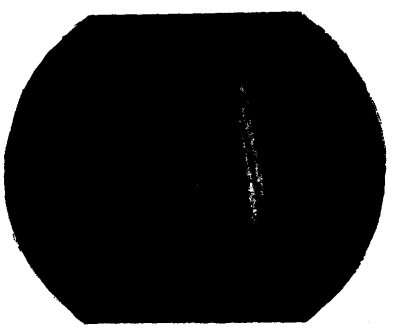


Fig. 7. Microstructure (× 50) of pyrographite, prepared by the authors[120] *in vacuo* at 2100° in a resistance furnace.

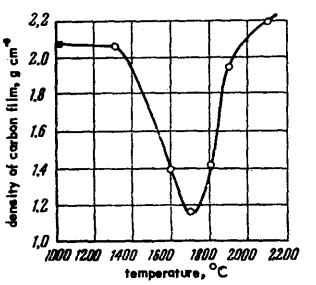



Fig. 9. Variation in density of pyrographite with temperature (after Brown and Watt[8]).

reorganisation of the crystallites); (2) the size of the hydrocarbon radical involved in the decomposition process at the surface.

In the temperature region 1000–1400° the mobility of carbon atoms is low and the hydrocarbon radicals are small, so that the resulting deposits are weakly oriented and have a high density (2.0–2.1 g $cm^{-3}$). Between 1400° and 1700° the activation energy of the dehydrogenation processes decreases, and the rate of formation of hexagonal carbon planes increases. At the same time, the hydrocarbon radicals become very much larger. The net result of these effects is to produce poorly oriented deposits of quite low density (as low as 1.29 g $cm^{-3}$ at 1700°).

At temperatures above 1700°, there is a sharp increase in the mobility of the hexagonal carbon planes, and fairly well oriented deposits of high density are formed in spite of the possibility of larger hydrocarbon radicals (the density exceeds 2.22 g $cm^{-3}$, and approaches the value of 2.26 g $cm^{-3}$ found in single crystals[9]).

The density and other properties of the deposits are not a function of the nature of the hydrocarbon[7,8,20,73,77].

Studies of gas permeability[19,73] have shown that open pores are absent. This suggests that the change in density of pyrographite is due exclusively to changes in the packing of the crystallites and of their constituent hexagonal layers.

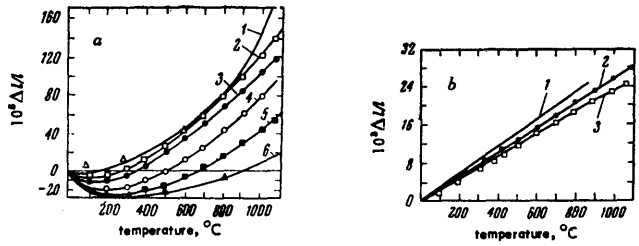



Fig.10. Temperature variation of linear thermal expansion for pyrographite and single crystals of natural graphite in two mutually perpendicular directions[80]:
*a*) along the *a* axis:
1) of specimens prepared at at atmospheric pressure;
2) of coarsely crystalline structures prepared *in vacuo* and heat treated for 3 h at 2700°;
3) of coarsely crystalline structures prepared *in vacuo*;
4) of microcrystalline structures prepared *in vacuo*;
5) of microcrystalline structures prepared *in vacuo* and heat treated for 3 h at 2700°;
6) of single crystals of natural graphite;
*b*) along the *c* axis:
1) of single crystals of natural graphite;
2) of pyrographite as prepared;
3) of pyrographite heat treated for 1 h at 3000°.

## 2. Hardness

The hardness of pyrographite is a function of the deposition temperature, and shows a maximum at 1000–1520° according to Tesner and Timofeeva[20]. This is because the material prepared at these temperatures has the maximal amount of structural disorder and the best developed system of cross-linking bonds.

The hardness of pyrographite has been found to be higher in the deposition direction than at right angle to it.

According to Lozier and Manofsky[9], pyrographite of density 2.2 g $cm^{-3}$ (deposited at 2000°) is nine or ten times harder in the deposition direction than ordinary polycrystalline graphite. Subsequent heat treatment at 3000° produces a four- or five-fold decrease in hardness, both in the deposition direction and perpendicular to it.

## 3. Linear Thermal Expansion

Pappis found[78-81] that the linear thermal expansion coefficient of pyrographite is directly related to the crystallographic anisotropy of the material. Fig. 10 shows the changes in linear thermal expansion of pyrographite specimens in two mutually perpendicular directions as a function of the temperature and method of preparation, and of heat treatment. An increase in the deposition temperature, and high-temperature heat treatment, cause the linear expansion coefficient in both directions to approach the corresponding values for single crystal specimens[9]. However, as Fig. 10 shows, the two values differ very considerably. This is because the linear expansion coefficient of pyrographite is sensitive not only to crystallographic factors but also to the microstructure, and to the internal stresses which develop in the material. Heat treatment at 3000°, by favouring the growth of structural anisotropy, also relieves internal stresses in the material. Specimens prepared at atmospheric pressure (unlike those prepared in a vacuum) do not show a negative temperature coefficient between 0° and 700° in the direction parallel to the deposition surface. This indicates a considerable decrease in the degree of preferential orientation of the hexagonal carbon layers.

The large difference (more than a factor of ten) between the linear thermal expansion coefficients in two mutually perpendicular directions causes the large internal thermal stresses which appear in pyrographite on cooling[69].

## 4. Mechanical Properties[4,74,78,80-84]

There are large discrepancies between results obtained by various authors, owing to the lack of a unique method of determining the mechanical properties of pyrographite. Hence, the statements made below should only be accepted as tentative. Like many of its other properties, the strength of pyrographite shows distinct anisotropy. It is highest in the direction parallel to the deposition surface.

(a) The tensile strength increases with temperature (as in the case of polycrystalline graphites). Pappis[80] explains this phenomenon in terms of the increase in plasticity of pyrographite on heating. However, it seems more likely that the increase in strength of pyrographite with temperature is associated with the relief of internal stresses, the closing up of microcracks, and the increase in area of contacting surfaces on heating.

The temperature coefficient of the tensile strength depends on the deposition temperature (Fig. 11), and to a lesser degree on the size of the conical fragments.

A decrease in grain size makes the appearance of internal stresses less likely, and thus raises the strength of these materials.

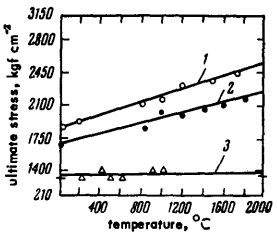



Fig.11. Temperature variation of the tensile and bend strengths of pyrographite:
1) bend strength[80] with load applied parallel to the *c* axis;
2) bend strength with load applied normal to the *c* axis;
3) ultimate tensile stress[85].

One of the main differences between pyrolytic graphite and the normal polycrystalline graphite carbons is the steady increase in strength of the former up to temperatures[83] in excess of 3000°.

(b) The bend strength increases with decreasing size of the conical formations, again because of the decreased probability of crack formation. This parameter also increases slightly with the temperature of the measurement (Fig. 11).

(c) The elongation increases from 0.1% at room temperature to 24% and 59.2% at 2500° and 2750° respectively[74]. At 1650° the elongation of pyrographite is higher than that of any other form of synthetic graphite.

## 5. Thermal Conductivity[8-9,69,71,73,74,80-82,84,86,87]

It is evident, from the data of Table 3, that the anisotropy coefficient at 300°K can vary from 50 to 100 according to the conditions under which the pyrographite is prepared[87]. In the direction parallel to the deposition surface the thermal conductivity can be as high as 320 kcal $m^{-1}$ $h^{-1}$ $deg^{-1}$, which is higher than the thermal conductivity of copper, whereas in the perpendicular direction it has a value of the order of 1–3 kcal $m^{-1}$ $h^{-1}$ $deg^{-1}$, which corresponds to the best high-temperature thermal insulants.

The temperature dependence of the thermal conductivity of various types of pyrographite is shown in Fig. 12. It is determined by phonon–phonon interactions and by the size of the crystallites. The curves go through a maximum at 50–100°K. Below these temperatures $K_\perp$ is proportional to $T^\alpha$, where $\alpha$ lies between 2.3 and 2.8. These data show that the anisotropy coefficient of the thermal conductivity of pyrographite is also a function of temperature.

TABLE 3. Thermal conductivity of pyrographite.

| Specimen | Density, g $cm^{-3}$ | Thermal conductivity, kcal $m^{-1}$ $h^{-1}$ $deg^{-1}$ | | | Thermal anisotropy $K_\parallel/K_\perp$ |
|---|---|---|---|---|---|
| | | measurement temperature, °K | $K_\perp$ | $K_\parallel$ | |
| Raytheon pyrographite (Ref. 87) | 2.10 | 300 | 2.25 | 215 | 95 |
| Raytheon pyrographite (Ref. 87) | 2.17 | 300 | 2.95 | 320 | 110 |
| General Electric pyrographite (Ref. 87) | 2.19 | 300 | 1.24 | 57 | 46 |

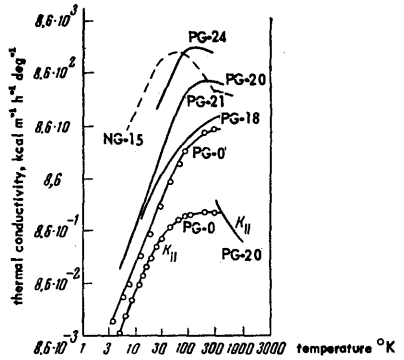



Fig.12. Temperature dependence of the thermal conductivity of various specimens of pyrographite (PG) and natural graphite (NG) at right angles to the *c* axis, after Slack[87]. Values of $K_\parallel$ (parallel to the *c* axis) are given only for two specimens. NG-15, Canadian natural graphite; PG-24, National Carbon pyrographite; PG-21, Royal Aircraft Establishment pyrographite; PG-20, Raytheon pyrographite; PG-18, National Carbon pyrographite; PG-0, General Electric pyrographite.

## 6. Electrophysical Properties

(a) Electrical resistivity. Fig. 13, based on Klein's results[88], shows the effect of deposition temperature on the electrical resistivity in a direction parallel to the deposition surface (see also Table 4).

The curve of Fig. 13 can be divided into sections corresponding to the following temperature ranges: 1100–1700°, in which the curve slopes gently; 1700–2000°, where the electrical resistance falls sharply (by about a factor of ten); above 2000°, where the curve slopes gently again.

This curve has a characteristic similarity to the behaviour of conventional well graphitised materials. However, the inflections occur at lower temperatures with the latter materials, and the resistance in the direction of the

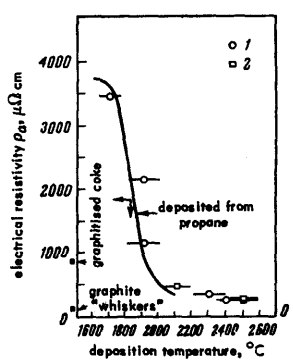



Fig.13. Effect of deposition temperature[88] on the electrical resistivity of pyrographite in the direction of the *a* axis:
1) pyrographite prepared in an induction furnace;
2) pyrographite prepared in a resistance furnace.

TABLE 4. Electrical resistivity at 20° of pyrographite and some graphites.

| Materials | Resistivity, Ω mm² m⁻¹ | | Anisotropy $\rho_a/\rho_c$ |
|---|---|---|---|
| | $\rho_a$ | $\rho_c$ | |
| Pyrographite[88] prepared at 2500° | 3 | 11000 | 3670 |
| Graphite single crystals[89,90] | 0.4 | 50 | 125 |
| Graphite "whiskers"[91] | 0.5 | — | — |
| Synthetic graphite | 10 | — | — |

deposition plane is much lower in the case of pyrographite. This is yet another manifestation of the sharp structural anisotropy of pyrographite. However, the electrical resistance in the direction of the *a* axis is about an order of magnitude higher than in a graphite single crystal.

For the reasons already discussed, the resistance at right angles to the deposition surface increases with deposition temperature. This gives rise to a large increase in the anisotropy of the electrical resistivity with increase in deposition temperature. As Klein points out[88], this effect is intimately related to the structural anisotropy of the material ($n_{max}/n_{min}$, measured by X-ray diffraction as described above).

(b) Magnetic susceptibility. The magnetic susceptibility of pyrographite, like that of other graphitic carbons, is of the diamagnetic type. This is explained by the aromatic structure of the carbon network.

Table 5 gives the diamagnetic susceptibility of pyrographite specimens (after Fishbach[10]), together with susceptibility data for single crystals.

The diamagnetic susceptibility of pyrographite was measured in two mutually perpendicular directions: $\chi_{\parallel}$ and $\chi_{\perp}$ (parallel and perpendicular to the deposition surface, respectively). The measurements were made by the Gouy balance method; the average susceptibility was calculated by the expression $\chi_{av} = \chi_{\perp} + 2\chi_{\parallel}$ CGS deg$^{-1}$.

It is clear from the data in Table 5 that the anisotropy of the diamagnetic susceptibility of pyrographite increases after heat treatment.

The effect of the heat-treatment temperature on the average magnetic susceptibility of pyrographite prepared at 2100–2300° is shown in Fig. 14. The susceptibility minimum found at 2900° is due to the removal of structural defects at these temperatures. Pyrographite prepared at 1900–2000° shows very small changes in susceptibility with the temperature of heat treatment.

TABLE 5. Diamagnetic susceptibility of pyrographite and of single crystals of natural graphite at 20°, $10^6$ CGS g$^{-1}$.

| Materials | $\chi_{av}$ | $\chi_{\perp}$ | $\chi_{\parallel}$ | $\chi_{\perp}/\chi_{\parallel}$ |
|---|---|---|---|---|
| Pyrographite prepared at 2100° (after Fishbach (Ref. 10) | 27.3 | 21.6 | 2.8 | 8 |
| Same specimen, heat treated at 2900° | 20.0 | 17.8 | 1.1 | 16 |
| Same specimen, heat treated at 3400° | 20.7 | 19.0 | 0.8 | 24 |
| Single crystals of natural graphite, data by Poquet *et al.* (Ref. 92) | 24.7 | 24.0 | 0.3 | 66 |
| data by Krishnan and Ganguli (Ref. 93) | 23.0 | 22.0 | 0.5 | 44 |

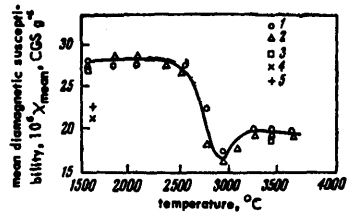



Fig. 14. Variation of the mean diamagnetic susceptibility of pyrographite with temperature of heat treatment (after Fishbach[10]):
1) pyrographite deposited at 2200–2300°;
2) pyrographite deposited at 2100°;
3) pyrographite deposited at 2200°;
4) from Ref. 92;
5) from Ref. 93.

(c) Hall coefficient. The following conclusion can be drawn from the variation of Hall coefficient and degree of graphitisation with deposition temperature[88], shown in Fig. 15.

(1) Pyrographite deposits offer a very wide range of electrophysical properties.

(2) The sign of the Hall coefficient changes twice over the range of deposition temperatures: from minus to plus when deposition occurs at 1500–1600° and from plus to minus at 2100–2200°.

(3) The highest value of the Hall coefficient in the *p*-region occurs at about 1800–1900°, as compared with 2000–2100° for conventional well-graphitised carbons. This same reduction by 200 deg in the critical temperature occurs also, as stated above, in the curve of electrical resistivity against deposition temperature: it is indicative of lower-temperature processes taking part in the formation of intermediate structures in the case of pyrographite.

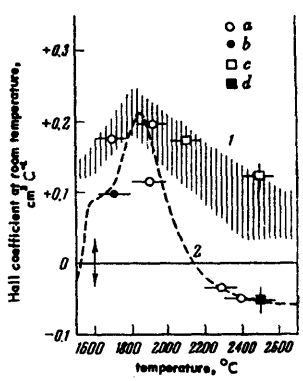



Fig. 15. Effect of deposition temperature on the Hall coefficient of pyrographite[88]:
1) carbon black region;
2) curve for pyrographite;
*a*) prepared in an induction furnace;
*b*) the same, after heat treatment;
*c*) prepared in a resistance furnace;
*d*) the same, after heat treatment.

TABLE 6. Hall coefficients of some graphitic structures.

| Materials | $R_H$, cm³ C⁻¹ |
|---|---|
| Pyrolytic graphite[88] prepared in a resistance furnace at 2000° | +0.12 |
| Pyrolytic graphite, heat treated[88] at 2600° | −0.05 |
| Single-crystal natural graphite[94] | −0.05 |
| Industrial *p*-type graphite | +0.30 |
| Industrial *n*-type graphite | −0.01 |

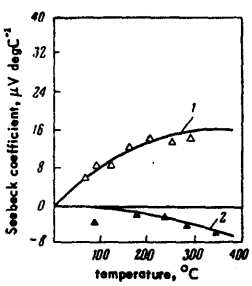



Fig.16. Temperature dependence of the Seebeck coefficient of pyrographite[89]:
1) as prepared;
2) heat treated at 3000°.

This can be explained in terms of the preferential orientation of the hexagonal layers in pyrographite, facilitating the subsequent structural transformations which ultimately determine the electronic properties.

(4) The *p*-region of the Hall curve corresponds to a degree of graphitisation $\gamma \leq 0.6$. In this region we observe the highest development of structural defects which act as "traps" for electrons and thus give rise to positive holes.

(5) Heat treatment which causes $\gamma$ to increase beyond $\gamma = 0.5$ can also convert pyrographite from the *p* to the *n* conduction type (see also Table 6).

(6) This latter circumstance offers the possibility of realising *p*–*n* junctions in thick layers of pyrographite heat treated at different temperatures. These can be used as high-temperature thermoelements.

Fig. 16 shows the change in Seebeck coefficient with temperature for a *p*–*n* junction in a flat wafer of pyrographite. The *p*-region of graphitised carbons is known[94-99] to conduct by both electrons and holes. The changes in Hall coefficient in this case are due to recombination effects arising from electron–hole interactions in the pyrographite. At the appropriate concentrations of the two types of carrier, and making allowance for the difference in mobility of electrons and holes, conditions for the minimal concentration of uncompensated positive charges (holes) can arise. These correspond to the maximum in the Hall curve.

## VI. USES OF PYROGRAPHITE

The high heat resistance, strength, and density of pyrographite, in conjunction with a highly anisotropic thermal conductivity, enable this material to be used in ultra-high-temperature technology as a highly heat-resisting constructional material and for thermal insulation[100-112]. It has been reported[3,6,83,86,101,108-110,113-115] that pyrographite can be used successfully as an erosion-resistant coating for the nozzles of rocket motors, combustion chambers, and nosecones. The properties of pyrographite are said to be superior to those of the best grades of graphite, previously used for these purposes.

Since pyrographite is a practically non-porous material, it has an interesting application as a moderator in nuclear technology. There has been a report[116] of particles of uranium or thorium dicarbide being covered with a 50–100 μm layer of pyrographite and mixed with graphite to produce the heat-evolving elements of a reactor.

The freedom from pores and high corrosion resistance of pyrolytic graphite enable it to be used in the chemical industry as a replacement for scarce metals. Furthermore, vacuum-tight and chemically stable high-temperature materials can be produced by filling the pores of conventional graphitised carbon ware with pyroltyic graphite[19-20].

Graphite tubes, coated with pyrolytic graphite, have proved highly satisfactory as heater elements for electrical resistance furnaces[117].

The unique electrical properties of pyrographite offer a wide scope for applications in electronics (various types of resistor, shunts, etc.)[16-18].

As stated above, the thermoelectric properties of pyrographite enable *p*–*n* junctions to be prepared in the material, and offer the possibility of using pyrographite in high-temperature thermocouples and thermoelements. The recent measurements by Rupprecht *et al.*[118] of the Seebeck coefficient of various pyrographites confirm this prediction.

Thin films of pyrographite show interesting optical properties[83], including that of optical anisotropy. The absorption coefficient for electromagnetic waves is a function of the direction of polarisation, as is the reflectivity. Thus, thin films of pyrographite can be used to polarise infrared radiation[119].

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# THERMODYNAMICS OF MOLTEN SALTS WITH A COMMON ION

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## 1. INTRODUCTION

According to Semenchenko's classification[1], ionic salt solutions belong to the group of homoeodynamic solutions. Hence, solutions of ionic salts can be expected to show the general properties of homoeodynamic solutions.

The theory of homoeodynamic solutions relies to a great extent on statistical methods. However, at least for the time being, any kind of statistical description can give no more than a relatively crude picture of real solutions. We believe, therefore, that simple and clearly defined physical models, whose conclusions can be put to simple experimental test, should prove very valuable in this field. The regular solution model is typical of such models.

According to the theory of regular solutions, the potential energy of formation of a solution, $\Delta E$, is given by the expression

$$\Delta E = \omega N_{AB}, \tag{1}$$

where $N_{AB}$ and $\omega$ are respectively, the number of bonds between atoms or molecules of different kinds in the case of atomic or molecular solutions and the average potential energy of one such bond (exchange energy). For solutions of ionic salts, these quantities refer to the number of bonds between ions of different kinds and the average potential energy of one bond. If the solution, composed of the salts $A_{n_1}C_{n_2}$ and $B_{n_3}C_{n_4}$, contains $n_1N_1$ ions of kind A and $n_3N_2$ ions of kind B, we have

$$N_{AB} = \frac{n_1N_1 \cdot n_3N_2}{n_1N_1 + n_3N_2}. \tag{2}$$

Since the chemical potential of the $i$th salt component is given by

$$\mu_i = \mu_{i0} + \frac{\partial \Delta E}{\partial N_i} - T\frac{\partial \Delta S}{\partial N_i}, \tag{2a}$$

it can also be expressed, using Eqns. (1) and (2), in the form

$$\mu_i = \mu_{i0} + \omega\beta_i(1 - x_i)^2 - T\frac{\partial \Delta S}{\partial N_i}, \tag{3}$$

where

$$\beta_1 = \frac{n_1}{\left(x_2 + \frac{n_1}{n_3}x_1\right)^2}, \quad \beta_2 = \frac{n_3}{\left(x_1 + \frac{n_3}{n_1}x_2\right)^2}, \quad x_i = \frac{N_i}{N_1 + N_2}; \tag{4}$$

and $\mu_{i0}$ denotes the chemical potential of the $i$th component in its standard state (taken to be the pure compound); $\Delta S$ is the entropy of mixing. In what follows, formulae relating to the first and to the second component of a solution or of a system will be written in that order.

The present article discusses the application of regular solution theory to solutions of ionic salts having a common ion, and considers the relation between the exchange energy $\omega$ and the properties of the individual constituents. Considerable use is made of published data as well as of values calculated by the writers.

## 2. DISTINGUISHABILITY OF THE COMMON ION

The earliest theories of ionic solutions[2,3,4], and some of the later ones[5,6], determine the potential energy of a solution in terms of the ionic radii and the composition. The entropy of mixing is usually assumed equal to the normal entropy of mixing of ideal solutions. This approximation can be too crude when ions of different valencies are involved, since the problem of the entropy of mixing is not considered in those papers.

From the thermodynamic point of view, the formation of an ideal solution presents three independent requirements:

1. The change in potential energy resulting from formation of the solution must be zero.

2. The volume change accompanying the formation of the solution must be zero.

3. The partial entropy of mixing of the $i$th component must equal $-k \ln x_i$ (where $k$ is Boltzmann's constant).

These conditions are usually assumed when dealing with molecular and atomic solutions belonging to the homoeodynamic class of solutions. The first two can also be adopted for solutions of ionic salts, but the third requires clarification.

The difference between ionic salt solutions on the one hand and atomic and molecular homoeodynamic solutions on the other is that in the former solutions the number of species (i. e. kinds of particles) is not the same as the number of solution components. For example, in a two-component KCl–RbCl solution we have three kinds of particles: potassium, rubidium, and chloride ions. The appearance of an additional species may give rise to an additional term in the entropy of mixing. Therefore, the third condition for the formation of ideal solutions of ionic salts should be formulated in the most general way, i. e. by stating that the particles (ions) in solution which determine the entropy of mixing must be distributed entirely randomly, according to the laws of chance.

The problem of ideal solutions of ionic salts appears to have been first discussed in a paper by Temkin[7], who used an ionic model of pure salts and their mixtures. The ions in pure salts and in solutions of salts are assumed to be distributed so that each cation is effectively surrounded by anions and vice versa. The electrostatic forces between ions are quite large, and therefore interchange of cations and anions must be excluded when computing the entropy of mixing. According to Temkin, the entropy of mixing is given by

$$\Delta S = \Delta S_+ + \Delta S_-;$$
$$\Delta S_+ = k \ln W_+; \quad \Delta S_- = k \ln W_-; \tag{5}$$

where $W_+$ and $W_-$ are the numbers of possible interchanges between cations only and between anions only.

Temkin applied Eqn. (5) only to solutions consisting of the salts AB and CD. For solutions of other salts, Temkin introduces the concept of activity coefficient by analogy with aqueous solutions. This is hardly justifiable, however[8]. It would be desirable, therefore, to apply Eqn. (5) to ionic salt solutions of any type. In fact, the entropy of mixing, determined by the interchange between distinguishable particles (i. e. those particles whose interchange produces a new microstate of the solution), is also the parameter which determines the formation of an ideal solution. This part of the entropy is given by Eqn. (5). We should also note that whereas Temkin's paper discusses liquid solutions (melts), the conclusions are equally applicable to solid solutions of ionic salts, since the state of aggregation is not taken into consideration.

Thus, the entropy of mixing of an ideal solution of ionic salts should be calculated from Eqn. (5). In accordance with this equation, the chemical potential of the $i$th salt component in an ideal solution is given by

$$\mu_i = \mu_{i0} - T\left(\frac{\partial \Delta S_+}{\partial N_i} + \frac{\partial \Delta S_-}{\partial N_i}\right). \tag{6}$$

We will discuss the application of Eqn. (6) to various binary solutions having a common ion. Although the formal discussion is confined to a common anion, all theoretical conclusions are equally applicable to solutions with a common cation. The general formulae of the salts which compose the solutions are $A_{n_1}C_{n_2}$ and $B_{n_3}C_{n_4}$: we shall refer to these as the first and the second component respectively. We shall use $N_1$ and $N_2$ for the number of "molecules" of $A_{n_1}C_{n_2}$ and $B_{n_3}C_{n_4}$ in the solution.

1. The cations A and B have the same valency. The chemical formulae of the salts forming the solution are $A_{n_1}C_{n_2}$ and $B_{n_1}C_{n_2}$. A solution composed of these salts has $n_1(N_1 + N_2)$ cation sites and $n_2(N_1 + N_2)$ anion sites. We shall assume that each cation can occupy only one cation site and each anion only one anion site. The anions corresponding to the cations A and B are indistinguishable, i. e. they form a "medium", within which cation interchange can take place. Then

$$W_- = 1, \ \Delta S_- = 0. \tag{7}$$

The cations in cation sites can be distributed in more than one way: two cases are possible.

(*a*) Cations of the two kinds are distributed randomly over the cation sites in such a way that "molecules" can be distinguished in the solution:

$$A_{n_1}C_{n_2}, \ A_{n_1-1}BC_{n_2}, \ A_{n_1-2}B_2C_{n_2}, \ \ldots, \ B_{n_1}C_{n_2}.$$

In this case the individual A and B ions can interchange places. Hence

$$W_+ = \frac{n_1N_1 + n_1N_2}{(n_1N_1)!\,(n_1N_2)!}. \tag{8}$$

Substituting Eqns. (7) and (8) into (5), and differentiating Eqn. (6), we find

$$\mu_1 = \mu_{10} + n_1kT \ln x_1;$$
$$\mu_2 = \mu_{20} + n_1kT \ln x_2. \tag{9}$$

(*b*) The different cations in solution are distributed in groups. Assume, for example, that the solution contains only "molecules" $A_{n_1}C_{n_2}$ and $B_{n_1}C_{n_2}$. In this case, A and B ions form a group of cation sites, and interchanges in cation sites are possible only in groups of $n_1$ A-cations and $n_1$ B-cations. If we assume that these groups are randomly distributed in the solution,

$$W_+ = \frac{(N_1 + N_2)!}{N_1!N_2!}. \tag{10}$$

Substitution of Eqns. (7) and (10) into (5), and differentiation of Eqn. (6), gives

$$\mu_1 = \mu_{10} + kT \ln x_1;$$
$$\mu_2 = \mu_{20} + kT \ln x_2. \tag{11}$$

Our general solution model cannot, of course, identify the solutions in which case *a* or case *b* is realised. We may conclude, however, on general grounds, that case *a* should obtain in solid solutions, since the formation of solid solutions requires that the cations A and B should have similar properties. In liquid solutions (melts), on the other hand, case *b* is also possible.

2. The cations A and B have different valencies. Here, the calculation of entropy of mixing for an ideal solution presents very real difficulties. With cations of the same valency we are able to treat the anions as a "medium" for the interchange of cations, but the situation has to be more accurately defined when cations of

different valency are envisaged. Consider, for example, the solution KCl–RbCl. According to our model, this solution consists of $N_1 + N_2$ cation sites and $N_1 + N_2$ anion sites. Let the cation and anion sites in the solution be distributed in a regular pattern, forming a lattice of cations and a lattice of anions. Interchange of cations within the cation lattice is possible, independently of any interchange of anions in the anion lattice. We can visualise a hypothetical spatial separation of the two lattices, which are then spatially reunited after carrying out cation and anion interchanges. Electrical neutrality of the final solution must, of course, be preserved. The criterion for indistinguishability of the anions is that cation interchanges shall be independent of anion interchanges.

Cation interchanges in solutions with cations of different valency cause either a change in the valency of one of the cations or the appearance of vacancies in the cation or the anion sublattice. These processes are needed to compensate the excess of charge arising from the exchange of cations of different valency in solution. Since excess charge compensation most frequently involves the formation of vacancies, we shall consider only this case. It must be clearly understood that these are not the familiar Schottky or Frenkel' vacancies, but simply vacancies resulting from the presence of cations of different valency in the solution. It may be thought that the appearance of vacancies must lead to an increase in the number of microstates, and that the entropy of mixing must be larger in the present of vacancies. It should be possible to calculate the increase in the entropy of mixing by taking into account the vacancy–ion interchanges. This procedure is followed in the papers by Flood, Förland, and others[9,10], but it meets serious difficulties because vacancies cannot be transferred to ionic sites without interchanging ions as well. Consequently, we are not in a position to calculate the number of interchanges by the normal procedure. An alternative approach seems more tractable[11]. Solutions of ionic salts can be subdivided into two classes:

1. Solutions in which cations of different kinds can be interchanged without interchanging anions.

2. Solutions in which cations of different kinds cannot be interchanged without interchanging anions.

Solutions of the first class include those in which the cations have the same valency, but solutions with cations of different valency may also belong to this class. Thus, if the formation of the solution can be described by the equation

$$A_{n_1}C_{n_2} + m\,B = A_rB_mC_{n_2} + (n_1 - r)\,A, \tag{12}$$

it is evident that interchange of unlike cations can occur without interchange of anions, and solutions of this type must therefore be assigned to the first class. However, cation migration can occur also by other mechanisms. We shall consider this in the concrete case of solutions with a univalent anion.

If, in the solutions formed by the salts $AC_{n_2}$ and $BC_{n_4}$, each cation occupies only one cation site, the additional anions will be located in additional anion sites. Interchange of unlike cations is impossible without anion interchange. Therefore, the anions must be treated as distinguishable species in systems of this type (with the obvious exception of $AC_{n_2}$–$BC_{n_2}$ solutions), and

$$W_+ = \frac{(N_1 + N_2)!}{N_1!\,N_2!};\quad W_- = \frac{(n_2N_1 + n_4N_2)!}{n_2N_1!\,n_4N_2!}. \tag{13}$$

Consequently

$$\mu_1 = \mu_{10} + kT\left(\ln x_1 + n_2 \ln \frac{n_2x_1}{n_2x_1 + n_4x_2}\right);$$
$$\mu_2 = \mu_{20} + kT\left(\ln x_2 + n_4 \ln \frac{n_4x_2}{n_2x_1 + n_4x_2}\right). \tag{14}$$

However, a solution with vacancies in the cation sublattice can be formed in the case of $AC$–$BC_2$, $AC$–$BC_3$, $AC$–$BC_4$, and $AC_2$–$BC_4$ solutions if $N_1 > N_2$, i.e. if the solution contains a higher proportion of the salt $AC_{n_2}$ than of $BC_{n_4}$ – we are confining the discussion to salts in which the valency of the cation does not exceed four. Formally, this means that the cation B must occupy two cation sites. For example, when B cations are added to AC, a B cation can take the place of an A cation. If the B cation is doubly charged, charge compensation requires that a neighbouring A cation site should be unoccupied. In such a solution, a B cation can be transferred to a pair of A cation sites without disturbing the anions. Hence, the anions can be treated as indistinguishable in this case, and for these solutions we have

$$W_+ = \frac{(N_1 + N_2)!}{N_1!N_2!};\quad W_- = 1. \tag{15}$$

Therefore,

$$\mu_1 = \mu_{10} + kT \ln x_1;$$
$$\mu_2 = \mu_{20} + kT \ln x_2. \tag{16}$$

Thus, depending on the mechanism of formation of the solution, the anions can be distinguishable or indistinguishable in solutions of the types $AC$–$BC_2$, $AC$–$BC_3$, $AC$–$BC_4$. and $AC_2$–$BC_4$.

We will now turn to a more complicated example. Consider solutions of the salts $A_4C_3$ and $B_4C$, in which the anion is quadrivalent. Assume that $N_1 > N_2$. The addition of B cations to $A_4C_3$ can be described as

$$A_4C_3 + 3B = A_3B_3C_3 + A, \tag{17}$$

a situation to which "reaction" (12) applies. We can think of the resulting solution as consisting of "molecules" of $A_4C_3$ and $A_3B_3C_3$. The excess of B cations in the $A_3B_3C_3$ "molecule" is located at additional cation sites. In this case the anions are, of course, indistinguishable.

The same procedure can be applied to other cases. Unfortunately, as was stated above, it is not always possible to decide unambiguously whether the anions are or are not distinguishable, but the essential features of the proposed method of evaluating the effect of the anions on the entropy of mixing are clearly illustrated by the examples given. In general, when dealing with solutions composed of the salts $A_{n_1}C_{n_2}$ and $B_{n_3}Cn_{n_4}$, we can write

$$\mu_1 = \mu_{10} + kT_{n_1} \ln \frac{n_1x_1}{n_1x_1 + n_3x_2};$$
$$\mu_2 = \mu_{20} + kT_{n_2} \ln \frac{n_3x_2}{n_1x_1 + n_3x_2}, \tag{18}$$

for indistinguishable anions, and

$$\mu_1 = \mu_{10} + kT\left(n_1 \ln \frac{n_1x_1}{n_1x_1 + n_3x_2} + n_2 \ln \frac{n_2x_1}{n_2x_1 + n_4x_2}\right);$$
$$\mu_2 = \mu_{20} + kT\left(n_3 \ln \frac{n_3x_2}{n_1x_1 + n_3x_2} + n_4 \ln \frac{n_4x_2}{n_2x_1 + n_4x_2}\right), \tag{19}$$

for distinguishable anions. The reader can easily verify that Eqn. (9) is a special case of Eqn. (18).

These expressions for the chemical potential in ideal solutions can be extended to real solutions in the usual way: by adding the term $kT \ln \gamma_i$ to the right-hand side of the equations, where $\gamma_i$ is the activity coefficient of the $i$th component. For dilute solutions (and, to a first approximation, for concentrated solutions as well), the parameter $\gamma_i$ can be taken to be constant. This allows the equations to be used with real solutions. Furthermore, the variation of $\gamma_i$ with solution composition can be calculated from regular solution theory.

This approach to the calculation of entropies of mixing for ideal solutions of ionic salts is based on Temkin's model. The extent to which it is justified by the behaviour of real systems will be demonstrated below. At this point we should mention that a model essentially different from Temkin's is proposed in the papers of Herasimenko[12] and Bradley[13]. In this model, the interchange of cations and anions is not excluded, i. e. anions and cations are treated as equivalent from the point of view of the entropy of mixing. The model fails to take account of the most important feature of ionic solutions (namely, that ionic solutions consist of ions, not of molecules!), and is therefore a cruder approximation to real solutions than is Temkin's model.

The form of the chemical potential in liquid solutions of ionic salts can be judged from the variation of melting point with composition when the system shows a simple eutectic. Thus, the equation of the liquidus curve can be written[14]

$$\alpha_{i0} \ln \frac{T_{i0}}{T} = \ln \frac{1}{a_i}, \qquad (20)$$

where $a_i$ is the activity of the $i$th component in the liquid phase, and $T_{i0}$ is the melting point of the pure $i$th component. The quantity $\alpha_{i0}$ is simply related to the entropy of fusion of the pure $i$th component, $\Delta S_f$:

$$\alpha_{i0} = \Delta S_f / kT_{i0}, \qquad (21)$$

since to a first approximation liquid salt solutions have the properties of regular solutions. Then, using Eqn. (3), we find

$$\ln a_i = \omega \beta_i (1 - x_i)^2 - T \frac{\partial \Delta S}{\partial N_i}. \qquad (22)$$

On the other hand, the entropy of mixing of a regular solution is equal to the entropy of mixing of an ideal solution. Therefore

$$(\mu_i - \mu_{i0})_{\text{ideal}} = -T \frac{\partial \Delta S}{\partial N_i}, \qquad (23)$$

where $(\mu_i - \mu_{i0})_{\text{ideal}}$ is determined by Eqns. (18) or (19).

Consider the fusion of the first component in the presence of the second component, with $x_1 > x_2$. Eqns. (18) and (19) for the chemical potential can be written, approximately, in the form

$$\mu_1 - \mu_{10} = kTn_3 \ln x_1, \qquad (24)$$

for Eqn. (18), and

$$\mu_1 - \mu_{10} = kT(n_3 + n_4) \ln x_1, \qquad (25)$$

for Eqn. (19). Substituting these expressions into Eqns. (22) and (20), we arrive at the general expression

$$Y = \alpha - KX, \qquad (26)$$

where

$$Y = \frac{\ln x_1}{\ln \frac{T}{T_{10}}}; \quad X = \frac{x_2^2}{T \ln \frac{T}{T_{10}}}. \qquad (27)$$

For indistinguishable anions

$$\alpha = \alpha_{10}/n_3, \qquad (28)$$

whereas for distinguishable anions

$$\alpha = \alpha_{10}/(n_3 + n_4). \qquad (29)$$

The quantity $K$ in Eqn. (26) is a constant, proportional to $\omega\beta_1$. For indistinguishable anions the proportionality coefficient is $1/kn_3$, whereas for distinguishable anions it is $1/k(n_3 + n_4)$. For more exact calculations, Eqn. (26) should be replaced by

$$Y = \alpha_{10} - \frac{\omega}{k} \beta_1 X, \qquad (30)$$

where the quantity $X$ is determined by the second Eqn. (27), and $Y$ by the equations given below:

$$Y = \frac{n_1 \ln \frac{n_1 x_1}{n_1 x_1 + n_2 x_2}}{\ln \frac{T}{T_{10}}} \qquad (31)$$

for indistinguishable anions, and

$$Y = \frac{n_1 \ln \frac{n_1 x_1}{n_1 x_1 + n_2 x_2} + n_2 \ln \frac{n_2 x_1}{n_2 x_1 + n_4 x_2}}{\ln \frac{T}{T_{10}}} \qquad (32)$$

for distinguishable anions.

Note that Eqns. (30) and (26) coincide for the case of indistinguishable anions and $n_1 = n_3$.

Table 1 gives the results of our calculations, by Eqn. (26), on 108 binary systems. The first component is taken as the major constituent. Values of $\alpha_{10}$ were calculated mainly from calorimetric data[15-18]. For lithium sulphate we used the calorimetric measurements of Voskresenskaya and Banashek[19]. For KSCN the values of $\alpha_{10}$ are taken from our calculations. Due to the large scatter in the heat of fusion values for $MgCl_2$, we were unable to choose a definite value of $\Delta S_f$ for this salt, and were again compelled to determine $\alpha_{10}$ from our calculations. Experimental liquidus data were taken mainly from a handbook[20]: column 9 of Table 1 gives the page references to this compilation. Other literature sources used in the calculations[21-26] are stated in column 10.

With the exception of systems 10–14 (as numbered in Table 1), we find $\beta_1$ = const for all other systems. For systems 10–14, $\beta_1 = 2/(2 + x_2)^2 \simeq 0.5 \simeq$ const. Therefore, experimental data from liquidus diagrams should give a straight line when plotted with the variables of Eqn. (26) as coordinates, and the values of $\alpha$ and $K$ should be obtainable from the parameters of the linear plots. In the vast majority of cases, the experimental data do give straight lines when plotted in the coordinates of Eqn. (26). Fig. 1 shows the agreement between Eqns. (26) and (30) and experimental results for a number of systems.

Table 1 also gives the values of the parameter $\omega$, calculated from the formula

$$\omega = \frac{n_3}{\beta_1} kK. \qquad (33)$$

For system 9, $n_3 = 2$; for all other systems, $n_3 = 1$. For system 9, $\beta_1 = 2$; for systems 10–14, $\beta_1 = 0.5$; for all other systems, $\beta_1 = 1$.

It is evident from the data of Table 1 that the systems can be divided into five groups: column 7 lists the group number of each system.

In the first group, $\alpha_{10}/\alpha = 1.02$ on the average, showing that the value of $\alpha$ obtained from liquidus data agrees with

TABLE 1. Results of calculations by Eqn. (26) for various binary salts systems.

| No. | Solvent | Solute | $\alpha_{10}$ | $\alpha$ | $\alpha_{10}/\alpha$ | Group | $\omega$, kcal | Page in Ref. 20 | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 1 | LiF | NaF | 2.90 | 2.95 | 0.98 | 1 | —0.24 | | 21 |
| 2 | » | KF | 2.90 | 2.50 | 1.16 | 1 | —1.57 | | 23 |
| 3 | » | RbF | 2.90 | 2.60 | 1.11 | 1 | —3.10 | | 22 |
| 4 | » | CsF | 2.90 | 3.05 | 0.95 | 1 | —2.30 | | 24 |
| 5 | LiCl | KCl | 2.70 | 2.60 | 1.04 | 1 | —1.70 | 347 | |
| 6 | » | RbCl | 2.70 | 2.20 | 1.23 | 1 | —2.00 | 468 | |
| 7 | » | CsCl | 2.70 | 2.10 | 1.28 | 1 | —3.30 | 264 | |
| 8 | LiBr | KBr | 2.56 | 2.45 | 1.04 | 1 | —1.70 | 332 | |
| 9 | $Li_2SO_4$ | $K_2SO_4$ | 0.80 | 0.35 | 2.28 | | 6.53 | | 25 |
| 10 | » | $BaSO_4$ | 0.80 | 0.67 | 1.19 | 1 | 1.30 | | 25 |
| 11 | » | $PbSO_4$ | 0.80 | 0.67 | 1.19 | 1 | 1.36 | | 25 |
| 12 | » | $SrSO_4$ | 0.80 | 0.60 | 1.33 | 2 | 4.50 | | 25 |
| 13 | » | $CaSO_4$ | 0.80 | 0.60 | 1.33 | 2 | 7.00 | | 25 |
| 14 | » | $CdSO_4$ | 0.80 | 0.60 | 1.33 | 2 | 6.62 | | 25 |
| 15 | $LiNO_3$ | $KNO_3$ | 5.78 | 4.10 | 1.41 | 2 | —0.80 | 401 | |
| 16 | » | $NaNO_3$ | 5.78 | 5.05 | 1.15 | 1 | 0.00 | 479 | |
| 17 | NaF | LiF | 3.12 | 4.38 | 0.72 | 4 | —2.35 | | 21 |
| 18 | » | RbF | 3.12 | 4.38 | 0.72 | 4 | —1.95 | | 22 |
| 19 | » | CsF | 3.12 | 4.38 | 0.72 | 4 | —0.70 | | 24 |
| 20 | » | $MgF_2$ | 3.12 | 3.15 | 1.00 | 1 | —10.30 | | 26 |
| 21 | » | $CdF_2$ | 3.12 | 3.11 | 1.01 | 1 | —2.46 | 238 | |
| 22 | » | $CaF_2$ | 3.12 | 3.11 | 1.01 | 1 | —1.79 | | 26 |
| 23 | NaF | $SrF_2$ | 3.12 | 3.11 | 1.01 | 1 | —0.37 | | 26 |
| 24 | » | $BaF_2$ | 3.12 | 3.11 | 1.01 | 1 | 0.00 | | 26 |
| 25 | NaCl | CsCl | 3.25 | 3.25 | 1.00 | 1 | —0.35 | 267 | |
| 26 | » | RbCl | 3.25 | 2.35 | 1.39 | 2 | 0.24 | 532 | |
| 27 | » | TlCl | 3.25 | 3.25 | 1.00 | 1 | 1.47 | 535 | |
| 28 | » | $BaCl_2$ | 3.25 | 3.40 | 0.95 | 1 | 0.00 | 120 | |
| 29 | » | $SrCl_2$ | 3.25 | 3.25 | 1.00 | 1 | —0.46 | 533 | |
| 30 | » | $CaCl_2$ | 3.25 | 3.25 | 1.00 | 1 | —2.25 | 188 | |
| 31 | » | $CdCl_2$ | 3.25 | 3.25 | 1.00 | 1 | —6.36 | 228 | |
| 32 | » | $MnCl_2$ | 3.25 | 2.35 | 1.39 | 2 | —3.50 | 515 | |
| 33 | » | $MgCl_2$ | 3.25 | 3.25 | 1.00 | 1 | —8.74 | 498 | |
| 34 | » | $ZnCl_2$ | 3.25 | 7.40 | 0.44 | 5 | —29.30 | 535 | |
| 35 | » | $NiCl_2$ | 3.25 | 7.40 | 0.44 | 5 | —52.90 | 531 | |
| 36 | » | $ZrCl_4$ | 3.25 | 0.16 | 21.25 | | 0.75 | 538 | |
| 37 | » | $Na_2CO_3$ | 3.25 | 2.35 | 1.39 | 2 | 1.68 | 735 | |
| 38 | » | NaF | 3.25 | 3.00 | 1.09 | 1 | 0.83 | 743 | |
| 39 | » | $Na_2SO_4$ | 3.25 | 3.00 | 1.09 | 1 | 0.83 | 750 | |
| 40 | » | $Na_4P_2O_7$ | 3.25 | 3.40 | 0.95 | 1 | 0.00 | 749 | |
| 41 | » | CuCl | 3.25 | 4.00 | 0.85 | 4 | —2.08 | 292 | |
| 42 | » | $SnCl_2$ | 3.25 | 4.00 | 0.85 | 4 | —3.82 | 533 | |
| 43 | » | $PbCl_2$ | 3.25 | 4.00 | 0.85 | 4 | —2.08 | 531 | |
| 44 | KF | LiF | 3.00 | 3.80 | 0.79 | 4 | —4.37 | | 23 |
| 45 | » | $BaF_2$ | 3.00 | 3.20 | 0.94 | 1 | —1.61 | 129 | |
| 46 | » | $LaF_3$ | 3.00 | 3.20 | 0.94 | 1 | —16.65 | 274 | |
| 47 | » | $ThF_4$ | 3.00 | 3.20 | 0.94 | 1 | —26.36 | 388 | |
| 48 | » | KCl | 3.00 | 3.08 | 0.97 | 1 | 0.00 | 649 | |
| 49 | » | KBr | 3.00 | 2.85 | 1.05 | 1 | 0.41 | 633 | |
| 50 | KF | KI | 3.00 | 3.08 | 0.97 | 1 | 0.86 | 670 | |
| 51 | » | $KVO_3$ | 3.00 | 3.08 | 0.97 | 1 | —0.74 | 675 | |
| 52 | KCl | AgCl | 2.95 | 2.90 | 1.00 | 1 | 0.00 | 26 | |
| 53 | » | LiCl | 2.95 | 2.90 | 1.00 | 1 | —0.88 | 347 | |
| 54 | » | CuCl | 2.95 | 2.10 | 1.39 | 2 | —4.25 | 285 | |
| 55 | » | $CdCl_2$ | 2.95 | 2.10 | 1.39 | 2 | —14.58 | 224 | |
| 56 | » | $MnCl_2$ | 2.95 | 2.90 | 1.00 | 1 | —6.50 | 353 | |
| 57 | » | $MgCl_2$ | 2.95 | 2.10 | 1.39 | 1 | —14.58 | 349 | |
| 58 | » | $ZnCl_2$ | 2.95 | 5.45 | 0.53 | 5 | —33.40 | 371 | |
| 59 | » | $K_2Cr_2O_7$ | 2.95 | 2.10 | 1.39 | 2 | 3.95 | 649 | |
| 60 | » | $K_2CrO_4$ | 2.95 | 2.10 | 1.39 | 2 | 1.69 | 648 | |
| 61 | » | $K_4P_2O_7$ | 2.95 | 2.90 | 1.00 | 1 | 4.67 | 658 | |
| 62 | » | $K_2SO_4$ | 2.95 | 2.10 | 1.39 | 2 | 3.88 | 658 | |
| 63 | KBr | LiBr | 3.03 | 3.60 | 0.85 | 4 | —2.90 | 332 | |
| 64 | $KNO_3$ | $LiNO_3$ | 2.32 | 2.10 | 1.10 | 1 | —1.01 | 401 | |
| 65 | » | $AgNO_3$ | 2.32 | 2.35 | 1.00 | 1 | —4.74 | 51 | |
| 66 | » | $Ba(NO_3)_2$ | 2.32 | 1.55 | 1.49 | 2 | 0.00 | 135 | |
| 67 | » | $Pb(NO_3)_2$ | 2.32 | 2.35 | 1.00 | 1 | —4.74 | 417 | |
| 68 | » | $Sr(NO_3)_2$ | 2.32 | 1.55 | 1.49 | 2 | 0.74 | 419 | |
| 69 | » | $Ca(NO_3)_2$ | 2.32 | 2.35 | 1.00 | 1 | —4.23 | 197 | |
| 70 | » | $K_2Cr_2O_7$ | 2.32 | 1.55 | 1.49 | 2 | 2.02 | 669 | |
| 71 | KSCN | KCl | 3.50 | 3.50 | 1.00 | 1 | 1.20 | 639 | |
| 72 | » | KBr | 3.50 | » | 1.00 | 1 | 1.20 | 631 | |
| 73 | » | KI | 3.50 | » | 1.00 | 1 | 1.20 | 640 | |
| 74 | » | NaSCN | 3.50 | 2.54 | 1.38 | 2 | 0.63 | 340 | |
| 75 | RbF | LiF | 2.88 | 3.05 | 0.95 | 1 | —3.10 | | 22 |
| 76 | » | NaF | 2.88 | 3.10 | 0.90 | 1 | —2.10 | | 22 |
| 77 | RbCl | LiCl | 2.85 | 2.10 | 1.35 | 2 | —2.00 | 468 | |
| 78 | RbCl | NaCl | 2.85 | 2.12 | 1.35 | 2 | 1.30 | 532 | |
| 79 | CsF | LiF | 2.61 | 2.82 | 0.93 | 1 | —3.20 | | 24 |
| 80 | » | NaF | 2.61 | 2.75 | 0.95 | 1 | 2.09 | | 24 |
| 81 | CsCl | LiCl | 2.63 | 2.70 | 1.00 | 1 | —5.50 | 264 | |
| 82 | » | RbCl | 2.63 | 1.80 | 1.15 | 1 | 0.61 | 32 | |
| 83 | AgCl | KCl | 2.05 | 2.10 | 0.98 | 1 | —1.66 | 26 | |
| 84 | » | $PbCl_2$ | 2.05 | 2.10 | 0.98 | 1 | 4.17 | 31 | |
| 85 | » | $InCl_3$ | 2.05 | 2.25 | 0.91 | 1 | 2.86 | 25 | |
| 86 | » | $AgNO_3$ | 2.05 | 2.60 | 0.77 | 4 | —0.32 | 585 | |
| 87 | » | $Ag_2SO_4$ | 2.05 | 1.85 | 1.11 | 1 | 1.60 | 587 | |
| 88 | AgBr | RbBr | 1.60 | 1.80 | 0.90 | 1 | —2.07 | 16 | |
| 89 | $AgNO_3$ | $LiNO_3$ | 2.85 | 2.50 | 1.14 | 1 | 1.40 | 53 | |
| 90 | » | $KNO_3$ | 2.85 | 2.90 | 1.00 | 1 | 0.00 | 51 | |
| 91 | » | $CsNO_3$ | 2.85 | 2.60 | 0.92 | 1 | —0.90 | 50 | |
| 92 | $MgF_2$ | $BaF_2$ | 4.53 | 4.90 | 0.93 | 1 | —0.46 | 130 | |
| 93 | » | KF | 4.53 | 4.90 | 0.93 | 1 | —10.76 | 380 | |
| 94 | » | RbF | 4.53 | 2.40 | 1.89 | 3 | —2.48 | 506 | |
| 95 | $MgCl_2$ | $CaCl_2$ | 7.40 | 7.40 | 1.00 | 1 | —9.89 | 184 | |
| 96 | » | $SrCl_2$ | 7.40 | 7.40 | 1.00 | 1 | —11.15 | 504 | |
| 97 | » | $BaCl_2$ | 7.40 | 7.40 | 1.00 | 1 | —8.88 | 117 | |
| 98 | » | NaCl | 7.40 | 3.60 | 2.05 | 3 | —1.50 | 498 | |
| 99 | » | KCl | 7.40 | 3.60 | 2.05 | 3 | —3.50 | 349 | |
| 100 | $MgCl_2$ | RbCl | 7.40 | 3.60 | 2.05 | 3 | —4.69 | 502 | |
| 101 | » | CsCl | 7.40 | 3.60 | 2.05 | 3 | —6.37 | 266 | |
| 102 | $BaF_2$ | $MgF_2$ | 1.42 | 1.50 | 0.95 | 1 | 0.78 | 130 | |
| 103 | » | LiF | 1.42 | 0.70 | 2.03 | 3 | 1.38 | 129 | |
| 104 | » | NaF | 1.42 | 0.70 | 2.03 | 3 | 2.67 | 128 | |
| 105 | » | KF | 1.42 | 0.70 | 2.03 | 3 | 4.00 | 132 | |
| 106 | » | RbF | 1.42 | 0.70 | 2.03 | 3 | 4.14 | 133 | |
| 107 | » | $BaCl_2$ | 1.42 | 1.50 | 0.95 | 1 | —2.12 | 595 | |
| 108 | » | $Ba_3(PO_4)_2$ | 1.42 | 1.50 | 0.95 | 1 | —7.66 | 600 | |

the value derived from calorimetric experiments. This is observed in the majority of systems (66 out of 108). For all these systems $n_3 = 1$. We may conclude from the observed agreement that in these systems the common ions are indistinguishable.

In the second group of systems $\alpha_{10}/\alpha = 1.39$ on the average: this is fairly close to unity, and there would be grounds for assigning these systems to the first group. However, the departure from unity can hardly be ascribed to experimental error, since it is found in an appreciable number of systems (19 out of 108). Evidently, we are dealing with a rather "subtle" anomaly in the entropy of mixing.

The third group, which includes the systems $MgF_2$–RbF; $MgCl_2$–NaCl, $MgCl_2$–KCl, $MgCl_2$–RbCl, $MgCl_2$–CsCl; $BaF_2$–LiF, $BaF_2$–NaF, $BaF_2$–KF, $BaF_2$–RbF (in all of which $n_3 = 1$), gives $\alpha_{10}/\alpha = 2$. We conclude that these systems form solutions in which the anions are distinguishable, since Eqn. (29) requires just this value of $\alpha_{10}/\alpha$ for systems with distinguishable anions. The lower part of Fig. 1 shows the results of our calculations by Eqn. (26) for $BaF_2$ containing additions of LiF, NaF, KF, and RbF. The upper part of the diagram illustrates our calculations by Eqn. (30) for $BaF_2$ containing LiF, NaF, KF, and RbF, and our calculations by Eqn. (26) for $BaF_2$ containing $MgF_2$, $BaCl_2$, and $Ba_3(PO_4)_2$. It can be seen that the straight lines of all the solutes meet at a common point when corrected for the distinguishability of the anions.

In the fourth group we find $\alpha_{10}/\alpha = 0.76$ on the average. This group comprises nine systems. It can be shown that the formation of limited solid solutions can account for an $\alpha_{10}/\alpha$ ratio below unity, but only small departures from unity can be expected.

In the fifth group of systems the ratio $\alpha_{10}/\alpha$ is close to 0.5, a value which can be explained by the formation of dimers of the solute in the melt. This group includes only three systems.

The NaCl–$ZrCl_4$ system, for which the ratio $\alpha_{10}/\alpha$ is anomalously high, is quite unique.

Calculations by Eqn. (26) give a value of 2.28 for the ratio $\alpha_{10}/\alpha$ of the system $Li_2SO_4$–$K_2SO_4$. But $n_3 = 2$ for this system, and the theoretical value of $\alpha_{10}/\alpha$ is 2 if the chemical potential is described by Eqn. (9). This agrees with the experimental value. We should point out that our calculations support Grjotheim and Urnes' view[27] that Temkin's ionic model is applicable to the $Li_2SO_4$–$K_2SO_4$ system. Grjotheim and Urnes' calculations have been questioned by Kordes[28], who put forward an explanation of the cryoscopic results in terms of complex formation, but, as we have seen, the criticism is unjustified.

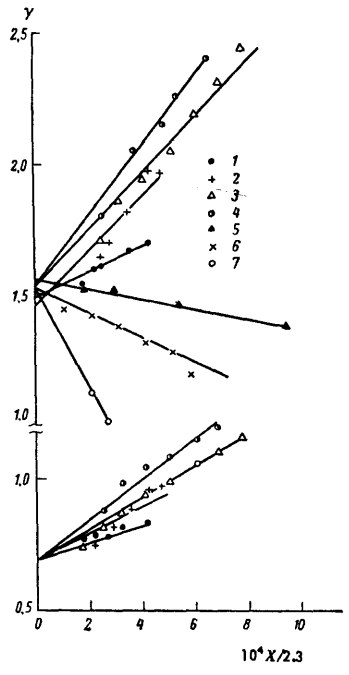



Fig. 1. Comparison of Eqns. (26) and (30) with experimental data for $BaF_2$ containing the following solutes:
1) LiF; 2) NaF; 3) KF; 4) RbF; 5) $MgF_2$; 6) $BaCl_2$; 7) $Ba_3(PO_4)_2$.

TABLE 2. Results of calculations by Eqn. (30) for a number of systems.

| No. | Solvent | Solute | $\alpha_{10}$ from Table 1 | $\alpha_{10}$ from Eqn. (30) | $\omega$, kcal |
|---|---|---|---|---|---|
| 1 | $BaF_2$ | LiF | 1.42 | 1.50 | 2.30 |
| 2 | » | NaF | 1.42 | 1.50 | 5.52 |
| 3 | » | KF | 1.42 | 1.50 | 6.16 |
| 4 | » | RbF | 1.42 | 1.50 | 6.72 |
| 5 | $MgCl_2$ | NaCl | 7.40 | 7.40 | —3.36 |
| 6 | » | KCl | 7.40 | 7.40 | —5.52 |
| 7 | » | RbCl | 7.40 | 7.40 | —9.43 |
| 8 | » | CsCl | 7.40 | 7.40 | —14.54 |
| 9 | $MgF_2$ | RbF | 4.53 | 4.90 | —6.67 |

Since the anion is distinguishable in systems 98–101 and 103–106, the value of $\omega$ should be calculated from the formula

$$\omega = \frac{n_3 + n_4}{\beta_1} kK, \qquad (34)$$

rather than from formula (33). However, this parameter was calculated even more precisely by using Eqn. (30). The results are set out in Table 2.

Returning to the data of Table 1, we see that the systems $AC_2$–BC exhibit anion distinguishability, as required by the theoretical considerations presented above. The $MgF_2$–KF system is exceptional in this respect, and does not have distinguishable anions. On the other hand, in the opposite type of system (AC–$BC_2$) anion distinguishability (and in some cases even cation distinguishability) is not observed. The possibility of loss of anion distinguishability in systems of this type has been discussed at the beginning of the present Section. Thus, the experimental information from liquidus diagrams which has been examined is in keeping, on the whole, with the theoretical considerations of anion distinguishability presented above. The proposition of anion distinguishability is supported also by data on crystallisation from aqueous solutions[29].

## 3. RELATION BETWEEN THE EXCHANGE ENERGY AND THE PROPERTIES OF THE CONSTITUENTS OF THE SOLUTION

The quantity $\omega$ reflects the change in interionic bond energy for the various components, and depends on the properties of the individual ions (charge, radius, structure of the electronic shell, etc.). The search for a relation between the value of $\omega$ and these properties is one of the major problems of the theory of ionic solutions.

Hildebrand and Salstrom[30] were the first to show that some binary mixtures of fused salts exhibit regular solution behaviour. These workers provided a theoretical basis for Eqn. (1) by a statistical procedure previously applied by Heitler[31] to non-electrolyte solutions. Among the systems examined by Hildebrand and his coworkers, those consisting of alkali metal bromides with silver bromide, and of lead halides with zinc halides, had the properties of regular solutions. The system were studied by an e. m. f. method, based on reactions between an electrode and the melt. Most of the experimental data now available for the activity of components in molten salts have been obtained by this method (see Table 3).

Data on heats of mixing are of the utmost importance in the thermodynamics of fused salts. Kleppa and coworkers[37,39,53] have undertaken a series of calorimetric measurements of the heats of mixing for the nitrates of metals in Groups I and II of the Periodic Table, and obtained some very interesting results, which show that these mixtures are regular solutions and have negative heats of mixing. Solid solutions of these salts have positive heats of mixing. The authors ascribe this difference to the fact that in solid solutions there is a loss of lattice energy due to the change in the distance between nearest neighbours, whereas in a melt the most important interactions are those between second nearest neighbours. They have shown[37] that the exchange energy for molten alkali metal nitrates is described by the empirical relation

$$\omega = -E\left(\frac{d_1 - d_2}{d_1 + d_2}\right)^2, \qquad (35)$$

where $E$ is the crystal lattice energy of the mixture, and $d_1$ and $d_2$ are the distances between the centres of the ions in the pure first and second component respectively.

We have already discussed calculations based on Eqn. (20). An alternative approach is to use the familiar form of Schröder's equation:

$$\ln a_i = \alpha_{i0}\left(\frac{T_{i0}}{T} - 1\right). \qquad (36)$$

Aukrust *et al.*[23] determined the activity of the components in the systems LiF–KF, LiCl–KCl, and LiBr–KBr from liquidus data by using Eqn. (36) in conjunction with the heat capacities of the components in the liquid and in the solid phase, and showed that solutions of these salts depart relatively little from regular solution behaviour.

TABLE 3. Experimental values of $\omega$ for various systems.

| No. | System | Temperature, °C | Method of measurement | $\omega$, kcal | Ref. |
|---|---|---|---|---|---|
| 1 | AgCl—LiCl | 500 | e.m.f. | 2.16 | 32,8,33 |
| | ditto | 600 | ditto | 2.14 | 32,8,33 |
| 2 | AgCl—NaCl | 900 | » | 0.75—1.10 | 34 |
| 3 | AgCl—KCl | 800 | » | —1.00—1.20 | 35 |
| 4 | AgBr—LiBr | 500 | » | 1.92 | 30,33 |
| | ditto | 550 | » | 1.86 | 30 |
| | » | 600 | » | 1.82 | 30 |
| 5 | AgBr—NaBr | 550 | » | 0.96 | 30 |
| | ditto | 600 | » | 0.94 | 30 |
| 6 | AgBr—KBr | 500 | » | —1.56 | 30 |
| | ditto | 550 | » | —1.58 | 30 |
| | » | 600 | » | —1.60 | 30 |
| 7 | AgBr—RbBr | 500 | » | —2.54 | 30 |
| | ditto | 550 | » | —2.58 | 30 |
| | » | 600 | » | —2.62 | 30 |
| 8 | $AgNO_3$—$LiNO_3$ | 209.6 | cryoscopy | 0.12 | 36 |
| | ditto | 350 | calorimetry | 0.65 | 37 |
| 9 | $AgNO_3$—$NaNO_3$ | 320 | e.m.f. | 1.06 | 38 |
| | ditto | 350 | calorimetry | 0.59 | 37 |
| 10 | $AgNO_3$—$KNO_3$ | 209.6 | cryoscopy | —0.92 | 36 |
| | ditto | 350 | calorimetry | —0.45 | 37 |
| 11 | $AgNO_3$—$RbNO_3$ | 209.6 | cryoscopy | —1.08 | 36 |
| | ditto | 350 | calorimetry | —1.20 | 37 |
| 12 | $AgNO_3$—$CsNO_3$ | 209.6 | cryoscopy | 1.38 | 36 |
| 13 | $AgNO_3$—$TlNO_3$ | 209.6 | » | 1.79 | 36 |
| 14 | LiF—KF | 775 | » | —1.20 | 23 |
| 15 | LiCl—KCl | 775 | » | —0.9—1.0 | 23 |
| 16 | LiBr—KBr | 775 | » | —0.8 | 23 |
| 17 | $LiNO_3$—$NaNO_3$ | 345 | calorimetry | —0.46 | 39 |
| 18 | $LiNO_3$—$KNO_3$ | 345 | » | —1.76 | 39 |
| 19 | $LiNO_3$—$RbNO_3$ | 345 | » | —2.47 | 39 |
| 20 | $LiNO_3$—$CsNO_3$ | 450 | » | —3.00 | 39 |
| 21 | $NaNO_3$—$KNO_3$ | 345—450 | » | —0.41 | 39 |
| 22 | $NaNO_3$—$RbNO_3$ | 345 | » | —0.74 | 39 |
| 23 | $NaNO_3$—$CsNO_3$ | 450 | » | —0.06 | 39 |
| 24 | $KNO_3$—$RbNO_3$ | 345 | » | —0.06 | 39 |
| 25 | $KNO_3$—$CsNO_3$ | 450 | » | —0.09 | 39 |
| 26 | $RbNO_3$—$CsNO_3$ | 450 | » | 0.02 | 39 |
| 27 | $Li_2CO_3$—$CaCO_3$ | 20—1100 | measurement of $CO_2$ pressure | —2.40 | 40 |
| 28 | $Na_2CO_3$—$CaCO_3$ | 20—1100 | | —5.50 | 40 |
| 29 | $K_2CO_3$—$CaCO_3$ | 20—1100 | | —11.50 | 40 |
| 30 | $K_2CrO_4$—$K_2Cr_2O_7$ | 650 | not stated | +0.5 | 41 |
| 31 | $Na_2CrO_4$—$Na_2Cr_2O_7$ | 450 | ditto | +0.3 | 41 |
| 32 | NaCl—KCl | 25 | calorimetry | +4.20 | 42 |
| 33 | KCl—RbCl | 50 | » | +0.85 | 43 |
| 34 | $PbCl_2$—$ZnCl_2$ | 500 | e.m.f. | —2.40 | 8,44 |
| | ditto | 600 | ditto | —2.80 | 8,44 |
| 35 | $PbBr_2$—$ZnBr_2$ | 400 | » | 0.80 | 8,45 |
| | ditto | 450 | » | 0.50 | 8,45 |
| | » | 500 | » | 0.30 | 8,45 |
| 36 | KCl—$PbCl_2$ | 550 | » | —12.40 | 8,46 |
| | ditto | 600 | » | —12.40 | 8,46 |
| 37 | KCl—$MgCl_2$ | 650 | » | —11.80 | 8,47,48 |
| | ditto | 750 | » | —13.10 | 8,47,48 |
| | » | 850 | » | —13.60 | 8,47,48 |
| | » | 950 | » | —14.30 | 8,47,48 |
| 38 | AgCl—AgBr | 500 | » | 2.25 | 49 |
| 39 | LiCl—LiBr | 800 | not stated | +0.15 | 41 |
| 40 | KCl—KBr | 50 | calorimetry | 0.93 | 43 |
| | ditto | 800 | not stated | 0.53 | 41 |
| 41 | NaCl—NaBr | 50 | calorimetry | 1.32 | 43 |
| | ditto | 800 | not stated | 0.35 | 41 |
| 42 | CsCl—CsBr | 25 | calorimetry | 1.05 | 50 |
| 43 | TlCl—TlBr | 25 | » | 0.64 | 51 |
| 44 | $MgCl_2$—$MgBr_2$ | 800 | not stated | —0.32 | 41 |
| 45 | $PbCl_2$—$PbBr_2$ | 450 | e.m.f. | 0.87 | 8,52 |
| | ditto | 500 | ditto | 0.83 | 8,52 |
| | » | 550 | » | 0.77 | 8,52 |

Margulescu and Sternberg[54,55], using the equations

$$kT_1 \ln \gamma_1 = \omega x_2^2; \quad kT_2 \ln \gamma_1 = \omega x_2^2, \tag{37}$$

written explicitly for the two temperatures $T_1$ and $T_2$, arrived at the expression

$$\ln a_1(T_2) = \frac{T_1}{T_2} \ln a_1(T_1) + \frac{T_2 - T_1}{T_2} \ln x_1. \tag{38}$$

They used this equation to compare activity values obtained from liquidus diagrams with the values obtained at higher temperatures by the e.m.f. method. The results were satisfactory.

Sinistry proposed[36,38,56] the use of the equation

$$\frac{\Delta T}{1 - x_l} = fK_0 + b(1 - x_l). \tag{39}$$

for determining the value of $\omega$, where $\Delta T$ is the depression of the freezing point caused by addition of the solute, $K_0$ is the cryoscopic constant, $f$ is the number of particles into which the solute dissociates, and $b$ is a constant. Eqn. (39) was derived by Haaze[57]; unlike the van't Hoff equation[58]

$$\frac{\Delta T}{1 - x_l} = fK_0, \tag{40}$$

it can be applied to moderately concentrated solutions. According to Sinistry[38],

$$\omega = -\frac{b}{fK_0}. \tag{41}$$

The values of $\omega$ obtained by Sinistry from cryoscopic data and Eqn. (41) are sometimes in serious disagreement with Kleppa's calorimetric results. It should be noted that Eqn. (39) can be derived from Eqn. (20) for the case of dilute solutions with unlike ions of the same valency.

Flood *et al.*[40] measured the activity of $CaCO_3$ in $CaCO_3$–$M_2CO_3$ mixtures (where M is an alkali metal) by measuring the amount of carbon dioxide evolved in the decomposition of the mixture. These mixtures were found to behave like regular solutions.

Published experimental values of $\omega$ for various molten salts with a common ion are listed in Table 3. Data relating to the solid solutions NaCl–NaBr, KCl–KBr, CsCl–CsBr, and TlCl–TlBr are also tabulated. A comparison of the data of Tables 1 and 3 clearly shows that one of the two values of $\omega$ obtained from Eqn. (26) agrees satisfactorily with the corresponding value in Table 3 (systems LiF–KF, LiCl–KCl, KCl–AgCl, AgBr–LiBr, and KCl–$MgCl_2$). It is interesting to note, in this connection, that the value of $\omega$ determined in the crystallisation region of the first salt does not agree numerically with the $\omega$ value determined in the crystallisation region of the second salt for the same system (see Table 1). Yet, these two values should be identical if a regular solution treatment is strictly applicable. The discrepancy may be due to a difference in properties between the crystallisation regions of the first and the second salt. In particular, this behaviour has been reported[65] for the composition–property curves close to the eutectic temperature.

As already pointed out, the value of $\omega$ depends on the individual properties of the ions. Using available data we have tried to identify the functional relation between $\omega$ and the radii of the cations and anions present in the solution. The value of $\omega$ is plotted against the radius of the common ion in Fig. 2 for six families of salts with a common ion. It is obvious that the straight-line plots for salts with a common cation and those for salts with a common anion respectively converge to a point: this means that the salt solutions achieve ideality when the anion (for the case of salts with a common anion) or the cation (for the case of salts with a common cation) reaches a certain size. It is also found that the slope of the straight lines of Fig. 2 is proportional to the difference between the radii of the non-common ions present in the solution. The general equation for families of salts with a common ion is

$$\omega = 31 \left(\frac{r_1 - r_2}{r_1 + r_2}\right)\left(1 - \frac{r}{r_0}\right), \tag{42}$$

where $r_1$ and $r_2$ are the radii of the non-common ions of the first and second component, $r$ is the radius of the common ion, and $r_0 = r$ for $\omega = 0$. The value of $r_0$ is 3.06 for the particular family of salts with a common anion examined

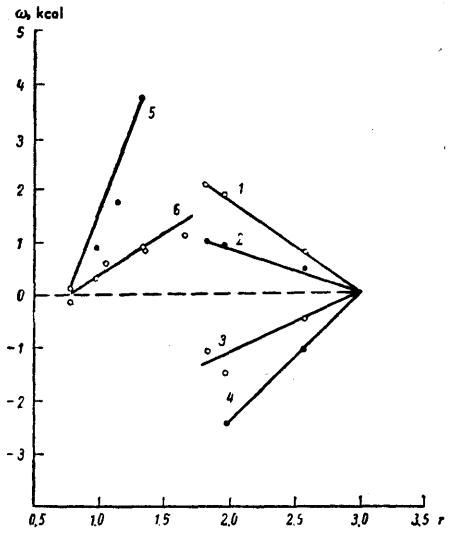



Fig. 2. Variation of the exchange energy in binary systems with radius of the common ion:
1) AgX–LiX; 2) AgX–NaX; 3) AgX–KX; 4) AgX–RbX (where X = Cl, Br, $NO_3$); 5) MCl–$M_2SO_4$; 6) MCl–MBr (where M = Li, Mg, Na, Tl, Ag, Pb, K, Cs).

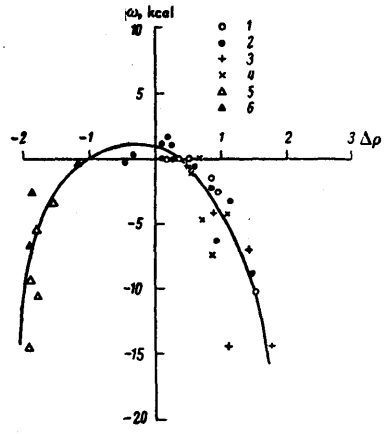



Fig. 3. Variation of exchange energy with difference in generalised moments:
1) NaF (with additions of Ba, Sr, Ca, Cd, Mg fluorides);
2) NaCl (with additions of Cs, Rb, Ba, Sr, Ca, Mn, Mg chlorides);
3) KCl (with additions of Ag, Li, Cu, Mn, Mg chlorides);
4) $KNO_3$ (with additions of Ba, Sr, Ca nitrates);
5) $MgCl_2$ (with additions of Cs, Rb, K, Na chlorides);
6) $MgF_2$ (with additions of Rb, Ba, Ca fluorides).

in Fig. 2, and 0.78 for the family of salts with a common cation.

The value of $\omega$ in Eqn. (42) is expressed in kcal. Ionic radii, here and elsewhere in the present paper, are the Goldschmidt values for the crystalline state[69], expressed in Ångström units.

Table 4 gives the numerical values of the crystal lattice energy for the salts to which Eqn. (42) applies. $E_1$ and $E_2$ are the crystal lattice energies of the first and second salt component, taken from a handbook[69]. The quantity $\Delta E$ is the difference $E_1 - E_2$. The mean value of $\Delta E$ for all the salts listed in Table 4 is 23.1, i.e. of the same order of magnitude as the constant coefficient in Eqn. (42).

Semenchenko[59] proposed the use of generalised moments for characterising the properties of particles such as ions, atoms, and molecules. The physical significance of the generalised moment is quite simple: it corresponds to the force due to the charge on the particle. For ions, the generalised moment gives the potential at the surface of the ion, considered as a sphere of radius $r$.

Using the concept of generalised moments, Semenchenko developed a general approach[68] to solubility phenomena. According to his theory, the mutual solubility of substances is higher, the smaller the absolute difference between their generalised moments. Thus, plots of $\Delta\rho$ against solubility (where $\Delta\rho$ is the difference in generalised moments between solvent and solute) give a curve with a maximum at $\Delta\rho = 0$.

Our results for the variation of $\omega$ with $\Delta\rho$ give a curve similar to that of Semenchenko (Fig. 3). In these calculations, the salt present in solution at the lower concentration is treated as the solute. The generalised moment is found by dividing the charge on the ion by the ionic radius.

The relation between $\omega$ and the difference in generalised moments shown in Fig. 3 refers to salts with a common anion. An analogous relation for salts with a common cation does not appear to exist, at least judging from the data of Table 1. This is not surprising, since generalised moments are not a very accurate way of characterising the energetics of anions.

TABLE 4. Crystal lattice energies of various salts.

| System | $E_1$, kcal | $E_2$, kcal | $\Delta E$, kcal | System | $E_1$, kcal | $E_2$, kcal | $\Delta E$, kcal |
|---|---|---|---|---|---|---|---|
| LiCl—LiBr | 195.6 | 185.2 | 10.4 | AgBr—LiBr | 210.0 | 185.20 | 24.8 |
| NaCl—NaBr | 181.9 | 172.5 | 9.4 | AgCl—NaCl | 213.7 | 182.0 | 31.7 |
| KCl—KBr | 166.6 | 159.0 | 7.6 | AgBr—NaBr | 210.0 | 173.0 | 37.0 |
| $MgCl_2$—$MgBr_2$ | 592 | 568.5 | 11.6 | AgCl—KCl | 213.7 | 167 | 46.7 |
| $PbCl_2$—$PbBr_2$ | 524.7 | 511 | 6.8 | AgBr—KBr | 210.0 | 160 | 50.0 |
| AgCl—LiCl | 213.7 | 196.0 | 17.8 | | | | |

## 4. CALCULATION OF EXCHANGE ENERGIES

In theory, the exchange energy can be calculated if a procedure for calculating the crystal lattice energy of the solution is available. The energy of a crystal lattice is calculated most simply by means of Born's formula[60]

$$E = \frac{ANe^2z_1z_2}{d}\left(1 - \frac{1}{u}\right), \qquad (43)$$

where $A$ is Madelung's constant, $N$ is Avogadro's number, $e$ is the electronic charge, $z_1$ and $z_2$ are the numbers of electronic charges on the cation and the anion, and $u$ is a quantity which characterises the repulsive forces.

X-Ray diffraction experiments have shown that the average distance between oppositely charged ions in a

solution varies in the simplest case (Vegard's law) according to the expression

$$d = d_1x_1 + d_2x_2. \quad (44)$$

Various attempts have been made[2,3,4] to substitute an expression of this type into the Born formula. The result is that the energy of formation of the solution, which should be identified with the potential energy of formation of the solution, is always positive: this is, of course, contrary to experience. In subsequent papers the energy of the solution is calculated more exactly.

Lumsden[5] treats the excess energy $\Delta E$ of a solution as the sum of two terms:

$$\Delta E = \Delta E_1 + \Delta E_p, \quad (45)$$

where $\Delta E_1$ is the interaction energy of ions of a given kind in the immediate neighbourhood of an arbitrarily chosen ion, and $\Delta E_p$ the polarisation energy of the anions.

The quantity $\Delta E_1$ is calculated by the London formula

$$E_1 = -\frac{P}{d^6}, \quad (46)$$

where $P$ is a constant. In an ionic solution of the type AC–BC (the theory is concerned only with solutions of alkali metal halides) each cation is effectively surrounded only by anions, and each anion only by cations. Hence, in the immediate surroundings of any cation the energy of the C–C bond has to be considered, and in the immediate surroundings of any anion the energy of the A–A, B–B, and A–B bonds is relevant. The bond energy of cations is small in comparison with the bond energy of anions, and it is legitimate to consider only the energy of the C–C bonds. The C–C distance in the pure salts AC and BC is $2^{0.5}d_{AC}$ and $2^{0.5}d_{BC}$ respectively, where $d_{AC}$ and $d_{BC}$ are the distances A–C and B–C. In the solution, this distance has the value $(d_{AC}^2 + d_{BC}^2)^{0.5}$. Hence the energy of the solution due to London forces is

$$E_1 = -\left[\frac{P_{AA}}{(2d_{AC}^2)^3}N_{AA} + \frac{P_{BB}}{(2d_{BC}^2)^3}N_{BB} + \frac{P_{AB}}{(d_{AC}^2 + d_{BC}^2)^3}N_{AB}\right], \quad (47)$$

where $P_{AA}$, $P_{BB}$, and $P_{AB}$ are the constants of Eqn. (46) for the appropriate bonds; $N_{AA}$, $N_{BB}$, and $N_{AB}$ are the numbers of A–A, B–B, and A–B bonds in the solution. For a regular solution

$$N_{AA} = \frac{Z}{2}x_1^2(N_1 + N_2); \quad N_{BB} = \frac{Z}{2}x_2^2(N_1 + N_2);$$
$$N_{AB} = Zx_1x_2(N_1 + N_2), \quad (48)$$

where $Z$ is the coordination number. Substituting (48) into (47), and after some rearrangement, we obtain

$$\Delta E_1 = \omega_1 x_1 x_2 (N_1 + N_2), \quad (49)$$

where

$$\omega_1 = \frac{Z}{2}\left[\frac{P_{AA}}{(2d_{AC}^2)^3} + \frac{P_{BB}}{(2d_{BC}^2)^3} + \frac{2P_{AB}}{(d_{AC}^2 + d_{BC}^2)^3}\right]. \quad (50)$$

If the anion is surrounded by cations of different size it becomes polarised. The force $F_0$ of the field acting on an anion surrounded by oppositely distributed A and B cations is

$$F_0 = e\left(\frac{1}{d_{AC}^2} - \frac{1}{d_{BC}^2}\right). \quad (51)$$

The energy due to polarisation of the anions in solution is

$$\Delta E_p = \frac{mF_0^2}{2}N_{AB}, \quad (52)$$

where $m$ is the polarisability of the anion. Substituting (51) into (52), and using (48), we obtain

$$\Delta E_p = \omega_p x_1 x_2 (N_1 + N_2), \quad (53)$$

where

$$\omega_p = \frac{Z}{2}me^2\left(\frac{1}{d_{AC}^2} - \frac{1}{d_{BC}^2}\right)^2. \quad (54)$$

Lumsden[5] allowed also for the polarisation of the anion due to the second layer of cations, when Eqn. (54) becomes

$$\omega_p = \left(\frac{4}{5}\right)^2\frac{Z}{2}me^2\left(\frac{1}{d_{AC}^2} - \frac{1}{d_{BC}^2}\right). \quad (55)$$

However, the occupancy of the second layer of cations is rather indeterminate: this causes inaccuracies in the computed second-layer polarisation, which is therefore best ignored.

Adding (49) and (53) we obtain

$$\Delta E = (\omega_1 + \omega_p)x_1x_2(N_1 + N_2). \quad (56)$$

This equation can be used to calculate the properties of real solutions. The constants $P_{AA}$ and $P_{BB}$ for alkali halides have been calculated by Mayer[61]. For the constant $P_{AB}$, Lumsden assumes

$$P_{AB}^2 = P_{AA} \times P_{BB}. \quad (57)$$

Values of $m$ for the anions $F^-$, $Cl^-$, $Br^-$, and $I^-$ have been determined by Kordes[62]: they are 0.462, 1.63, 2.29, and 3.56 cm$^3$ respectively. The parameters $d_{AC}$ and $d_{BC}$ are equal to the anion–cation distances in the crystal. Values of $\omega$ obtained by Lumsden for a number of systems are reproduced in Table 5. A comparison between experimental liquidus curves and similar curves calculated from theoretical values of $\omega$ is given in Lumsden's paper[5]. On the whole, the calculated values agree with experiment. It should be noted, however, that whereas one branch of the liquidus curve coincides with the experimental data, the other branch usually shows some departure. This is further confirmation that the $\omega$ values for different components in a given binary system with simple eutectic are different.

The excess free energy can also be calculated with the help of the theory proposed by Vasastjerna[6] for solid

TABLE 5. Comparison of $\omega$ values obtained according to Lumsden and to Vasastjerna with the values derived from the liquidus diagram data by Eqns. (26) and (30).

| No. | System | $\omega_1$, kcal (after Lumsden) | $\omega_1$, kcal (after Vasastjerna) | From Eqns. (26) and (30) | | |
|---|---|---|---|---|---|---|
| | | | | $\omega_1$, kcal | $\omega_2$, kcal | $\bar{\omega}$, kcal |
| 1 | LiF—NaF | —1.60 | +0.96 | —0.24 | —2.35 | —1.30 |
| 2 | LiF—KF | —4.20 | +3.10 | —1.57 | —4.37 | —2.97 |
| 3 | LiF—RBF | —4.50 | — | —3.10 | —4.00 | —3.55 |
| 4 | LiF—CsF | —4.70 | — | —2.30 | —3.20 | —2.75 |
| 5 | NaF—KF | —0.40 | +0.85 | — | — | — |
| 6 | NaF—RbF | —0.10 | — | —2.00 | —2.10 | —2.05 |
| 7 | NaF—CsF | +0.90 | — | —0.70 | +2.09 | +0.70 |
| 8 | LiCl—NaCl | —1.10 | +0.99 | — | — | — |
| 9 | LiCl—KCl | —4.00 | +2.20 | —1.70 | —0.88 | —1.30 |
| 10 | LiCl—RbCl | —4.60 | — | —2.00 | —2.00 | —2.00 |
| 11 | LiCl—CsCl | —5.90 | +4.60 | —3.30 | —5.50 | —4.40 |
| 12 | NaCl—KCl | —0.80 | +0.25 | — | — | — |
| 13 | NaCl—RbCl | —1.10 | +0.83 | +0.24 | +1.30 | +0.77 |
| 14 | NaCl—CsCl | —1.70 | +1.40 | —0.35 | —1.06 | —0.70 |
| 15 | KCl—CsCl | —0.10 | — | — | — | — |
| 16 | LiBr—KBr | —3.40 | — | —1.70 | —2.90 | —2.30 |
| 17 | LiBr—CsBr | —5.90 | +2.70 | — | — | — |
| 18 | LiI—NaI | —0.90 | +0.89 | — | — | — |
| 19 | LiI—CsI | —5.90 | +2.84 | — | — | — |
| 20 | NaI—CsI | —2.10 | +1.22 | — | — | — |
| 21 | $LiNO_3$—$KNO_3$ | —1.90 | — | —0.80 | —1.01 | —0.90 |

solutions of ionic salts. According to this theory, the excess energy of mixing and the entropy of mixing are given by the expressions

$$\Delta E = \frac{Ae^2}{d}\left(\frac{\Delta d}{d}\right) x_1 \quad x_2(N_1+N_2)\left\{\frac{\theta_1}{8}[1+\sigma(1-4x_2)]+\right.$$
$$\left.+\frac{\theta_2}{8}[1+\sigma(1-4x_1)]+\frac{1}{2}(1+\sigma)\right\}; \quad (58)$$

$$\Delta S = -k(N_1 \ln x_1 + N_2 \ln x_2) - k(\varkappa \ln \varkappa + \lambda \ln \lambda + \mu \ln \mu + \nu \ln \nu). \quad (59)$$

In these expressions

$$\theta_i = \frac{3+4Tv}{\frac{\epsilon Ae^2}{6d_i^4 - Tv}}; \quad \varkappa = \frac{x_1}{x_1 - x_2\sigma};$$
$$\lambda = x_1x_2(1+\sigma); \quad \mu = \frac{x_1x_2}{x_2 - x_1\sigma}; \quad \nu = \frac{x_2}{x_2 - x_1\sigma}, \quad (60)$$

where the degree of short-range order, $\sigma$, is defined by

$$\sigma = \frac{1-2x_1 \quad x_2 l - \sqrt{1-4x_1x_2 l}}{2x_1 \quad x_2 l};$$
$$l = 1 - \exp\left\{\frac{Ae^2}{d}\left(\frac{\Delta d}{d}\right)^2 \frac{\theta_1(1-4x_2)+\theta_2(1-4x_1)+4}{8kT}\right\}, \quad (61)$$

$\Delta d = d_1 - d_2$, $v$ is the coefficient of thermal expansion, and $\epsilon$ the compressibility coefficient. The quantity $d$ in Eqn. (58) denotes the distance between cation and anion, which can be calculated by Vegard's law. The quantity $d_i$ refers to the distance between cation and anion in the corresponding pure salt.

In Hovi's papers[51,52,63] the theory of Vasastjerna is used to calculate the free energy of solid solutions, thus making it possible to predict critical separation temperatures. Unfortunately, these calculated results lack direct experimental confirmation. Heats of mixing calculated by Eqn. (58) for solid solutions are in tolerably good agreement with experiment[42,51,52,63].

Vasastjerna's theory can also be applied to molten salts. Margulescu and Sternberg[64] have applied it to the systems AgBr–LiBr, AgBr–NaBr, AgCl–NaCl, and AgBr–AgCl. The excess energies of mixing derived from experimental data are in general agreement with the calculated values.

The present writers have evaluated Eqn. (58) for a number of systems, using $d$ values taken from Levy *et al.*[66] and $\epsilon$ and $v$ values taken from Bockris and Richard[67]. The calculations were made for the composition $x_1 = x_2 = 0.5$. The value of $\omega$ was found from the relation

$$\omega = \frac{1}{x_1 \quad x_2} \quad \Delta E = 4\Delta E.$$

It should be noted that $\omega$ is required by Eqn. (57), to be a function of solution composition, but in a rough comparison with experiment it may be taken as constant.

The results of this calculation are entered in Table 5. For comparison, the table gives also the values of $\omega_1$, which relate to crystallisation of the first component, and of $\omega_2$, which relate to the region of crystallisation of the second component. These values are taken from Table 1, i.e. they were calculated by Eqns. (26) and (33). The arithmetic mean of $\omega_1$ and $\omega_2$ is tabulated as $\bar{\omega}$. Inspection of Table 5 shows that Lumsden's theory agrees, on the whole, with values taken from liquidus diagrams. In some cases, however, there is serious discrepancy. Thus, in the NaF–CsF system, $\omega_1 < 0$ and $\omega_2 > 0$, whereas Lumsden gives $\omega > 0$. For the NaCl–RbCl system $\omega_1$ and $\omega_2$ are positive, but according to Lumdsen $\omega < 0$. In the other systems the value of $\omega$ calculated by Lumsden's method is close to $\bar{\omega}$. On the other hand, the theory of Vasastjerna does not lead to satisfactory results.

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The results presented in this review provide evidence that the theory of regular solutions is applicable to molten salts. A collection of exchange energy data more comprehensive than any hitherto available[41,54] is also presented. The data of Table 3 show that the absolute value of $\omega$ decreases or increases with increasing temperature according to whether $\omega$ is positive or negative, respectively. These changes are small, however, and the assumption made when using Eqns. (26) and (30) that $\omega$ is independent of temperature is, on the whole, justified. Hence, these equations can be used to interpret experimental data from liquidus diagrams. Furthermore, analysis of the liquidus curves in systems with a simple eutectic can provide information on the entropy of mixing of ionic salt solutions.

We have stated that Lumsden's theory is in agreement with experiment. However, its conclusions are still only applicable to solutions of uni-univalent salts. The variation of the exchange energy with difference of generalised moments can be used to give an approximate estimate of this quantity in solutions of salts with different cations and a common anion.


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# ADVANCES IN THE CHEMISTRY OF CARBENES

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## I. INTRODUCTION

Some years ago the journal "Uspekhi Khimii" published a comprehensive review of carbenes by Knuyants *et al.*[1], covering the literature up to and including 1957. In view of the exceptionally rapid development of the chemistry of carbenes and the fundamental interest of this field for a wide variety of investigators, we thought it useful to review the work on carbenes which has been published in the subsequent five years — from 1958 to 1962 inclusive. Some papers published in 1963 have also been covered.

Although the literature dealt with in the present review covers a short period, the data accumulated on carbenes are extensive and often scattered in papers dealing with other problems. It is therefore not impossible that some data on the synthesis or a practical application of carbenes or a particular treatment of a reaction mechanism including the formation of a carbene have been omitted.

## II. THE STRUCTURE OF CARBENES

No definite new evidence for the geometrical and electronic structure of carbene has been obtained since the appearance of the review of Knunyants *et al.*[1] Of the work in this field, it is only necessary to mention that of Herzberg[2], who investigated methylene by ultraviolet spectroscopy and showed that it has a triplet ground state, the singlet state having a somewhat higher energy. This is to some extent confirmed by the reactions of free methylene, particularly by its addition to carbon–carbon double bonds. The point is that the carbene being in a triplet state adds to the double bond in several stages, the first involving the formation of a 1,3-biradical in which rotation about the carbon–carbon bond is possible, so that the formation of cyclopropanes is non-stereospecific. However, it is possible to obtain methylene in the singlet state, for example photolytically; such methylene adds to double bonds stereospecifically. If it then passes to its ground (triplet) state, having given up part of its excess energy in a collision, for

example non-stereospecific addition of methylene to carbon–carbon double bonds occurs again[3-6]. In the case of substituted methylenes a wide variety of situations arises, depending on the nature of the substituents linked with the key carbon atom. Thus it has been established that dihalogenocarbenes add to double bonds stereospecifically[7], while diphenylcarbene adds non-stereospecifically[8]; the latter result is also consistent with physical data: it has recently been shown by electron paramagnetic resonance[9] that phenylcarbene, diphenylcarbene, and fluorenylidene obtained by the photolysis of the corresponding diazo-compounds have triplet ground states.

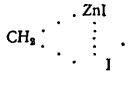
It must be borne in mind that the key carbon atom in carbenes has a lone pair of electrons as well as an unfilled orbital so that, in addition to its electrophilic properties, which until recently have been the only ones to be investigated experimentally, it also has nucleophilic properties, which will be discussed below (pp. 75, 76, 77).

## III. PREPARATION AND CHARACTERISTIC PROPERTIES OF INDIVIDUAL CARBENES

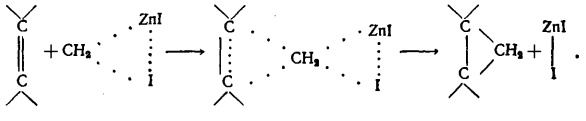
### 1. Methylene

Although there is no direct proof that free methylene is produced in the reaction between methylene iodide and the zinc–copper couple, the fact that cyclopropanes are obtained in the presence of olefins in the reaction mixture can be explained by the intermediate formation of methylene[10,11]. The reaction of methylene iodide with the zinc–copper couple in dry ether is known to yield iodomethylzinc iodide[12], from which cyclopropanes can be obtained in two ways.

a. Iodomethylzinc iodide may be regarded as a complex of methylene and zinc iodide which breaks down spontaneously into zinc iodide and free methylene, the latter reacting with double bonds:



b. The $\pi$-bond of the olefin can replace zinc iodide in iodomethylzinc iodide with the formation of cyclopropane[11]:



Comparatively recently a study of ultraviolet, visible, and infrared spectra has established that the photolysis of diazomethane in nitrogen at 90°K yields a complex mixture of products including ethylene, cyclopropane, and a number of other stable and unstable substances. Possibly, free methylene is also present, but its formation in the reaction mixture has not been rigorously demonstrated. The presence of certain substances in this mixture can be accounted for by reactions of methylene with diazomethane[13].

Keten is formed in the photolysis of diazomethane in a mixture of nitrogen and carbon monoxide. However, even when the concentration of carbon monoxide is eighteen times greater than that of diazomethane, the yield of keten is only 50%. This is probably due to the simultaneous occurrence of two competing reactions: reaction of carbon monoxide with methylene and of diazomethane with methylene. Furthermore, it is known that keten itself breaks down into carbon monoxide and methylene when it is irradiated with ultraviolet light[14,15] and therefore a definite equilibrium exists between carbon monoxide and methylene on the one hand and keten on the other, which reduces the yield of the latter.

### 2. Dihalogenocarbenes

a. Difluorocarbene. In 1960 Simons and Yarwood[16] showed that the photolysis of *sym*-dichlorotetrafluoroacetone in the vapour phase results in the formation of difluorocarbene and proceeds as follows:

$$CF_2ClCOCF_2Cl + h\nu \rightarrow CF_2ClCOCF_2\cdot + Cl\cdot,$$
$$CF_2ClCOCF_2\cdot \longrightarrow CF_2Cl\cdot + CO + CF_2.$$

The authors draw attention to the low reactivity of difluorocarbene.

Haszeldine and coworkers[17] obtained difluorocarbene by decarboxylation of sodium chlorodifluoroacetate:

$$ClCF_2COO^- \rightarrow Cl^- + CF_2 + CO_2.$$

Difluorocarbene readily reacts with water, fluoride ions, and chlorine[18]:

$$CF_2 + H_2O \xrightarrow{H_2O} \begin{cases} \longrightarrow CO + 2HF \\ \longrightarrow HCOOH + 2HF, \end{cases}$$
$$CF_2 + F^- \xrightarrow{H_2O} CHF_3 + OH^-,$$
$$CF_2 + Cl^- \xrightarrow{H_2O} CHClF_2 + OH^-.$$

It can also be obtained by the reaction of potassium isopropoxide with chlorodifluoromethane in isopropanol[18]:

$$(CH_3)_2CHO^- + CHClF_2 \rightleftarrows (CH_3)_2CHOH + CClF_2^-,$$
$$CClF_2^- \rightarrow CF_2 + Cl^-.$$

Hine and Porter[19] obtained difluorocarbene by the action of sodium methoxide on difluoromethylphenylsulphone:

$$CF_2H-S(O)(O)-C_6H_5 \xrightarrow{NaOCH_3} CF_2.$$

Under suitable conditions difluorocarbene dimerises to tetrafluoroethylene with a yield reaching 95%[20]:

$$2CF_2 \rightarrow CF_2=CF_2.$$

b. Dichlorocarbene. The generally known method of preparing dichlorocarbene is by alkaline hydrolysis of chloroform[21]. A modification of this method is the reaction of chloroform with potassium t-butoxide in an inert solvent such as pentane[22]:

$$CHCl_3 + (CH_3)_3CO^- \rightleftarrows (CH_3)_3COH + CCl_3^-,$$
$$CCl_3^- \rightleftarrows CCl_2 + Cl^-.$$

The advantage of t-butoxides compared with other alkoxides is probably to a large extent associated with the weak reactivity of the anions of the sterically hindered tertiary alcohol[23].

The synthesis of dichlorocarbene from carbon tetrahalides and lithium alkyls in ethereal solution appears to be very promising[24]:

$$CCl_3X + RLi \rightarrow CCl_3Li + RX,$$
$$CCl_3Li \rightarrow CCl_2 + LiCl.$$

The effectiveness of this method of synthesising dichlorocarbene is evident from Table 1, which lists the yield of dichloronorcarane obtained by the addition of dichlorocarbene to cyclohexene. The reaction of lithium alkyls with chloroform finds a useful application when the dichlorocarbene formed is trapped by the nucleophilic triphenylphosphine. One then obtains alkylidenephosphorane which can be converted into substituted vinyl chlorides by the Wittig reaction[25]:

$$(C_6H_5)_3P + CCl_2 \rightarrow (C_6H_5)_3P=CCl_2,$$
$$(C_6H_5)_3P=CCl_2 + \rangle C=O \rightarrow \rangle C=CCl_2 + (C_6H_5)_3PO.$$

Recently a new method has been proposed for the preparation of dichlorocarbene, by the reaction of chloroacetate esters with alkoxides in an inert solvent:

$$CCl_3COR + RO^- \rightarrow CCl_3\overset{\overset{O^-}{|}}{C}-OR \rightarrow CCl_2 + Cl^- + RO-\overset{\overset{O}{\|}}{C}-OR.$$

The effectiveness of this method may be judged from the yield of cyclopropanes formed when olefins are introduced into the reaction system. When t-butyl dichloroacetate is allowed to react with potassium t-butoxide and isobutene, 1,1-dichloro-2,2-dimethylcyclopropane is obtained in only 10% yield[26]; Parham and coworkers[27] were able to increase the yield of cyclopropanes to 72–88% by carrying out the reaction with ethyl trichloroacetate and potassium t-butoxide, sodium ethoxide, or sodium methoxide. Thus the above reaction can give higher yields of cyclopropanes than the reaction in which chloroform is used as a source of dichlorocarbene. The use of readily available sodium methoxide is also an advantage of this method.

Table 2 lists the yields of cyclopropane derivatives obtained by the two methods described above. Wagner[30] proposed a modification of Parham's method[26,27] consisting in thermal decomposition of sodium trichloroacetate in an inert solvent:

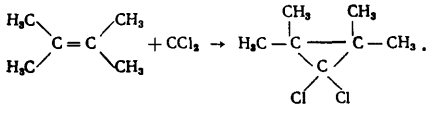
$$CCl_3COONa \xrightarrow{t} CCl_2 + NaCl + CO_2.$$

It has recently been established by polarography that the electrochemical reduction of carbon tetrachloride in solution in acetonitrile proceeds via a stage in which dichlorocarbene is formed[31]:

$$CCl_4 + 2\bar{e} \rightarrow CCl_3^- + Cl^-,$$
$$CCl_3^- \rightleftarrows CCl_2 + Cl^-,$$
$$CCl_2 + 2\bar{e} \rightarrow CCl_2^{2-},$$
$$CCl_2^{2-} + 2CH_3CN \rightarrow CH_2Cl_2 + 2CH_2CN^-.$$

This is also confirmed by the synthesis of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane when the electrolysis of carbon tetrachloride is carried out at -20° in the presence of tetramethylethylene[31]:

$$CCl_4 + 2\bar{e} \rightarrow CCl_3^- + Cl^-,$$
$$CCl_3^- \rightleftarrows CCl_2 + Cl^-,$$



In 1963 it was found[32] that dichlorocarbene can add to the double bond of tetrachloroethylene with the formation of hexachlorocyclopropane. Bearing in mind the fact that tetrachloroethylene is resistant to electrophilic attack, the authors suggest that dichlorocarbene behaves in this reaction either as a nucleophilic or a radical reagent.

Dichlorocarbene has been more thoroughly investigated than any other carbene, and we shall therefore return to its various reactions throughout this review.

c. Dibromocarbene. This compound can be formed as an intermediate either by the alkaline hydrolysis of bromoform[18,33,34] or by treatment of a mixture of the latter in anhydrous alcohol with alkali metal alkoxides[7,18,28]:

$$CHBr_3 + :B \rightleftarrows CBr_3^- + HB,$$
$$CBr_3^- \rightleftarrows CBr_2 + Br^-.$$

Strong bases such as methyllithium and n-butyllithium have also been tested in the synthesis of dibromocarbene. Closs and Closs[39] allowed these bases to react with dibromomethane and Miller and Kim[24] with carbon tetrabromide. It was found that, whereas n-butyllithium and carbon tetrabromide convert olefins into dibromocyclocyclopropanes albeit in very small yields, it was impossible to demonstrate the formation of dibromocarbene in the reaction of methyllithium with dibromomethane.

d. Diiodocarbene. Hine *et al.*[21] recently succeeded in synthesising diiodocarbene by the action of sodium ethoxide on iodoform:

$$CHI_3 + C_2H_5O^- \rightleftarrows CI_3^- + C_2H_5OH,$$
$$CI_3^- \rightleftarrows CI_2 + I^-.$$

The diiodocarbene so formed reacts with the excess of ethoxide ions, yielding acetaldehyde and methylene iodide:

$$CI_2 + C_2H_5O^- \longrightarrow CH_3CHO + CHI_2^-,$$
$$CHI_2^- + C_2H_5OH \longrightarrow CH_2I_2 + C_2H_5O^-.$$

TABLE 1. Yields of dichloronorcarane obtained by the reaction of cyclohexene with carbon tetrahalides and different organolithium compounds.

| Carbon tetrahalide | Lithium alkyl | Yield of dichloro-norcarane, % |
|---|---|---|
| $CCl_4$ | $CH_3Li$ | 8 |
| $CCl_4$ | $n\text{-}CH_3(CH_2)_3Li$ | 50 |
| $CCl_3Br$ | $CH_3Li$ | 67 |
| $CCl_3Br$ | $n\text{-}CH_3(CH_2)_3Li$ | 91 |
| $CCl_3I$ | $CH_3Li$ | 71 |

TABLE 2. Comparison of the yields (%) of cyclopropane derivatives obtained from olefins by the "ethyl trichloroacetate" and "chloroform" methods.

| Reaction products | Initial chloride | | | |
|---|---|---|---|---|
| | $CCl_3COOC_2H_5$[27] | | $CHCl_3$ | |
| | 1,1-dichloro-2,2-dimethyl-cyclopropane | 7,7-dichloro-norcarane | 1,1-dichloro-2,2-dimethyl-cyclopropane | 7,7-dichloro-norcarane |
| In the presence of: | | | | |
| Potassium t-butoxide | 86 | 72 | 65[28] | 59[28] |
| Sodium ethoxide | 82 | — | — | — |
| Sodium methoxide | 76 | 88 | — | 38[29] |

e. Chlorofluorocarbene. This compound probably forms as an intermediate in the thermal decomposition (70–100°) of dichlorofluoroacetic acid in aqueous solution:

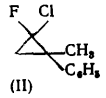
$$Cl_2CFCOO^- \longrightarrow Cl_2CF^- + CO_2,$$
$$Cl_2CF^- \longrightarrow CClF + Cl^-.$$

It later undergoes rapid hydrolysis as follows[36]:

$$CClF \xrightarrow{H_2O} HCl, HF, CO, \text{ and } HCOOH.$$

It has been shown recently that *sym*-tetrachlorodifluoroacetone can serve as a source of chlorofluorocarbene[37]. When the former was allowed to react with cyclohexene in the presence of potassium t-butoxide, 7-chloro-7-fluorobicyclo[4,1,0]heptane (I) was obtained and when 1,1-methylphenylethylene was used instead of cyclohexene, the product was 1-chloro-1-fluoro-2-methyl-2-phenylcyclopropane (II):


(I)


(II)

3. Monohalogenocarbenes

a. Alkoxyhalogenocarbenes. Hine and Tanabe[38] showed that fluoroisopropoxycarbene is formed in the decomposition of chlorodifluoromethane by potassium isopropoxide in isopropanol. Probably, initially difluorocarbene is formed[18] and then reacts with isopropanol, undergoing conversion into fluoroisopropoxycarbene:

$$CHClF_2 + (CH_3)_2CHO^- \rightleftharpoons CClF_2^- + (CH_3)_2CHOH,$$
$$CClF_2^- \longrightarrow CF_2 + Cl^-,$$
$$(CH_3)_2CHOH + CF_2 \longrightarrow (CH_3)_2CH\overset{+}{O}-\overset{-}{C}F_2 \xrightarrow{-HF} \underset{H}{\overset{OCH(CH_3)_2}{C}}\!\!<_{F}.$$

Fluoroisopropoxycarbene is also formed in the reaction of dichlorofluoromethane with a dilute solution of potassium isopropoxide, but in this case the intermediate is chlorofluorocarbene and not difluorocarbene[21].

It seems strange why the above reaction has only a single final product, triisopropyl orthoformate in 71% yield. Under the same conditions chloroform and bromoform yield in addition carbon monoxide, propene, and isopropyl ether. Evidently the difference is due to the fact that the halogen in fluoroisopropoxycarbene is less strongly bound than in chloroisopropoxy- or bromo-carbene. The latter compound loses a halide anion forming the cation (A) which then undergoes the following chain of reactions:

$$\underset{(A)}{(CH_3)_2CHOC^+} \xrightarrow{-CO} (CH_3)_2CH^+ \xrightarrow[-H^+]{(CH_3)_2CHO^-} CH_3CH{=}CH_2 + (CH_3)_2CH{-}O{-}CH(CH_3)_2.$$

b. Chlorocarbene. This compound forms when methyllithium[39], n-butyllithium[35,25], or phenyllithium[25] react with methylene chloride in dry ether:

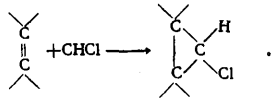
$$CH_2Cl_2 + RLi \longrightarrow LiCHCl_2,$$
$$LiCHCl_2 \longrightarrow CHCl + LiCl.$$

When methylene chloride reacts with n-butyllithium in the presence of triphenylphosphine, the corresponding alkylidenephosphorane forms in 65% yield, which falls to 40% when phenyllithium is used to form chlorocarbene[25]. This reaction is very important, since substituted vinylidene chloride can be obtained from the alkylidene phosphorane and aldehydes or ketones by the Wittig reaction[25]:

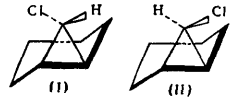
$$(C_6H_5)_3P + CHCl \longrightarrow (C_6H_5)_3P{=}CHCl,$$
$$>C{=}O + (C_6H_5)_3P{=}CHCl \longrightarrow >C{=}CHCl + (C_6H_5)_3PO.$$

Like the majority of carbenes, chlorocarbene is an electrophilic agent which reacts with olefinic double bonds, forming chlorocyclopropanes, whose yield depends on the nucleophilic properties of the olefins[35,40]:

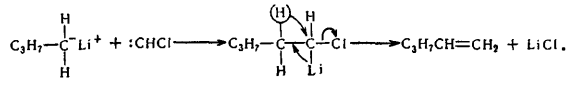
$$CH_2Cl_2 + n\text{-}C_4H_9Li \longrightarrow LiCHCl_2 \longrightarrow CHCl + LiCl,$$



Thus 2,3-dimethylbut-2-ene yields 1-chloro-2,2,3,3-tetramethylcyclopropane in 67% yield and *trans*-but-2-ene yields 1-chloro-2,3-*trans*-dimethylcyclopropane in 40% yield. Cyclohexene gives a 31% yield of a mixture of the two stereoisomeric 7-chlorobicyclo[4,1,0]heptanes (I) and (II) in 1 : 2 ratio, their reduction with sodium in liquid ammonia giving bicyclo[4,1,0]heptane[41]:

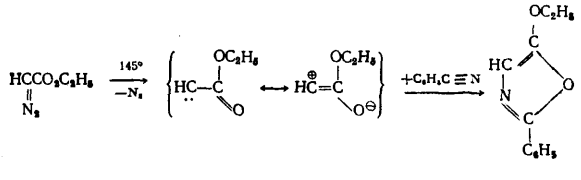

(I) (II)

In the absence of an olefin in the reaction medium, chlorocarbene reacts with n-butyllithium to give 1-chloro-n-pentyllithium which then undergoes $\alpha$-elimination of lithium chloride, forming pent-1-ene following the rearrangement of the hydride anion[35,41]:



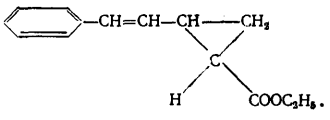
4. Keto- and Thioketo-Carbenes

Since by ketocarbenes we understand any carbenes containing the C=O group in their molecules, we think it appropriate to include in this Section some information about ethoxycarbonylcarbene. It can be obtained by the removal of nitrogen from diazoacetate ester, for example. Thus by the thermolysis of diazoacetate ester in benzonitrile, Huisgen *et al.*[42] obtained in 42% yield 5-ethoxy-2-phenyloxazole which is a product of the 1,3-dipolar cyclo-addition of ethoxycarbonylcarbene to benzonitrile:



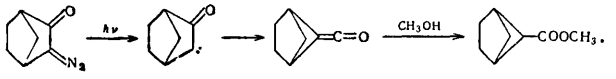
The high yield of the substituted oxazole is probably associated with the inability of ethoxycarbonylcarbene to undergo the Wolff rearrangement. Acetonitrile and phenylacetonitrile[42] also react with ethoxycarbonylcarbene, giving 2-substituted 5-ethoxyoxazole. When the decomposition of diazoacetate ester is catalysed by copper in the presence of tolane, the corresponding derivative of cyclopropene is formed[43]; the replacement of copper by copper sulphate sharply alters the mode of reaction, 2-ethoxy-4,5--diphenylfuran being formed[44,45]. Unfortunately this fact has not as yet been adequately explained (see pp. 81 and 82).

Comparatively recently the addition of ethoxycarbonylcarbene to phenylbutadiene has been described[46]. The reaction results in the formation of the following cyclopropane derivative:

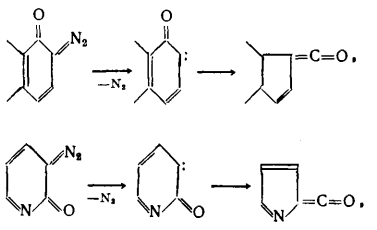


Other reactions of ethoxycarbonylcarbene are described on pages 81, 82, and 85.

Among the latest investigations of other ketocarbenes the work of Wiberg *et al.*[47], for example, is of interest; by irradiating diazonorcamphor in methanol, they obtained methylbicyclo[2,1,1]hexane-5-carboxylate:

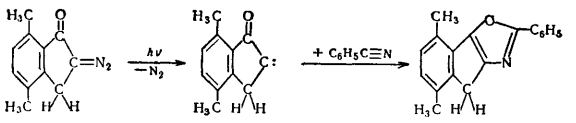


Similar ring contraction as a result of a Wolff rearrangement occurs in the photochemical[48,49] and thermal[50] decomposition of quinone diazides and naphthalene diazo-oxide, in the photochemical decomposition of diazopyridones[51],

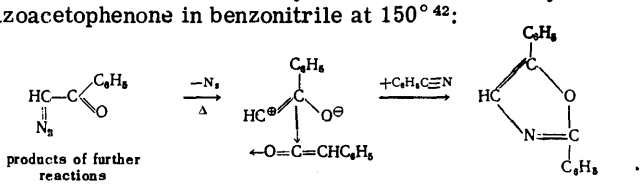


and in the photolysis of 4,7-dimethyl-4-diazoindan-1-one in aqueous tetrahydrofuran[52,53].

In the last case the Wolff rearrangement is somewhat retarded, probably as a result of the large amount of strain in the ring, so that when the reaction is carried out in benzonitrile it is possible to obtain the 1,3-adduct of the dipolar cyclo-addition of the intermediate ketocarbene to benzonitrile (the corresponding condensed oxazole)[54]:

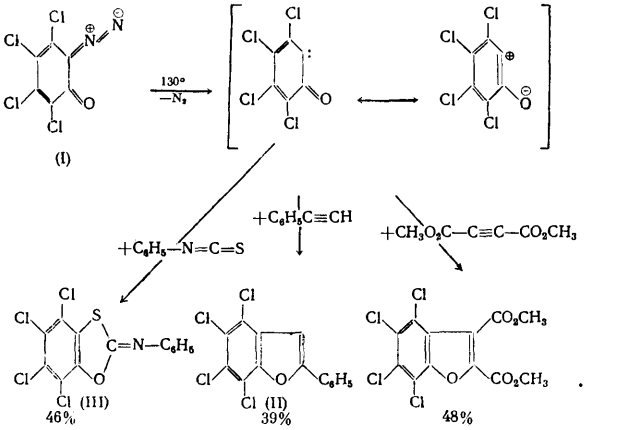


In other cases the formation of ketocarbenes was also confirmed by introducing into the reaction mixture various dipolarophiles which resulted in the formation of the corresponding 1,3-adducts. For example, 2,5-diphenyloxazole was isolated in 0.4% yield after the thermolysis of diazoacetophenone in benzonitrile at 150°[42]:

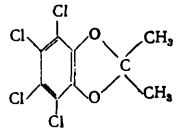


The very low yield of the 1,3-adduct in this case is due to the high rate of the Wolff rearrangement as a result of which a large part of the initially formed benzolycarbene is converted into the corresponding keten. When the carbene is stabilised with metallic copper or certain cuprous and cupric compounds, the product of 1,3-dipolar cyclo--addition can be obtained in higher yields. For example, when the above reaction is carried out in the presence of copper powder, cuprous cyanide, or cupric acetylacetonate, 2,5-diphenyloxazole is obtained in 16–17% yield[42]. By stabilising the ketocarbene with copper, Novak and coworkers[55] were able to obtain acylcyclopropanes in the decomposition of a diazoketone in the presence of olefins. It is interesting that, when the decomposition of diazoacetonephenone is catalysed with copper in the presence of tolane, 2,3,5-triphenylfuran is formed[54]. The formation of the corresponding adducts of acetonitrile and acetone with ethoxycarbonyltrifluoroacetylcarbene has recently been described[56].

Aromatic ketocarbenes are distinguished by a long "life-time" in the absence of substances capable of reacting with them. This is because such carbenes would lose their aromatic character by undergoing a Wolff rearrangement. For example, the carbene formed in the photolysis of 3,4,5,6-tetrachlorobenzene-*o*-diazo-oxide (I) is so resistant to rearrangement than in methanol it gives the monoethyl ether of tetrachlorocatechol in 70% yield[54]. On the other hand, thermolysis of 2,3,4,5-tetrachlorobenzene-*o*--diazo-oxide in phenylacetylene at 130° gives the 1 : 1 adduct of the corresponding ketocarbene and the solvent; the adduct is 4,5,6,7-tetrachloro-2-phenylbenzo(b)furan (II).[42] If the decomposition of the diazo-oxide (I) is carried out in styrene, the 2,3-dihydro-derivative of the above adduct is obtained while in dimethyl fumarate the product is the diester of dihydrobenzo[b]furandicarboxylic acid. The intermediate ketocarbene also readily forms the corresponding adduct (III) with phenylisothiocyanate, whose C=S double bond is an active dipolarophile. The reactions undergone by the ketocarbene formed in the thermolysis or photolysis of 3,4,5,6-tetrachlorobenzene-*o*-diazo-oxide (I) can be represented schematically as follows:

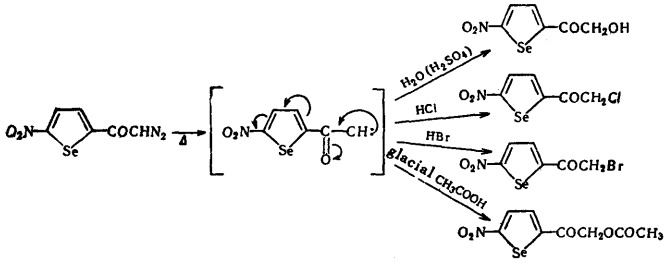


In the photolysis of the diazo-oxide (I) in acetone the carbene adds to the keto-group of acetone forming 1,3-benzodioxole in 30% yield:

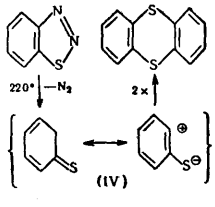


The low dependence of the rate of decomposition of the diazo-oxide (I) on the nature of the dipolarophile used as solvent is a definite indication that the reaction between these components takes place after the removal of the nitrogen molecule from the diazo-oxide (I), i.e. the corresponding aromatic carbene really exists.

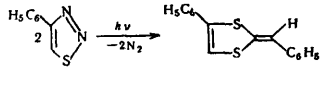
Ketocarbenes are longer-lived than alkylcarbenes, for example, which may be due to the conjugation of the lone pair of electrons of the key carbon atom and the carbonyl double bond[1]. However, the usual ketocarbenes nevertheless fairly readily undergo the Wolff rearrangement (particularly in the presence of colloidal silver), giving the corresponding ketens. The resistance of the ketocarbenes to rearrangement increases with increase in the extent of conjugation in the molecule. Thus it is reasonable that aromatic ketocarbenes are the most stable. Using aromatic ketocarbenes or ketocarbenes with a fairly long conjugation chain, it is possible to obtain high yields of the products of their direct reaction with alcohols, amines, water, hydrogen halides, etc., without resorting to additional stabilisation of the carbene with copper[57]. Thus it proves possible[58] to obtain ketones derived from selenophen, starting with 2-diazoacetyl-5-nitroselenophen:



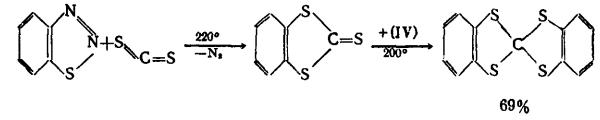
Turning now to thioketocarbenes, we must mention that as early as 1893 Jacobson and Janssen[59] obtained thianthrene by the thermolysis of 1,2,3-benzothiadiazole, which probably involves the intermediate formation of the corresponding thioketocarbene (IV):



The formation of the derivative of dithiafulvene in the photolysis of 4-phenyl-1,2,3-thiadiazole[60] may be explained by the 1,3-addition of phenylthiocarbene to the product of its rearrangement — phenylthioketen:



In contrast to the ketocarbene obtained by the degradation of the diazo-oxide (I), the thiocarbene (IV) exhibits a striking tendency towards dimerisation. Only the most active dipolarophiles with a C=S double bond can give the corresponding adducts with this thioketocarbene. Such dipolarophiles are, in particular, carbon disulphide and phenyl isothiocyanate:

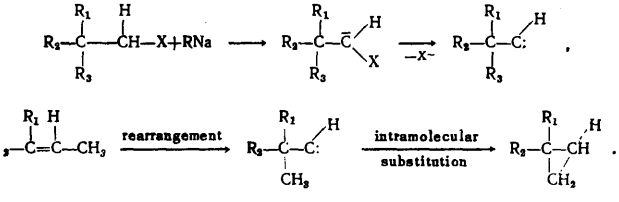


69%

There is as yet little information in the literature about the reactions of the thioketocarbene (IV) obtained in the photolysis of 1,2,3-thiadiazole[61].

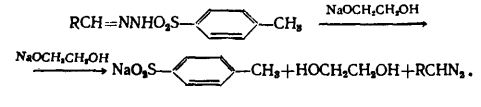
## 5. Other Carbenes

a. Alkylcarbenes. These compounds are obtained by the dehydrohalogenation of alkyl halides, the reaction being greatly affected by the strength of the base used for the dehydrohalogenation and by steric factors. For example, phenylsodium is more effective for the preparation of alkylcarbenes than sodium methoxide. When a secondary or a tertiary alkyl group is linked to the $\alpha$-carbon atom of the alkyl halide, the main products of the reaction are olefins and cyclopropanes formed from the carbene by rearrangement or intramolecular substitution (see below) respectively[62,63]:



It is also significant that alkyl iodides are dehydrohalogenated more sluggishly than the corresponding bromides and chlorides.

Bamford and Stevens[66] developed a method for the preparation of diazoalkanes which consists in the reaction of the corresponding tosylhydrazones with sodium in ethyleneglycol:



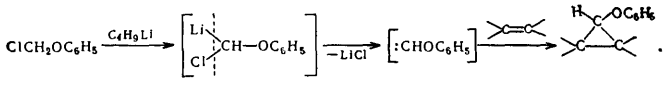
This reaction has been widely used for the preparation of alkylcarbenes. For example, it has been established that

TABLE 3. Extent of dehydrohalogenation of alkyl halides (%) as a function of the base used.

| Base | Alkyl halide | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | n-butyl (Ref. 64) | | | isobutyl (Ref. 64) | | | neopentyl (Ref. 65) | | neohexyl (Ref. 65) |
| | Cl | Br | I | Cl | Br | I | Cl | Br | Cl |
| $C_6H_5Na$ | 94 | 94 | 65 | 89 | 62 | 13 | 70 | 25 | 67 |
| $NaNH_2$ | 30 | 15 | — | 7 | 1 | — | 60 | — | — |
| $NaOCH_3$ | 10 | — | — | 0 | — | — | — | — | — |

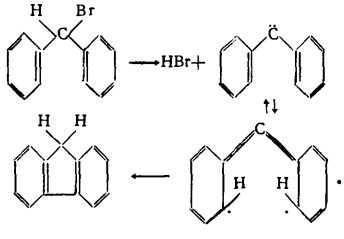
the tosylhydrazones of aromatic[63,67], aliphatic[63,68], and alicyclic[69] aldehydes and ketones react with bases in aprotic solvents, such as diethyl Carbitol, forming diazo-compounds which on thermal decomposition between 160° and 220° generate the corresponding carbenes. Alkylcarbenes obtained from aliphatic tosylhydrazones tend to undergo rearrangement with formation of olefins, and intramolecular substitution resulting in cyclopropanes. The rearrangement takes place to a greater extent in view of the higher yields of olefins.

b. Alkoxy- and phenoxy-carbenes. Schöllkopf and Paust[70] obtained in high yields a number of alkoxycyclopropanes by the reaction of dichloromethyl alkyl ethers with olefins in the presence of methyllithium. They believe that this reaction proceeds with the intermediate formation of the alkoxycarbene. Later these workers and Lerch[71] described a synthesis of phenoxycyclopropanes by the reaction of chloromethyl phenyl ether with olefins in the presence of butyllithium. They believe that the reaction proceeds as follows:

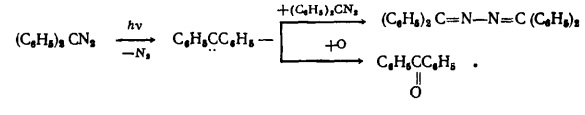


The addition of phenoxycarbene to the double bond takes place stereospecifically, like *cis*-addition.

c. Diphenylcarbenes. By pyrolysing diphenylmethyl bromide, Harrison and Lossing obtained fluorene and hydrogen bromide[72]. Probably diphenylcarbene forms as an intermediate and is then converted into fluorene as a result of migration of hydrogen atoms:

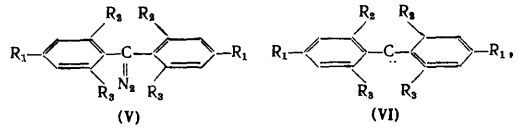


Photolysis of diphenyldiazomethane at low temperatures also result in the formation of diphenylcarbene, the latter rapidly reacting with diphenyldiazomethane and oxygen to give benzophenone azine [bis(diphenylmethylene)hydrazine] and benzophenone[73]:



Diphenylcarbene can also be obtained by the thermal decomposition of diphenyldiazomethane, the nature of the final reaction products depending on the solvent used. When the reaction is carried out with solvent or in benzene, benzophenone azine is formed exclusively. When petroleum ether is used, benzophenone azine, *sym*-tetraphenylethane, and a molecular complex of tetraphenylethane and benzophenone azine are formed. The authors believe that in this case diphenylcarbene reacts with petroleum ether forming diphenylmethyl radicals which on dimerisation give the substituted ethane.

Fairly stable substituted diphenylcarbenes (VI) were obtained by the pyrolytic and photolytic decomposition of the corresponding diazo-compounds (V):[74]



(V) (VI)

Va, VIa; $R_1$, $R_2$, $R_3$=$CH_3$;

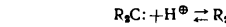
Vb, VIb; $R_1$, $R_2$, $R_3$=Cl;

Vc, VIc; $R_1$=$CH_3$, $R_2$=$R_3$=$OCH_3$.

The low reactivity of carbenes of type (VI) is a consequence of steric hindrance. Paskovich's dissertation deals in particular with sterically hindered carbenes[75].

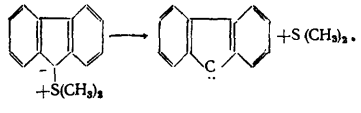
It is interesting that diphenylcarbene exhibits radical properties[76]; for example its addition to olefins is non-stereospecific[8]†.

Recently Kirmse[78] observed nucleophilic behaviour in the case of diphenylcarbene: the latter was converted into the diphenylcarbenium cation after its synthesis by the photolysis of diphenyldiazomethane in alcohol. Thus the equilibrium

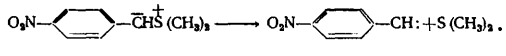


which previously was regarded as purely formal, found practical confirmation. The author notes that diphenylenecarbene obtained from diazofluorene shows much weaker nucleophilic activity.

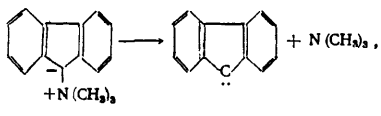
d. Fluorenylidene and cyclopentadienylidene. Johnson and La Count[79] showed that when dimethylsulphonium 9-fluorenylide is decomposed the corresponding carbene, fluorenylidene, is formed as an intermediate:



Swain and Thornton[80] found that other dimethylsulphonium compounds also break down with the formation of the corresponding carbenes. Thus decomposition of *p*-nitrobenzyldimethylsulphonium *p*-toluenesulphonate in the presence of sodium hydroxide at 60° yields *p*-nitrobenzylcarbene, which dimerises to *cis*- and *trans*-*pp'*-dinitrostilbenes:

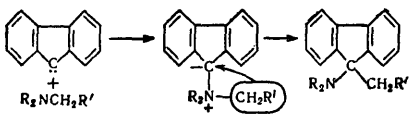


Franzen[81] showed that trimethylammonium 9-fluorenylide also decomposes into fluorenylidene,

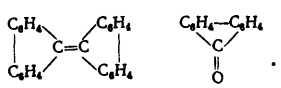


† Somewhat later Skell and Klebe[77] observed radical properties in the case of another carbene — propargylidene (HC≡C–C̈–H).

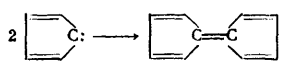
which then reacts, with amines for example[81,82] in the following way:



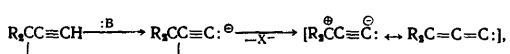
In the absence of suitable reagents fluorenylidene dimerises to difluorenylidene or reacts with oxygen to form fluorenone[13]:



The photochemical decomposition of diazocyclopentadiene yields fulvalene; this is probably due to the formation of a carbene (cyclopentadienylidene) as an intermediate, which subsequently dimerises[13]:

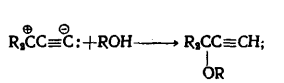


e. Vinylidenecarbenes. Hartzler[83] made a thorough study of the rearrangement of acetylene systems into allene systems in the presence of alkoxide and hydroxide ions and concluded that the formation of vinylidenecarbene is an intermediate stage in this reaction:

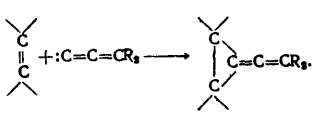


where R = $CH_3$, $C_6H_5$, H; and X = Cl, Br, OH, $OCOCH_3$.

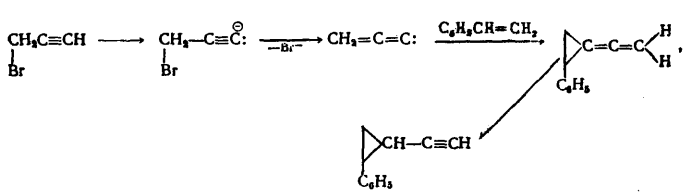
In the presence of alcohol the vinylidenecarbene reacts in the "propargyl form" with the formation of the corresponding propargyl ether[84],



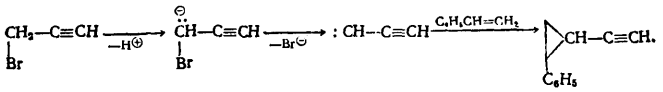
while in the presence of olefins it reacts in the "allenyl form" and is converted into cyclopropanes[83-85]:



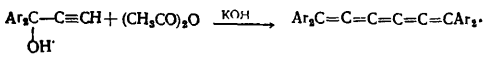
The reaction of propargyl bromide with potassium t-butoxide in styrene yields 1-ethynyl-2-phenylcyclopropane. This compound can form in two ways: either via the vinylidene carbene[83]:



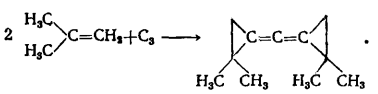
or by $\alpha$-elimination of hydrogen bromide with subsequent addition of the resulting propargylidene to styrene[83]:

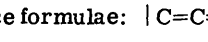


According to Hartzler[83], the formation of tetraarylhexapentaenes in the reaction of diarylethynylmethanols with acetic anhydride and potassium hydroxide in dry ether[86] also proceeds via vinylidenecarbene:



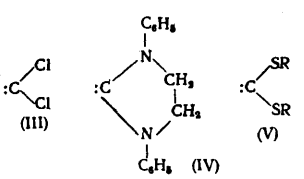
The dicarbene $C_3$ observed recently in the atmosphere of comets proved to be the main constituent of gaseous carbon[87]. This dicarbene is obtained by evaporating carbon into a vacuum corresponding to $10^{-3}$–$10^{-5}$ mmHg. It can enter into a variety of reactions on the walls of the reaction vessel cooled to -196°. For example, the reaction of the dicarbene $C_3$ with isobutene yielded a compound of a new class — the bisethanoallene series. The structure of the products, whose yield was 40%, was demonstrated by infrared and nuclear magnetic resonance spectroscopy[88,89]:



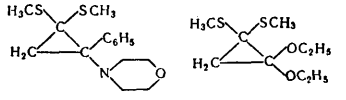
The reaction of the dicarbene with *cis*- and *trans*-but-2-enes is stereospecific to the extent of 90–95%, i.e. 90–95% of the dicarbene molecules are in the singlet state at the instant of the reaction and the remainder in the triplet state. Skell and Wescott[88] suggest that the structure of the $C_3$ molecule should be represented by a combination of the following two resonance formulae:  .

f. 1,3-Diphenylimidazolidin-2-ylidene. By reacting dianilinoethane with orthoformates, Wanzlick and coworkers[90-92] were able to synthesise an olefin which readily dissociated into two molecules of a carbene–1,3-diphenylimidazolidin-2-ylidene. This carbene, which we shall henceforth call stable carbene, is markedly nucleophilic probably because of the strong electron-donor properties of the nitrogen atoms, and does not react with the usual olefins. The authors isolated only the product of the reaction of stable carbene with tetracyanoethylene, in which the electron density at the double bond is known to be greatly reduced[91]. The structure of this product has not as yet been elucidated.

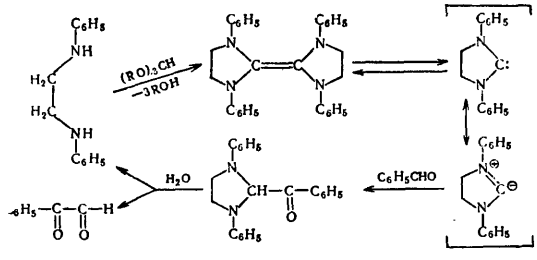
The electrophilic or nucleophilic properties of a carbene depend on the electron-acceptor (or correspondingly the electron-donor) properties of the atoms linked to the key carbon atom. In this connection it is interesting to compare dichlorocarbene (III), stable carbene (IV), and the carbene (V) in which two sulphur atoms are linked to the key carbon atom, since sulphur is intermediate between nitrogen and chlorine in its electron-donor properties.



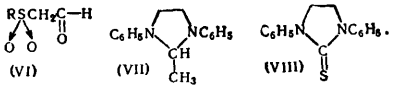
Dichlorocarbene (III), being a typical electrophilic agent, readily reacts with the usual olefins and only to a very slight extent with olefins whose double bond is markedly deactivated, the reaction mechanism being evidently different in the latter case[32]. The stable carbene (IV) is a nucleophilic compound and does not react at all with the usual olefins. Schöllkopf and Wiskott[93] have established that the di(methylcapto)carbene (V) (R = $CH_3$, for example), does not react with a solution of cyclohexene in the dimethyl ether of ethylene glycol, because the sulphur atoms greatly reduce its electrophilic properties by virtue of their lone pairs of electrons. Nevertheless, in certain cases di(methylmercapto)carbene also shows electrophilic properties. Thus it is capable of adding to double bonds with enhanced electron density, yielding, for example, cyclopropane derivatives on reaction with 1-morpholino-1--phenylethylene or keten diethyl acetal:



Although the chemistry of the nucleophilic carbene has only just begun to be investigated, its possible synthetic applications are already apparent. Its preparation and certain reactions can be shown schematically as follows:

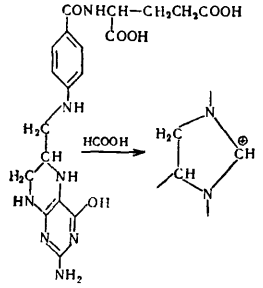


Apart from its use in the synthesis of keto-aldehydes, the stable carbene provides, for example, a possible pathway to the synthesis of the as yet unknown class of $\beta$-sulphone-aldehydes (VI).[94] Hydrolysis of the primary product of the reaction of the stable carbene with acetic anhydride yields 2-methyl-1,3-diphenylimidazolidine (VII) and monoacetylated dianilinoethane. The stable carbene reacts with sulphur even at room temperature, giving the corresponding derivative of thiourea (VIII):



While in their reaction with dichlorocarbene diazo--compounds eliminate a molecule of nitrogen[95], with the nucleophilic carbene they yield ketazines. On treatment with carboxylic acid chlorides, the stable carbene gives imidazolidinium salts acylated at the carbon atom in position 2, which are readily hydrolysed.

It is nowadays believed that tetrahydrofolic acid combines with formic acid or formaldehyde and participates in the metabolism of certain substances in living organisms, promoting transformylation, transhydroxymethylation, and certain other reactions[96]. It is interesting that tetrahydrofolic acid itself is structurally related to dianilinoethane, while the product of its reaction with formic acid, the so--called "anhydrocitrovorum factor", is none other than the protonated form of a carbene very similar in structure to the stable carbene[97]:



Hence it is not impossible that reactions involving the participation of carbenes occur also in nature. Quite recently Wanzlick and coworkers[98] have described the synthesis of new compounds of the type of bis(1,3-diphenylimidazolidin--2-ylidene).

## IV. SOME ASPECTS OF THE SYNTHETIC APPLICATIONS OF CARBENES

### 1. Substitution of Carbenes in C–H, C–Halogen, and Other Bonds

a. Intermolecular substitution of carbenes. Franzen and Fikentscher[99] allowed methylene labelled at the carbon atom to react with ethyl ether and showed that this results in the formation of ethyl n-propyl ether by direct substitution of methylene in the C–H bond of the ethyl group. Franzen and Kuntze[100] described similar reactions with other alkyl ethers, tetrahydrofuran, and *N*-methylpyrrolidine.

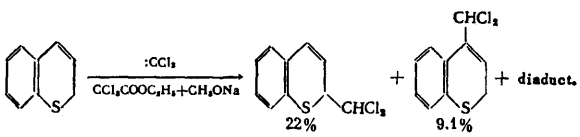
Doering and coworkers[101] showed that methylene obtained by the photochemical decomposition of diazomethane readily interacts with the C–H bonds of saturated hydrocarbons, for example n-pentane, 2,3-dimethylbutane, cyclopentane, etc., the products of the substitution of methylene in various C–H bonds being formed in amounts corresponding to the number of these bonds in the hydrocarbon molecule regardless of the nature of the bond. In view of the absence of selectivity in this reaction, Doering suggested that its activation energy is close to zero[101,102].

However, Frey[103] was able to show that methylene obtained by gas-phase photolysis of diazomethane reacts selectively with $\rangle$CH, $\rangle CH_2$, and $-CH_3$ bonds in hydrocarbons, in the ratios 1.5 : 1.2 : 1.0. Richardson *et al.*[4] carried out liquid-phase photolysis of diazomethane in solution in isomeric octanes and arrived at the same conclusions as Doering. They believe that the difference between the reactivity of methylene in the gas phase and in solution can be readily explained on the basis of Herzberg's spectroscopic data on its structure[3,104]. During photolysis in solution excited singlet methylene forms initially, almost each of its collisions with the solvent molecules resulting in reaction. Since the frequency of collisions is much greater than the frequency of the singlet–triplet transition, non-selective substitution of methylene in carbon–hydrogen bonds occurs. In the gas-phase reaction the frequency of the collisions of methylene with hydrocarbon molecules is approximately the same as that of the singlet–triplet transition and therefore methylene reacts selectively as a typical radical agent.

This interpretation is consistent with a number of experimental data[4,103,105,106]. Doering and Knox[102] showed that the replacement of hydrogen atoms in methylene by electronegative groups greatly increases the selectivity of the reaction of the carbene with C–H bonds. The ratios of the rates of substitution at tertiary, secondary, and primary carbon atoms of the alkane greatly increase in the following sequence of carbenes: $CH_2 < CHCOOC_2H_5 < C(COOC_2H_5)_2$. Doering and Knox suggest that the presence of the alkoxycarbonyl group increases the activation energy for the reaction and favours the reaction at the tertiary carbon atom relative to that at the primary atom.

Recently it proved possible to substitute methylene in the C–H bond of pyridine, with 83% yield of α-picoline[107]. The specificity of the reaction was explained by the initial addition of methylene to the nitrogen atom with subsequent rearrangement.

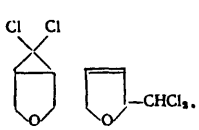
Until 1961 it was regarded as generally accepted[108] that dihalogenocarbenes cannot be substituted in C–H bonds. However, Parham and Koncos[109] showed that this reaction is possible:




They suggest that the benzothiopyranate anion forms initially under the action of sodium methoxide.

Since the formation of tetrachloroethylene from dichlorocarbene and chloroform is never observed in the liquid phase, its formation in the pyrolysis of chloroform probably involves the substitution of dichlorocarbene in the C–H bond of chloroform, the resulting pentachloroethane being converted into tetrachloroethylene after losing the elements of hydrogen chloride[97].

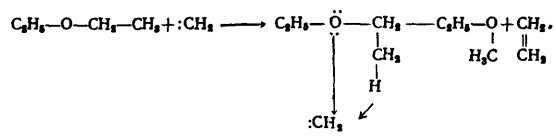
Anderson and Reese[110] showed that the addition of dihalogenocarbenes to carbon–carbon double bonds and their substitution in C–H bonds of olefins may compete with one another. Thus when 2,5-dihydrofuran is treated with a slight excess of dichlorocarbene obtained from ethyl ether, trichloroacetic acid, and sodium methoxide at 0°, a mixture of 6,6-dichloro-3-oxabicyclo[3,1,0]-hexane and 2-dichloromethyl-2,5-dihydrofuran is formed with an overall yield of 62%:



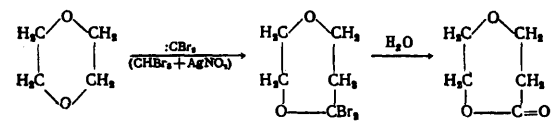

In the case of dibromocarbene a mixture of the corresponding bromo-compounds forms with an overall yield of 28%.

Of the latest work on the substitution of free methylene in C–halogen bonds, the investigation of Bradley and Ledwith[111] must be mentioned. They were able to substitute methylene in C–Cl bonds of primary, secondary, and tertiary alkyl chlorides. The substitution of methylene in C–halogen bonds is described in greater detail in D'yakonov's review[112].

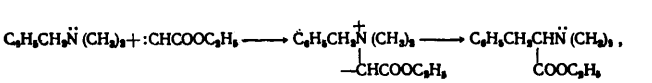
The C–O bond is fairly vulnerable with respect to carbenes. For example, methylene is not only substituted in the C–H bonds of alkyl ether but the latter are actually split with the formation of olefins and the corresponding methyl alkyl ethers. The reaction probably proceeds as follows[99]:

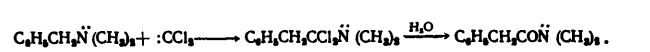



Phenylcarbene and ethoxycarbonylcarbene[99], obtained by the photolysis of the corresponding diazo-compounds, react similarly. The reaction of dibromocarbene with dioxan in aqueous solution is also an example of substitution in the C–O bond[113]:

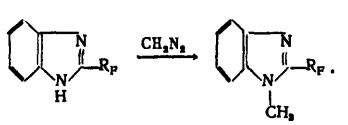



The substitution of carbenes in C–N bonds usually occurs only in those cases where the amino-nitrogen is linked to the benzyl radical, which is distinguished by exceptional cationoid activity[108,110,114]. The reaction probably takes place by a "ylid" mechanism:

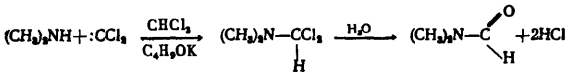



Braz *et al.*[115] showed that methylene is readily substituted in N–H bonds of benzimidazoles with a perfluoroalkyl substituent in the 2-position, which greatly increases the mobility of the hydrogen atom in the imino-group:




Other examples of substitution of carbenes in N–H bonds are known[116,117]:

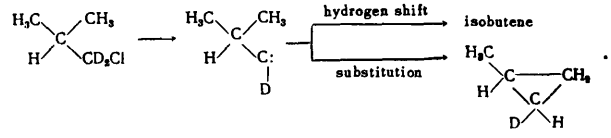



It has recently been shown that this reaction can be used also for the preparation of thioformamides[118].

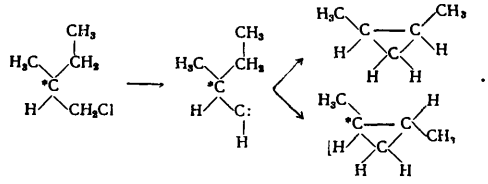
Reutov and Lovtsova[119] suggest that dichlorocarbene can be substituted in the Hg–Cl bond with the formation of trichloromethylorganomercury compounds.

b. Intramolecular substitution of carbenes. In the case of alkylcarbenes the substitution in C–H bonds often takes place intramolecularly. Kirmse and Doering[120] found that the formation of methylcyclopropane and isobutene under the conditions of the Wurtz reaction from isobutylene chloride labelled with deuterium

proceeds via α-elimination of deuterium chloride, i.e. in the intermediate dehydrohalogenation stage carbene is formed and then gives the final product by intramolecular substitution:

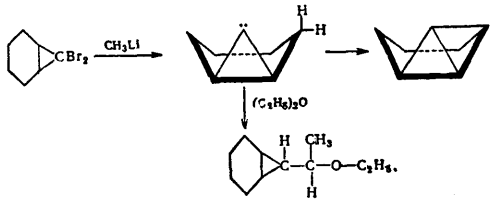



Doering and Kirmse[121] found an elegant application for the above reaction: they used it to establish the *cis*- and *trans*-configurations of the isomeric 1,2-dimethylcyclopropanes. This depends on the fact that the carbene formed from the optically active 2-methylbutyl chloride can react further in several ways: with formation of an olefin, ethylcyclopropane, and two dimethylcyclopropanes. Of the last two, only the *trans*-isomer can be optically active and therefore the presence of optical activity in the case of one of the dimethylcyclopropanes proves that it has the *trans*--configuration:

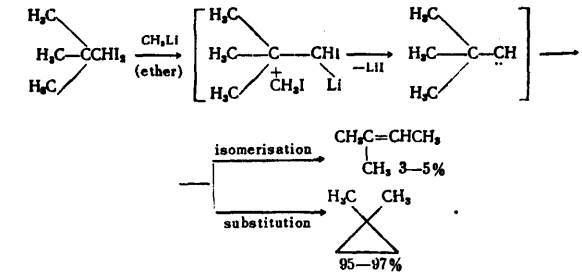


Skell and Krapcho[122] confirmed the mechanism of formation of the cyclopropanes, involving the α-elimination of the elements of hydrogen chloride, using the reaction of dideuteroneopentyl chloride with metallic sodium.

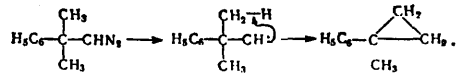
Another example of intramolecular substitution is the reaction of 7,7-dibromonorcarane with methyllithium yielding a carbene which reacts with the ether used as solvent: it is intramolecularly substituted in the C–H bond[123]:



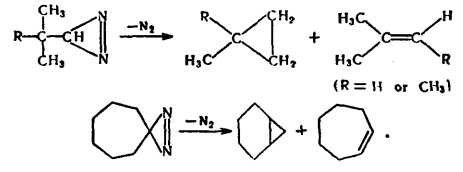

The reaction of the last type was investigated in greater detail by Kirmse and Wedel[124], who showed that, when lithium alkyls or metals (lithium, magnesium) are allowed to act upon *gem*-dihalogeno-compounds, both halogen atoms are eliminated with the formation of a mixture of the corresponding unsaturated compounds and cyclopropane derivatives. For example, the reaction between 1,1-dibromobutane and methyllithium or magnesium yields mainly but-1-ene, methylcyclopropane being formed only in small amounts. The tendency of the intermediate alkylcarbene towards intramolecular substitution in the C–H bond increases with the extent of branching of the alkyl group. Thus the reaction of 1,1-diiodo-2,2-dimethylpropane with methyllithium in ether gives a mixture of products consisting of 95–97% of 1,1-dimethylcyclopropane and 3–5% of 2-methylbut-2-ene.




The rearrangement which Philip and Keating[125] discovered and called "neophilic" rearrangement, is also an example of intramolecular substitution of a carbene in a C–H bond:



Schmitz *et al.*[126] showed that thermal degradation of diazirines yields carbenes which react further to give cyclopropane derivatives, products of intramolecular substitution, together with olefins formed as a result of rearrangement:




In contrast to the examples known until now, the solvent has no effect on the relative yields of the products in this case: whether the solvent contains hydroxy-groups or not, the yields of cyclopropanes and olefins are the same.

## 2. Addition of Carbenes to Carbon–Carbon and Other Double Bonds

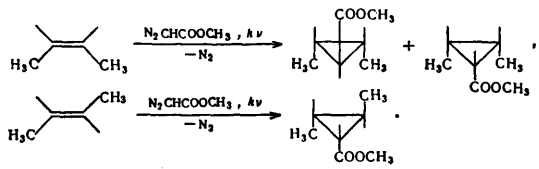
All the carbenes, except the so-called nucleophilic carbene (see p. 76) add to the double bonds of olefins with the formation of cyclopropanes. Although this reaction is often used to prove the existence of carbenes, it is necessary to exercise a certain caution in this respect. Thus in the synthesis of cyclopropanes in the reaction of Simmons and Smith[11,127,128] an organometallic compound and not a carbene is probably formed in the intermediate stage[11,127,128]. However, in most cases there is no doubt about the formation of carbenes as intermediates in the synthesis of cyclopropanes from olefins.

We shall mention first of all the series of carbenes (produced by the reactions shown below) through which an enormous number of substituted cyclopropanes have become readily available[129–133]:

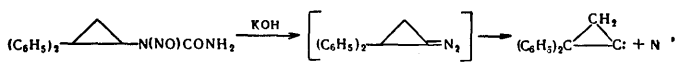
$$CF_2Br_2+RLi \rightarrow RBr+LiBr+ : CF_2,$$
$$ClH_2COR+RLi \rightarrow RH+LiCl+ : CHOR,$$
$$ClH_2CSR+RLi \rightarrow RH+LiCl+ : CHSR.$$

Having at their disposal the method at present available for the preparation of dihalogenocarbenes under neutral. conditions, which consists in the thermal decomposition of the salts of trihalogenoacetic acids, researchers are able to synthesise cyclopropanes from olefins which are sensitive to bases, for example allyl chloride[30,134].

While speaking of the characteristic features of the addition of carbenes to carbon–carbon double bonds, it must be mentioned that, as shown by Doering and Mole[135] and also D'yakonov and coworkers[136,137], alkoxycarbonylcarbenes, for example, add stereospecifically to the double bond in the *cis*-position:



2,2-Diphenylcyclopropylidene described by Jones[138],

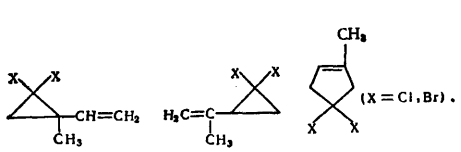


also probably adds stereospecifically to the isomeric but-2-enes[112].

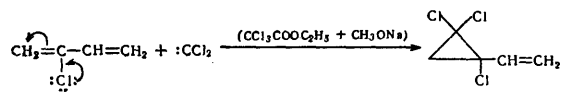
Skell and Etter[139] found that ethoxycarbonylcarbene, formed in the photolysis of diazoacetic ester, is much less stereoselective in the reaction with olefins than the same carbene prepared in a different way — by the decomposition of the diazoacetic ester in the presence of copper. Possibly under the conditions of copper catalysis the complex of the carbene with copper (or copper ions) reacts, and not the free carbene. Complex formation may increase the dimensions of the carbene reacting with the double bond and at the same time reduce its electrophilic activity[139].

Skell and Etter[140] established that the reactivity of ethoxycarbonylcarbene with respect to olefins of different structure varies in the same sense as that of the electrophilic bromonium cation. The rate of reaction in both cases diminishes as the nucleophilic properties of the olefin are weakened. This constitutes further evidence that the additions of carbenes to olefins are electrophilic reactions. In this connection we may mention that the rate of addition of the nucleophilic trichloromethyl anion to the same olefins varies in the opposite sense in the same sequence.

The reaction of dihalogenocarbenes with isoprene has been studied[141,143] and it has been found that the addition takes place mainly in the 1,2-position. Orchin and Herrick[141], who obtained a small amount of the product of 3,4-addition as well as that of the 1,2-addition, suggested that a very small amount of the product of the 1,4-addition is also formed:

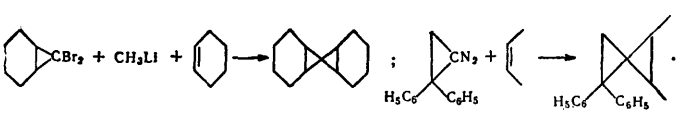


Later D'yakonov and coworkers[144] showed that dichlorocarbene also adds to chloroprene, mainly in the 1,2-position:

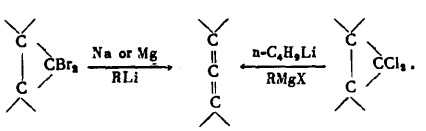


D'yakonov[112] explains this result by suggesting that during the reaction the important feature is not the negative inductive effect of the chlorine atom in the chloroprene molecule but its positive conjugation effect, which makes the 1,2-bond more nucleophilic than the 3,4-bond. It should be noted that the mode of addition to chloroprene of an electrophilic agent such as hydrogen chloride or bromide is consistent with the above explanation; in both cases the proton of the hydrogen halide is directed to the first carbon atom of chloroprene[145]. When dihalogenocarbenes are allowed to react with hexa-1,3,5-triene, mono- and di-adducts are formed. Clearly the more nucleophilic double bonds of the terminal vinyl groups of hexa-1,3,5-triene are involved in the reaction. Vinylcyclopropanes may be of interest as monomers. Thus polymerisation of vinylcyclopropane in the presence of $Al(C_2H_5)_3.TiCl_3$ gave a crystalline polymer[146,147].

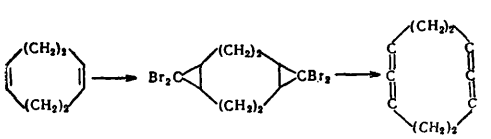
Using the addition of cyclic carbenes (cyclopropylidenes) to olefins[138,148], it is possible to obtain spiran derivatives:



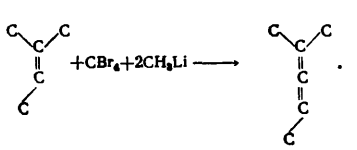
It is interesting that, when the adducts of olefins and dichloro- or dibromo-carbenes are acted upon by various alkaline agents, they lose two halogen atoms and are converted into allenes[10,148-150]:



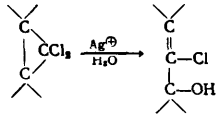
Skatteböl[149] used this reaction to convert cycloocta-1,5-diene into cyclodeca-1,2,6,7-tetraene:



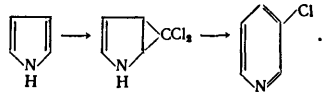
Since lithiumalkyls are among the reagents which convert dihalogenocyclopropanes into allenes and since, on the other hand, the reaction of lithiumalkyls with carbon tetrahalides can give dihalogenocarbenes, there is a possibility of converting olefins into allenes in one step, which Skatteböl[149] in fact achieved:



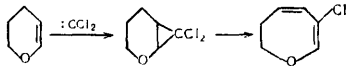
Dihalogenodicyclopropanes can be converted into allyl compounds as well, for example by treatment with an aqueous solution of silver nitrate[151]:



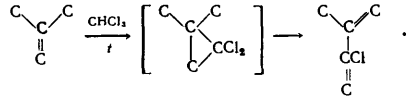
The rearrangement into allyl compounds takes place also with adducts of cyclopentene[152] and bicyclo[2,2,1]-heptadiene[153], the latter forming bicyclo[3,2,1]octadiene. The removal of a molecule of hydrogen halide together with the opening of the cyclopropane ring takes place particularly readily if an aromatic compound or a compound with conjugated multiple bonds is the product of the reaction[154]:



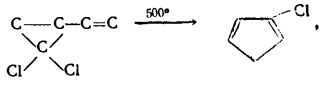
Chlorobenzene and β-chloronaphthalene are obtained in the same way from cyclopentadiene[159] and indene[156]. Monochlorocarbene, formed from methylene chloride and a lithium alkyl, gives pyridine on reaction with pyrrole[157]. Other dichlorocyclopropanes require more severe conditions for reactions of this kind. For example, the adduct of dichlorocarbene and dihydropyran is converted into chlorodihydrooxepin in boiling quinoline[158]:



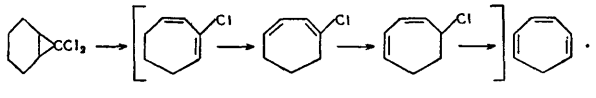
Pyrolysis of suitable adducts also gives dienes. Since chloroform, for example, is pyrolysed to dichlorocarbene[159], it is possible to obtain chlorobutadiene by the pyrolysis of chloroform in the presence of isobutene[160]:



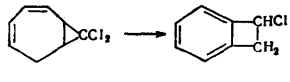
In a number of cases the pyrolysis of the adduct of an olefin and dichlorocarbene does not give the expected chlorodiene; for example, the adduct of butadiene is converted into chlorocyclopentadiene on pyrolysis[161]:



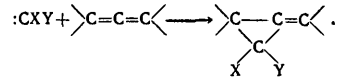
while 7,7-dichloronorcarane yields cycloheptatriene[29,162]:



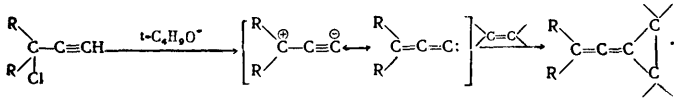
The pyrolysis of the adduct of cycloheptatriene results in the formation of chlorobenzocyclobutene[155] and not chlorocyclooctatetraene:



Comparatively recently alkylidenecyclopropanes were obtained by the addition of carbenes to allenes[163-165]:



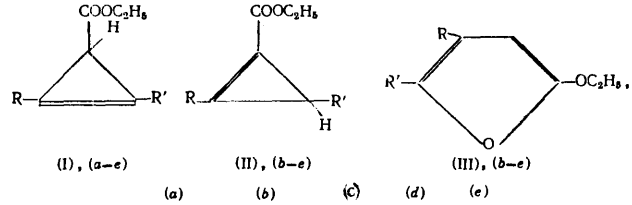
Hartzler established that αγ-elimination of the elements of hydrogen halide from a 3-halogenoalk-1-yne results in an intermediate compound of the carbene type which adds to olefins with the formation of alkenylidenecyclopropanes[83,85,166]:



As regards the addition of carbenes to double bonds other than carbon-carbon, for example the carbonyl group, we may mention the hypothesis of Knunyants *et al.*[1] concerning the possibility of the participation of carbenes in the Darzen reaction. The formation of epoxy-derivatives of alkenes from keto-derivatives of diazomethane probably occurs without the intermediate formation of the carbene[167]. The 1,3-dipolar cyclo-addition of suitable carbenes to the carbonyl groups of ketones has already been mentioned on page 73. Fields and Sandri[168] observed the addition of dichlorocarbene to the C=N double bond of *N*-benzylideneaniline.

### 3. Carbene Synthesis of Cyclopropene Derivatives

By allowing ethoxycarbonylcarbene to react with various acetylenic hydrocarbons, D'yakonov and coworkers[44,169,170] showed that, depending on the experimental conditions, the reaction can yield either two isomeric compounds or only one of them. Initially it was assumed that both isomers are esters of cyclopropenecarboxylic acids, (I) and (II), differing in the position of endocyclic double bonds. (I) forms in the high-temperature reaction without catalyst or in the presence of very small amounts of copper sulphate [in the latter case there is an admixture of (I)], and (II) forms in the low-temperature reaction in the presence of large amounts of copper sulphate[44,169,170]:



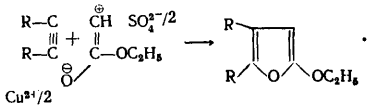
(I), (*a–e*) (II), (*b–e*) (III), (*b–e*)

| | (*a*) | (*b*) | (*c*) | (*d*) | (*e*) |
|---|---|---|---|---|---|
| R | $C_6H_5$ | $CH_3C_6H_4$ | $C_6H_5$ | $C_3H_7$ | $C_4H_9$ |
| R′ | $CH_3$ | $CH_3$ | $C_6H_5$ | $C_3H_7$ | $C_4H_9$. |

Later it was found that (I) also forms in the presence of copper as a catalyst.

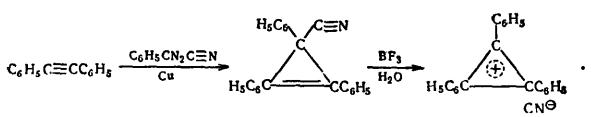
Breslow and Chipman[45] suggested that the properties of the compound hitherto assumed to be (II*c*) are more consistent with 5-ethoxy-2,3-diphenylfuran (III*c*). Similarly they suggested that the formulae (II*d*) and (II*e*) should be changed to (III*d*) and (III*e*) respectively. D'yakonov and coworkers made an additional investigation of the above compounds whose results[169] proved to be in complete agreement with the remarks of Breslow and Chipman.

The American workers explained the formation of 5-ethoxyfurans by 1,3-addition of ethoxycarbonylcarbenes to the triple bond, possibly as a complex with copper sulphate. There is also a possibility that the presence in the reaction medium of cupric and sulphate ions bearing opposite charges stabilises the 1,3-dipolar form of ethoxycarbonylcarbene, since in the absence of copper sulphate or the presence of metallic compounds which Breslow used[43], 1,1-adducts are formed:

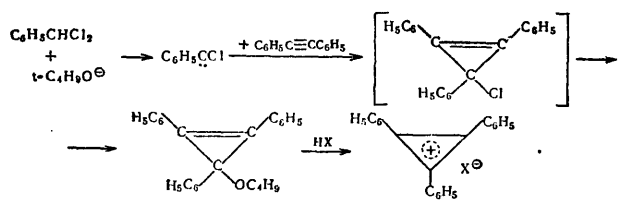


D'yakonov and coworkers succeeded in obtaining derivatives of dicyclobutane from the corresponding cyclopropene derivatives (Id) and (Ie) and the diazoacetate ester in the presence of copper[171].

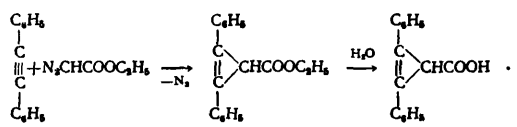
The cyclopropene derivative prepared by Breslow[172,173] from phenylcyanocarbene and tolane was used to form a new aromatic system — the *sym*-triphenylcyclopropenyl cation:



Breslow and coworkers[174,175] also obtained the same cation by the reaction of benzylidene chloride with potassium t-butoxide in the presence of diphenylacetylene, with subsequent acid treatment of the resulting cyclopropenyl ether:

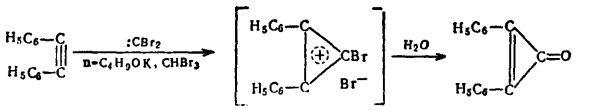


Breslow also carried out reactions between tolane and the diazomalonic ester and between tolane and the diazoacetic ester[176], with formation in the latter case of 1,2-diphenylcycloprop-1(2)-ene-3-carboxylic acid, identical with that synthesised by D'yakonov from the ester (Ic) (see p. 81):



Doering and Mole[135] carried out a photochemical reaction between diazomethane and but-2-yne which resulted in the formation of 1,2-dimethylcyclopro-1(2)-ene. Frey[177] attempted to obtain cyclopropene by the addition of methylene, produced by the photolysis of diazomethane, to acetylene in the gas phase, but only allene, methylacetylene, and a large amount of polymeric products were actually formed. When this reaction is carried out with acetylene labelled with deuterium, the final products are 1,3-dideuteropropyne and 1,1-dideuteropropadiene which suggest the formation of dideuterocyclopropene as an intermediate.

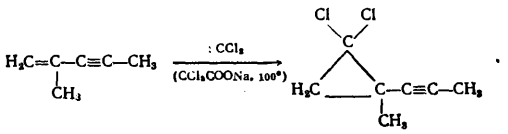
The addition of a dihalogenocarbene to a triple bond was first achieved by Vol'pin *et al.*[178,179] in the reaction between dibromocarbene and tolane:



Somewhat earlier Breslow *et al.*[180] obtained diphenylcyclopropenone from phenylchlorocarbene and the acetal of phenylketen. The authors explained the unusual properties of this ketone in terms of the concept of the cyclopropenyl cation as an aromatic species.

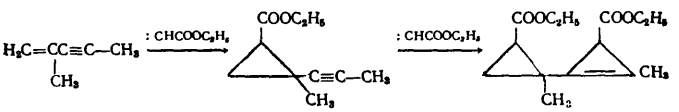
Dipropylcyclopropenone, which Breslow and Peterson[181] obtained from oct-4-yne and dichlorocarbene, proved to be even more stable.

D'yakonov and coworkers[182] showed that enyne hydrocarbons also react with carbenes:



It is reasonable that the electrophilic dichlorocarbene should add to the double bond since the latter is more nucleophilic than the triple bond. This corresponding diadduct could not be obtained. The authors explained this both by the weakening of the nucleophilic properties of the triple bond and the low reactivity of dichlorocarbene. Later Vo-quang and Cadiot[183], who studied the reactions of dichloro- and dibromo-carbenes with other enynes, confirmed that the reaction stops at the stage in which the dihalogenocarbene adds to the double bond of the enyne hydrocarbon.

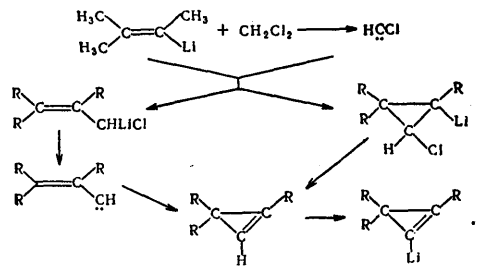
D'yakonov and Danilkina[184] studied the action of ethoxycarbonylcarbene, obtained by the decomposition of diazoacetic ester in the presence of copper or its sulphate, on 2-methylpent-1-en-3-yne. In this reaction the diadduct was obtained in addition to the monoadduct, and it was shown in a separate experiment[112] that the reaction proceeds in two stages as follows:



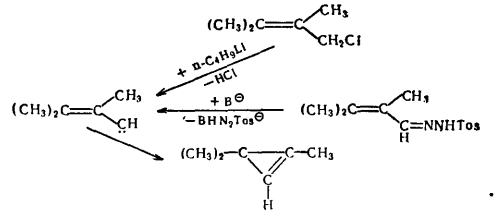
In this reaction ethoxycarbonylcarbene is more reactive and more selective than dichlorocarbene, which is consistent with the comparative characteristics of these reagents established by Skell and coworkers[140,185].

There exist two other possible ways of synthesising cyclopropenes from carbenes: (a) by the reaction between methylene chloride and lithium alkenyls[186] and (b) by intramolecular carbene–olefin addition using vinylcarbene. Let us consider the first of these reactions. In this case the monochlorocarbene formed initially can react with lithium alkenyls in two ways: (1) the carbene can add to the double bond of the lithium alkenyl with $\alpha\beta$-elimination of lithium chloride, and (2) the carbene can be substituted in the C–Li bond with subsequent $\alpha\alpha$-elimination of lithium chloride, resulting in vinylcarbene, which is then converted into cyclopropene by intramolecular addition. Since the

vinyl hydrogen in cyclopropenes is acidic[187], the product of the reaction is the lithium salt of the cyclopropene derivative. Under the given experimental conditions it can react further:

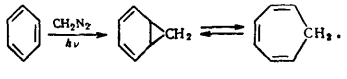


Like bromovinylcarbene, the above vinylcarbene can also be obtained by metal-substitution of mono- and di--halogeno derivatives of the allyl type[188] or from a tosylhydrazone[189] and then converted into cyclopropene:



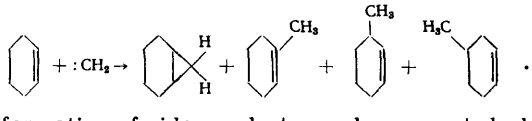
4. Ring Enlargement

The photochemical reaction of benzene with methylene resulting in the enlargement of the ring of the former has been known for a comparatively long time[190]; a mixture of cycloheptatriene and norcaradiene is formed. On heating, norcaradiene can be almost completely converted into cycloheptatriene. Nevertheless the problem of the relation between these two valence-tautomeric structures still cannot be regarded as resolved[191]:



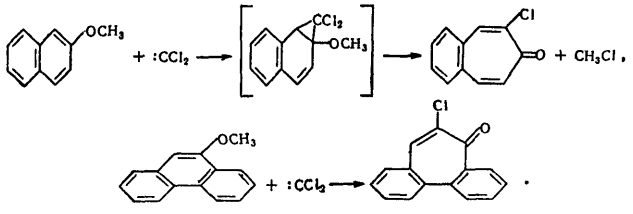
It is interesting that cycloheptatriene can be obtained by the reaction between benzene and diazomethane not only under the action of radiation but also in the presence of catalysts (cuprous chloride and bromide). According to Müller and Fricke[192], in the latter case benzene is subjected to electrophilic attack by the complex $\overset{+}{C}H_2CuBr_2$, formed from diazomethane and cuprous bromide.

A fairly large number of reactions of carbenes involving the enlargement of other rings are known. However, by no means all of them proceed equally smoothly. Kopecky and coworkers[6] established that the reaction between free methylene and cyclohexene yields a small amount of methylcyclohexene in addition to bicyclo[4,1,0]heptane (norcarane):

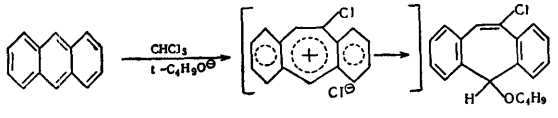


The formation of side-products can be prevented when methylene is produced by photolysis of diazomethane in solution using benzophenone as sensitiser, or by thermal–catalytic decomposition of diazomethane using powdered copper or iron dipivaloylmethide as catalysts.

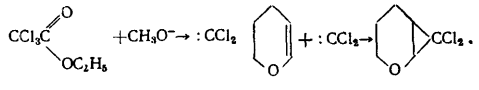
Generally speaking, aromatic double bonds combine with carbenes less readily than olefins. For example, dichlorocarbene does not react with benzene[193]. However, if the aromatic ring contains an electron-donor group, the addition is substantially facilitated. For example, the addition of dichlorocarbene, produced from ethyl trichloroacetate and sodium methoxide, to 1- and 2-methoxynaphthalenes and to 9-methoxyphenanthrene[194] results in the formation of the corresponding chlorotropones:



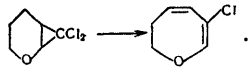
The hydrolysis of chlorotropone yields tropolone. Anthracene, in which certain positions have an enhanced electron density, reacts with dichlorocarbene and undergoes ring enlargement[195]:



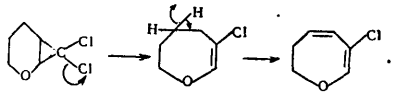
Dichlorocarbene, produced from ethyl trichloroacetate, was also used for the enlargement of certain heterocyclic rings. Thus when ethyl trichloroacetate is added to a mixture of dihydropyran and sodium methoxide in pentane, 7,7-dichloro-2-oxanorcarane is formed[158]:



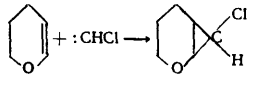
When it is heated with quinoline at 140–150° and a reduced pressure, 6-chloro-2,3-dihydrooxepin is obtained[158]:



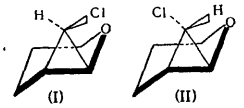
The conversion of 7,7-dichloro-2-oxanorcarane into 6-chloro-2,3-dihydrooxepin proceeds via the allyl carbonium ion, which then loses a proton:



Schweizer and Parham[158] found that chlorocarbene is also suitable for the enlargement of heterocyclic and aromatic rings. For example, when dihydropyran reacts with this carbene, a racemic mixture of the *endo*- and *exo*-forms of 7-chloro-2-oxanorcarane is obtained in 1 : 1.5 ratio:

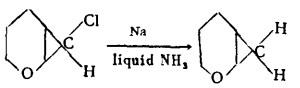


The above workers ascribed the structure (I) to the predominating isomer and structure (II) to the minor isomer, on the grounds that the formation of structure (II) in the activated complex is difficult due to the shielding of the ring by the large chlorine atom of chlorocarbene, whereas the influence of the small hydrogen atom is less marked and isomer (I) forms more rapidly.

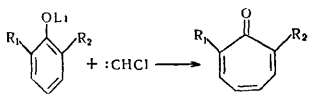


(I) (II)

Consequently isomer (I) is *exo*-7-chloro-2-oxanorcarane while isomer (II) is the *endo*-compound. Isomer (II) distils at atmospheric pressure, while the *exo*-compound decomposes even at 120° and when it is distilled with quinoline at a reduced pressure ring enlargement occurs and 2,3-dihydrooxepin is formed. The ease of conversion of isomer (I) into 2,3-dihydrooxepin is due to the influence of the *trans*-oxygen atom at the instant of the removal of the chlorine atom. Both isomers are readily reduced to 2-oxanorcarane, and in high yield, by sodium in liquid ammonia:

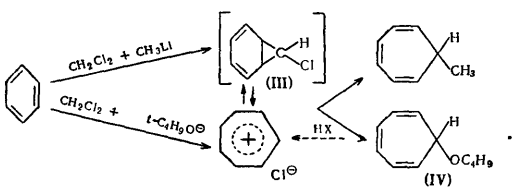



Chlorocarbene, obtained from methylene chloride and methyllithium, yields tropones on reaction with lithium phenoxides [39]:

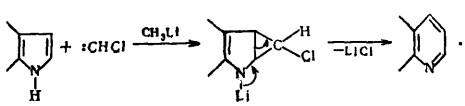



where $R_1$, $R_2$ = H (a), $R_1$ = H, $R_2$ = $CH_3$ (b), and $R_1$ = $R_2$ = = $(CH_3)_3C$ (c). The above synthesis of tropones is an example of the influence of electron-donor substituents on the reactivity of the benzene ring because chlorocarbene obtained in the above way reacts to only a slight extent with the benzene ring itself, the reaction involving, according to Closs and Closs [196], the initial formation of the hypothetical compound (III) which is subsequently converted into the tautomeric tropylium chloride; the latter then reacts with methyllithium to give 7-methylcyclohepta-1,3,5--triene.

When the reaction is carried out in the presence of a weak base, potassium t-butoxide [193], the ether (IV) is formed and subsequently yields the tropylium ion on interaction with acid:

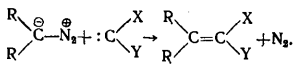



Addition of chlorocarbene to pyrrole and indole also results in the formation of ring-enlargement products, pyridine in 32% yield and quinoline in 13% yield respectively [157]:

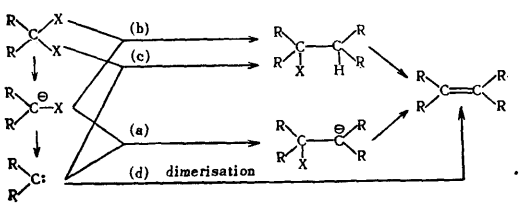



5. Carbene Syntheses of Olefins

As already pointed out (see p. 71), the phosphorus atom in triphenylphosphine, which has a free electron pair and is capable of passing to the pentavalent state, readily reacts with carbenes, yielding relatively stable alkylidenephosphoranes. The latter were obtained from dichloro-, difluoro-, and monochloro-carbenes [22,25,197,198]. When such alkylidenephosphoranes are introduced into the Wittig reaction, olefins which are otherwise difficult to obtain can be prepared. Such olefins can also be synthesised by another procedure also involving carbenes. When diazo--compounds are allowed to react with different carbenes, the latter attack the carbon atom of the diazo-compound marked with the minus sign, yielding olefins [95,199]:



A number of reactions are also known in which compounds of the type $R_1R_2CHX$ yield the olefins $R_1R_2C{=}CR_1R_2$ under the action of base. Since it is possible to visualise the participation in this reaction of three different types of species, the molecule $R_1R_2CHX$, the anion $R_1R_2XC^-$, and the carbene $R_1R_2C$, the olefin may form by several different pathways:



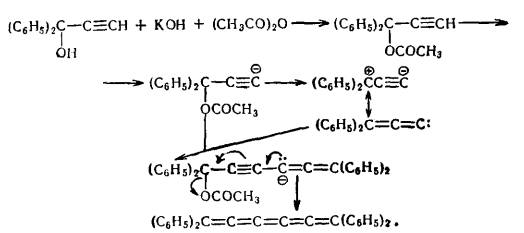

In view of the electrophilic properties of most carbenes, pathway (a), i.e. the interaction of the anion and carbene, is very probable. According to literature data, the following reactions proceed by this mechanism [80,200,201]:

$$p\text{-}NO_2C_6H_4CH_2\overset{\oplus}{S}(CH_3)_2 \rightarrow p\text{-}NO_2C_6H_4CH{=}CHC_6H_4\text{-}p\text{-}NO_2$$

(this reaction has already been mentioned on p. 75) and

$$(CH_3S)_3CH \rightarrow (CH_3S)_2C{=}C(SCH_3)_2.$$

As already pointed out in passing on p. 76, tetraphenylhexapentaene is also synthesised by this pathway:



Nucleophilic substitution of the anion in the molecule in pathway (b) should in the first place give ethane derivatives [202], which in fact have been isolated in a few cases but they could have been formed also by the substitution of the carbene in the C–H bond of the molecule by pathway (c).[1]

In recent years dimerisation of carbenes by pathway (d) has been put forward to account for the formation of olefins[203]:

$$p\text{-}NO_2C_6H_4CH_2Cl \rightarrow p\text{-}NO_2C_6H_4CH{=}CHC_6H_4\text{-}p\text{-}NO_2.$$

---o0o---

Carbenoids, the electronic analogues of carbenes, are fairly similar to the latter in chemical and certain physical properties. Although the key atoms in these compounds are not of carbon but of other elements, their most characteristic property, like that of carbenes, is the capacity to form two new covalent bonds in reactions. Fairly extensive data are at present available on the carbenoids, but their discussion is outside the scope of the present review.

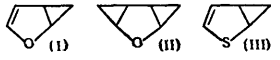
## ADDED IN PROOF

After our article had been sent to press, a number of interesting papers having direct relevance to the present review appeared, and we therefore felt bound to give at least a brief description of them. Thus we must mention a very thorough French review[204] as well as other review articles[205-207]. Of the experimental investigations, the work of Nefedov *et al.*[208], who proposed a new general method for the synthesis of carbenes, merits considerable attention. This method can be schematically represented as follows:

$$RR'CXX' \xrightarrow[\text{tetrahydrofuran}]{Li} RR'CLiX' \xrightarrow{-LiX'} RR'C:$$

where X and X′ are halogens and R and R′ are hydrogen, halogens, and aryl, alkyl, or alkylidene groups.

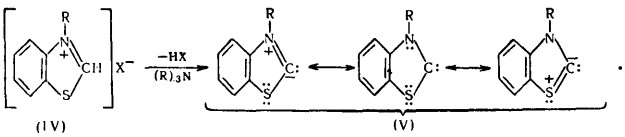
Among the latest spectroscopic studies of carbenes, that of Trozzolo *et al.*[209], who investigated *p*-phenylenebis-(phenylmethylene), is interesting. Another interesting paper is that of Russell and Hendry[210], who studied the effect of solvents on the reactions of methylene. The reaction of methylene radicals with acetylene in the gas phase has been investigated by Terao *et al.*[211] Müller *et al.*[212] discovered a reaction in which five-membered aromatic compounds are converted into their homologues by means of diazomethane. Using this reaction, compounds (I), (II), and (III) were obtained from furan and thiophen:




A number of papers have dealt also with the reactions of dihalogenocarbenes. Thus Skattebŏl[213] has continued the study of the reaction mentioned on p. 80. Certain olefins are known to be very inert towards dihalogenocarbenes prepared by the usual methods. For the preparation of *gem*-dihalogenocyclopropane from such olefins, Seyferth *et al.*[214] proposed a procedure involving the use of organomercury compounds: $C_6H_5HgCCl_2Br$, $C_6H_5HgCClBr_2$, and $C_6H_5HgCBr_3$. Landgrebe and Mathis[215] studied several examples of the substitution of dichlorocarbene in the carbon–mercury bond and also the thermal decomposition of compounds obtained in this way. The work of Ohno[216] dealing with the reaction of enamines with dichlorocarbenes is also interesting.

A paper has been published on the reaction of dichlorocarbene with benzofuran and benzothiophen[217]. Krapcho and Huyffer[218] described the thermal decarboxylation of sodium trichloroacetate in the presence of activated carbon and halogeno-compounds.

Kirmse[219,220] recently published two papers on alkylchlorocarbenes. Other communications deal with alkyl-, aryl-, and alkylidene-carbenes[221-224], allylcarbenes[225], and also with the rearrangements of carbenes obtained by the decomposition of 2,2,2-triaryldiazoethanes[226]. Several papers describe the reactions of ethoxycarbonylcarbene[227-229]. We may also mention that Schöllkopf and Küppers[230] obtained a number of phenylselenocyclopropanes starting with phenylselenocarbene and various olefins. In a quite recent paper Wanzlick and Kleiner[231] state that their attempts to find carbenes with "quasi-aromatic resonance stabilisation" have been successful. When *N*-alkylbenzothiazolium halides (IV) are treated with tertiary amines, the former lose the elements of hydrogen halide yielding substances which can be represented by the resonance hybrids (V):




(IV) (V)

The carbene (V) dimerises and also participates in a number of other chemical reactions.


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# PERCHLORIC ACID AND ITS COMPOUNDS IN ORGANIC SYNTHESIS

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## I. INTRODUCTION

In recent years acid catalysts, among which perchloric acid and its compounds occupy an important place, have been attracting increasing attention. During the past 10–15 years more than 300 papers and patents have appeared, dealing with the use of $HClO_4$ and its compounds in organic chemistry.

Perchloric acid is the strongest mineral acid but at ordinary temperatures its oxidising power is less than that of the other oxygen acids of chlorine, bromine, and iodine[1]. In many organic solvents perchloric acid is readily solvated and this changes the polarity of the bond between the hydrogen atom and the $ClO_4$ residue. In polar organic solvents (acetic acid[2-4], nitromethane[5], nitrobenzene[6], etc.) perchloric acid is ionised to a greater degree than other acids. Comparison of the ionisation constants of mineral acids in anhydrous acetic acid confirms that perchloric acid ($K = 1.6 \times 10^{-4}$) is tens or hundreds of times stronger than hydrobromic ($K = 4 \times 10^{-5}$), sulphuric ($K = 6 \times 10^{-7}$), hydrochloric ($K = 1.4 \times 10^{-7}$), nitric ($K = 4.2 \times 10^{-8}$), and trichloracetic ($K = 2.3 \times 10^{-10}$) acids.

For many years the wide use of perchloric acid in organic synthesis has been hindered by greatly exaggerated ideas about the danger of explosions. However, although work with the anhydrous acid is in fact not without danger, the use of an aqueous solution (30, 60, and 72%) involves practically no risk. Solutions of the anhydrous acid in acetic acid or acetic anhydride containing less than 55% of $HClO_4$ by volume, which are frequently used, are also quite safe[8].

Much experimental data on the use of perchloric acid and its compounds in various fields of organic chemistry has accumulated. This work requires to be correlated and systematised since the published reviews dealing with only parts of the problem are already out of date[8-10].

## II. PERCHLORATES OF ORGANIC COMPOUNDS

The study of organic perchlorates started in the 19th century when crystalline perchlorates of alkaloids were obtained[11]. Later it was found that perchloric acid readily forms perchlorates with ethers, ketones, weakly basic compounds containing nitrogen, and pyridine; this property is used successfully in the purification and identification of many basic organic compounds[12-15]. Organic perchlorates are usually obtained by treating solutions of organic compounds in polar or non-polar solvents (water, alcohols, ether, nitromethane, etc.) with perchloric acid in the cold[16-18].

In their structure the esters of perchloric acid are superficially similar to salts, the metal being replaced by a hydrocarbon radical. The bond between the perchlorate ion and the hydrocarbon radical is covalent or nearly ionic, depending on the degree of polarisation. Nearly all these compounds are unstable and only some of them can be obtained in the pure state. Among the various methods of

synthesising perchloric esters the most widely applicable method is based on the reaction of alkyl halides with silver perchlorate[19-22]:

$$RX + AgClO_4 \rightarrow RClO_4 + AgX.$$

The esters may also be obtained by the interaction of the alcohol with chlorine heptoxide or by the action of diazomethane on aqueous $HClO_4$:[23]

$$ROH + Cl_2O_7 \rightarrow RClO_4 + HClO_4,$$
$$CH_2N_2 + HClO_4 \rightarrow CH_3ClO_4 + N_2.$$

The esters of perchloric acid are widely used as alkylating agents. They are colourless low-boiling oils, miscible with alcohol and insoluble in water, which slowly hydrolyses them[24].

The introduction of aryl residues into the perchlorate molecule has a considerable polarising effect on the C–O ester bond. As the number of aryl groups in an aralkyl perchlorate molecule increases, the C–O bond approaches the ionic type. Aralkyl perchlorates are obtained by the methods used for the preparation of esters.

However, when 72% perchloric acid acts on diphenylmethylmethanol in nitromethane, a mixture of diphenylmethyl ether, diphenylmethane, and benzophenone is obtained instead of the expected diphenylmethyl perchlorate[25].

In the reaction of diphenylmethyl chloride with silver perchlorate in benzene solution diphenylmethyl perchlorate, which has considerable alkylating power, was obtained[26].

Benzyl perchlorate is also highly reactive but this could not be obtained pure, because it rapidly polymerised at the moment of formation[27-30].

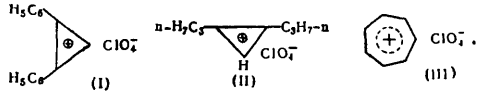
The most interesting of the aralkyl perchlorates are the triarylmethyl perchlorates, as these can be used in hydride displacement reactions.

Experimental data on electrical conductivity[31-33] and absorption spectra[34,35] indicate that the triarylmethyl perchlorates are typical carbonium salts. They are conveniently obtained by the addition of 70% $HClO_4$ to a solution of triarylmethanol in acetic anhydride at room temperature or by the exchange reaction of triarylalkyl chlorides with $AgClO_4$ in a polar solvent[36,37].

Interesting organosilicon perchlorates have been recently obtained by slowly mixing benzene solutions of trialkyl- or triaryl-silicon chloride and silver perchlorate in a stream of dry nitrogen[38,39]. The trialkylsilicon perchlorates ($Alk_3SiClO_4$) were isolated as colourless liquids fuming in air and exploding at 180–200°; they can be distilled under vacuum without decomposition. The triarylsilicon perchlorates are crystalline compounds insoluble in benzene; they evidently have an ionic structure, which was confirmed by a study of their infrared spectra and chemical properties. Recently the synthesis of new heteroorganic perchlorates, $Alk_3\overset{+}{S}ClO_4^-$ and $(CH_3)_3\overset{+}{S}nClO_4^-$, has been reported; they were obtained in the crystalline state[40,41]. Compounds of the first type are easily obtained by the action of perchloric acid on a mixture of thioether and the corresponding alcohol.

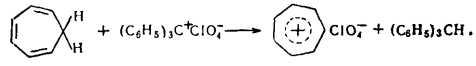
Among diverse carbonium salts[42,43] a special place is occupied by aromatic cations, of which the cyclopropenyl cation is the simplest representative; this cation has the properties of an aromatic system. However, salts of the unsubstituted cyclopropenyl cation are still unknown.

In the reaction of 1,2-diphenylcyclopropene-3-carboxylic acid with 10% $HClO_4$ in acetic anhydride a 70% yield of diphenylcyclopropenyl perchlorate (I) was obtained[44]:



The entirely stable dipropylcyclopropenyl cation (II) has been obtained by this method, acetyl perchlorate in acetic anhydride acting on dipropylcyclopropenecarboxylic acid[45]; this shows that the hypothesis that phenyl groups are required to stabilise the cyclopropenyl cation is untenable.

The properties of cyclopropenyl perchlorates are in many ways similar to the properties of tropylium salts (III). Tropylium perchlorate is easily obtained by the action of triphenylmethyl perchlorate, which is an effective hydride ion acceptor, on cycloheptatriene[46]:



The same method has been used to synthesise some homologues of tropylium salts and vinyltropylium perchlorate[47,48].

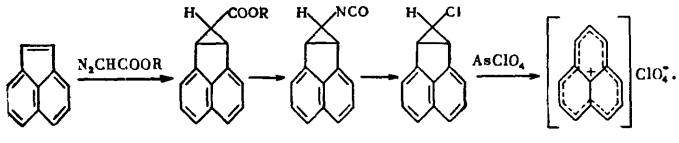
Tropylium perchlorate is also obtained in high yield from cycloheptatriene, phosphorus pentachloride, and 50% perchloric acid in dry carbon tetrachloride solution by the method of Kursanov and Vol'pin[49,50].

A British patent indicates the possibility of preparing tropylium perchlorate by the acid oxidation with perchloric acid of cycloheptatriene with no more than one substituent at the methylene group[51].

A report on the preparation of tropylium perchlorate by the autoxidation of cycloheptatriene in acetic acid solution in the presence of perchloric acid is noteworthy[52].

The reaction in which fundamental groups R are eliminated from 1-substituted cyclohepta-2,4,6-trienes $C_7H_7R$ (R = COOH, COCl, CN) has been studied with the object of preparing tropylium salts[53]. Tropylium perchlorate was obtained by the action on the latter of silver perchlorate in nitromethane.

Among the various polycyclic systems the perinaphthenyl system has attracted attention; this can exist as a cation, anion, or free radical. The perinaphthenyl cation was obtained[54,55] as the perchlorate from acenaphthylene and diazoacetic ester by the method developed for the synthesis of tropylium salts[53]:

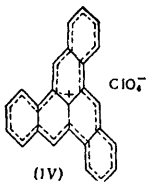


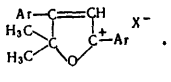
Theoretically it is possible to obtain perinaphthenyl perchlorate by the reaction of silver perchlorate with the perinaphthenyl radical[56]:

$$C_{13}H_9 + AgClO_4 \rightarrow C_{13}H_9^+ ClO_4^- + Ag.$$

The perinaphthenyl cation is more stable than the triarylmethyl cation but less stable than the tropylium cation. Perinaphthenyl perchlorate is insoluble in non-polar solvents but soluble in strong acids; it is readily hydrolysed

and is unstable in air. Tribenzoperinaphthenyl perchlorate (IV) has similar properties[57]:


(IV)


(V)

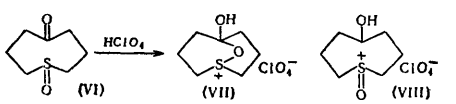
A very interesting synthesis is that of 4,6,8-trimethylazulenium perchlorate, obtained by boiling 4,6,8-trimethylazulene with an excess of 70% $HClO_4$ in acetic acid for a short time[58]. The crystalline perchlorate melts with decomposition at 168–171°; it is stable in air but is decomposed by water.

Kirby and Reid have shown that substituents in positions 4 and 8 are necessary for the formation of azulenium perchlorate.

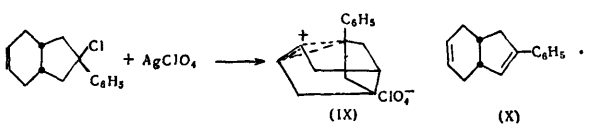
Dihydrofurylium perchlorate is obtained in almost quantitative yield by the action of an ethereal solution of $HClO_4$ on hydroxydihydrofuran[59]. The product (V) is a yellow compound, insoluble in ether and benzene and slightly soluble in alcohol. A resemblance between dihydrofurylium salts and salts of benzopyrylium, xanthylium, and chromylium has been noted.

The stable 4,5,5-trimethyl-2-phenyldihydrofurylium perchlorate has been prepared[60]; 2,2,3,5-tetramethyl-5-phenyl-2,5-dihydrofuran is obtained by the action of methylmagnesium iodide on this perchlorate. The reactivity of 4-methyldihydrofurylium salts has been studied[61].

The perchlorate of 1-oxo-1-thiacyclooctan-5-one (VI) has been prepared[62,63]; this may have structure (VII) or (VIII).


(VI) (VII) (VIII)

Leal and Pettit obtained a characteristic stable non-classical carbonium ion by the following reaction[64]:


(IX) (X)

Compound (IX) is a yellow saltlike product, insoluble in hexane, chloroform, carbon tetrachloride, and benzene. With water or alcohol it forms the diene (X).

## III. ELECTROPHILIC SUBSTITUTION REACTIONS

### 1. Perchlorylation of Organic Compounds

The electrophilic substitution reaction, which is widely used in organic chemistry, proceeds readily when halogens or mineral acids act on compounds of the aromatic series. However, the introduction of the $ClO_3$ residue into organic compounds by the action of perchloric acid on aromatic compounds is not possible. A direct method of perchlorylation of organic compounds was not developed until 1958.[65,66] Perchloryl compounds of the aromatic series are easily formed by the action of $FClO_3$ in the presence of $AlCl_3$ or $AlBr_3$ on benzene and other aromatic hydrocarbons containing no electron-acceptor groups:

$$ArH + FClO_3 \xrightarrow{AlCl_3} ArClO_3 + HF.$$

The spectra[65] and chemical properties of the perchloryl compounds confirm that they have the $ArClO_3$ and not the ester structure $ArOClO_2$.[65-68].

Perchlorylation in the *para*-position also proceeds smoothly with anisole[65] and with fluoro-,[65] chloro-,[67] and bromo-benzene[67]. The perchlorylarenes are stable liquids or solid compounds; some of them can be distilled without decomposition. They are entirely stable in neutral and acid media, but are hydrolysed to phenols by concentrated alkali solutions. The perchloryl compounds are detonated by a sharp blow or when the temperature is raised; they decompose explosively. When perchlorylbenzene is hydrogenated by hydrogen in alcoholic solution, the perchloryl group is smoothly eliminated and benzene is formed[68]. Perchlorylbenzene is nitrated in the *meta*-position and its nitro-compound can be reduced to the amine[65]. It is also possible to reduce *m*-nitroperchlorylbenzene completely; the reaction proceeds with the absorption of 7 moles of hydrogen and the elimination of the perchloryl group[68].

The action of nucleophilic reagents on perchloryl compounds has been studied and it has been shown that although perchlorylbenzene does not react with metallic lithium or magnesium, it does react vigorously even at -33° with $NaNH_2$ and $ArNH_2$ in liquid ammonia with the formation of triphenylamine[67]. The formation of dehydrobenzene from perchlorylarenes is confirmed by study of the elimination of the perchloryl group which proceeds readily to the extent of 87% under the action of the $NH_2^-$ anion in liquid ammonia.

Measurement of the dipole moment of $FClO_3$ has shown that, although the molecule is electrically neutral, the $ClO_3$ group is the electropositive end of a dipole and the fluorine atom is the electronegative end[69]. Therefore, in the presence of Brønsted or Lewis acids (as occurs in the perchlorylation reaction) the organic compound will be attacked by the electrophilic cation $ClO_3^+$. In contrast, in an alkaline medium, because of an inductomeric shift, $FClO_3$ may act as an effective fluorinating agent with electropositive fluorine. Thus, when $FClO_3$ acts on 1-ethoxycyclohexene in pyridine at 0°, 2-fluorocyclohexanol is formed. Compounds with an active methylene group (acetylacetone, diethyl malonate, etc.) are smoothly fluorinated by perchloryl fluoride[70,71].

Perchloric acid and its derivatives may be used in the halogenation[72-76], nitration[77-79], nitrosation[80,81], and diazotization[82-85] of organic compounds.

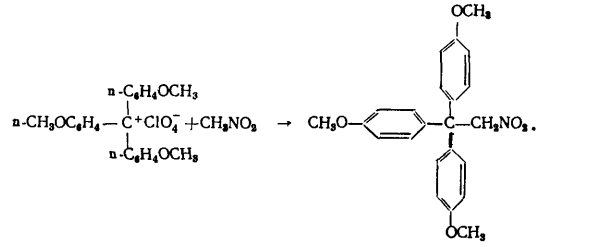
### 2. Alkylation

Alkyl perchlorates may be used as alkylating agents. Thus, methyl perchlorate, obtained from methyl iodide and silver perchlorate, slowly reacts with anisole at ordinary temperatures to give *p*-methylanisole[86,87]. Methyl perchlorate reacts much less rapidly with benzene. Ethyl, propyl, and n-butyl perchlorates have similar properties.

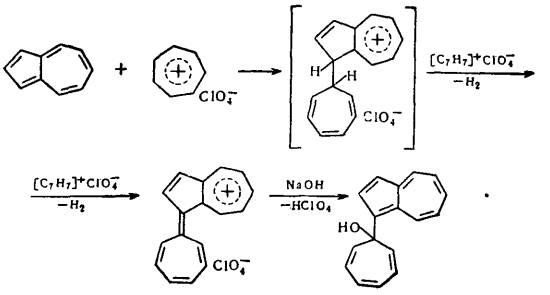
It is interesting that isobutyl perchlorate isomerises to t-butyl perchlorate, and when anisole and benzene are alkylated with isobutyl iodide and $AgClO_4$, t-butylanisole

(76%) and t-butylbenzene are obtained. There are data on the alkylation of toluene by cyclohexyl perchlorate[88,89].

Aralkyl perchlorates are very reactive. Benzyl perchlorate, prepared in solution of the compound to be alkylated, smoothly reacts with benzene and toluene forming diphenylmethane and *p*-methyldiphenylmethane in good yield[86]. Diphenylmethyl perchlorate readily combines with benzene to give triphenylmethane (65%) in two hours at room temperature[26]. When trityl perchlorate ($Tr^+ClO_4^-$) acts on a mixture of phenol and aniline, *p*-aminotetraphenylmethane is obtained in 78–84% yield[90]. At room temperature $Tr^+ClO_4^-$ converts anisole into *p*-methoxytetraphenylmethane in 63% yield; the same product is obtained from anisole and triphenylmethanol in the presence of 72% $HClO_4$ in nitromethane. Hydroxytetraphenylmethane was obtained from $Tr^+ClO_4^-$ and phenol in nitromethane at room temperature in yields of 23% (8 hours) and 68% (7 days). It is interesting that, when heated with 72% $HClO_4$ in nitromethane for 7 days, tri-*p*-methoxyphenylmethanol forms 1,1,1-tri-*p*-methoxyphenylnitroethane in good yield[26]:



Azulene and triphenylmethyl perchlorate in boiling acetic acid form a mixture of 1-triphenylmethyl- and 1,3-bis(triphenylmethyl)-azulene[91]. The reaction of azulene and its methyl homologues with tropylium perchlorate in dimethylformamide has been studied[81]; it proceeds according to the following scheme:



When unsubstituted azulene is alkylated under the conditions mentioned, a 1,3-dicycloheptatrienyl derivative of azulene is formed.

When an attempt was made to alkylate benzene and anisole with allyl perchlorate, obtained from allyl chloride and silver perchlorate, only resinous products were obtained[29].

Perchloric acid can be used for the alkylation of phenol by different alcohols[25,92-94]. When phenol is alkylated with t-butyl alcohol in 50% perchloric acid, 4-t-butylphenol and 2,4-di-t-butylphenol are formed[92].

Diphenylmethanol, phenol, and 72% $HClO_4$ give 63% of *p*-hydroxytriphenylmethane or 86% of 2,4,6-tris(diphenylmethyl)phenol, depending on the molecular proportions employed[25,26]. Similarly anisole forms *p*-methoxytriphenylmethane (89%), which is further converted to 2,4-bis-(diphenylmethyl)anisole (93%). Trisubstituted anisole could not be isolated. In the presence of perchloric acid hydroxymethyldimethylamine reacts with azulene to form mono- and bis-(dimethylaminomethyl) derivatives[95].

The patent literature contains references to the use of perchloric acid[96] and its salts[97,98] in the alkylation of phenols by olefins. In the presence of crystalline aluminium or iron perchlorate or aqueous lead perchlorate, *o*-cresol reacts with dodecene to give 4-s-dodecyl-*o*-cresol in excellent yield; similarly octene and aluminium perchlorate gives 4-s-octyl-*o*-cresol[98]. Phenylethylphenols (*o*- and *p*-) have been obtained by allowing styrene and perchloric acid in acetic acid to react with phenol[99].

The interaction of β-acetoxyethylmercury acetate with anisole to form β-(*p*-anisyl)ethylmercury acetate is an interesting case of alkylation[100].

Recently a method of alkylating phenols with ketones using small amounts of perchloric acid has been developed[101,102], and it has been shown that when benzyl phenyl ethers are treated with acetic anhydride and perchloric acid they are smoothly debenzylated[29,103].

### 3. *C*-Acylation

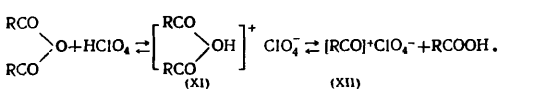
There are a number of serious disadvantages in the use of the usual catalysts such as $AlCl_3$, $ZnCl_2$, HF, etc. in acylation. It is sufficient to mention that the acylation of many organic compounds in the presence of these catalysts is associated with great difficulties arising from resinification of the starting materials, their isomerisation, degradation, and polymerisation. Extremely large amounts of catalyst are required. There are also difficulties in separating the products from the catalysts. Some of these difficulties can be overcome by the use of perchloric acid and its compounds as catalysts.

In 1927 Diels and Alder published the first account of the use of perchloric acid in the acylation of toluene and *o*-xylene by hot acetic anhydride[104].

In 1944 Berlin, who was studying the *N*-acylation of amines difficult to acylate, found that, when pyrrole is heated with acetic anhydride in the presence of catalytic quantities of 30% perchloric acid, a mixture of 1- and 2--acetylpyrroles is formed; he suggested that 2-acetylpyrrole (yield 33%) is a product of the thermal isomerisation of 1-acetylpyrrole[105].

In 1950 Burton and Praill commenced extensive studies of the catalytic properties of 72% perchloric acid, and showed that reactive aromatic compounds (*m*-xylene and anisole) could by acylated by carboxylic acid anhydrides in the presence of half-molar quantities of this catalyst[106-109]. In the same year Foster obtained a patent for the catalytic acylation of aromatic compounds in the presence of perchloric acid[110]. Aqueous (usually 60–72%) perchloric acid is generally employed in acylation.

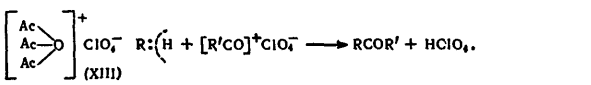
Perchloric acid reacts with acid anhydrides evidently forming an oxonium ion (XI) which dissociates in solution to form an electrophilic acylium carbonium ion (XII) and a carboxylic acid[106]:



The existence of the triacetyloxonium cation (XIII), obtained from acetyl perchlorate and acetic anhydride, has also been

suggested[111]. The possibility that these ions exist has been confirmed by electrical conductivity measurements of solutions of perchloric acid in acetic anhydride[111,112] and also by kinetic studies[112-114].

Acylium carbonium ions (XII) are effective acylating agents and are therefore used for the acylation of reactive compounds of aromatic character[106-109,115,116].



(XIII)

Acyl perchlorates of various structures are also easily obtained by the reaction of equimolar quantities of acid chlorides with silver perchlorate in solution in nitromethane, absolute ether, or acetonitrile[107-109]:

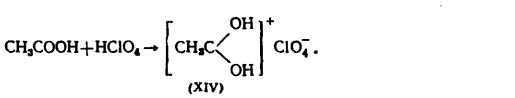
$$RCOCl + AgClO_4 \rightarrow [RCO]^+ClO_4^- + AgCl.$$

"Pure" acyl perchlorates obtained in this way are more effective acylating agents than those formed from acid anhydrides and perchloric acid[107], since in the latter case the acylating reagent consists of a mixture of carbonium (XII) and oxonium (XI) ions.

When a solution of perchloric acid in acetic anhydride is allowed to stand for a long time, or when freshly prepared acetyl perchlorate is added to acetic anhydride even at 20°, self-acylation occurs, probably in the following way[13]:

$$(CH_3CO)_2O + CH_3CO^+ \rightarrow CH_3COCH_2CO^+ + CH_3COOH.$$

At room temperature perchloric acid reacts with acetic acid to form an acidium complex (XIV) with no *C*-acylating properties[106,116]. This explains the negative results obtained in attempts to acylate a number of aromatic compounds by carboxylic acids in the presence of perchloric acid[116]. However, when a dehydrating agent is added to the complex, it is converted to the acylium cation (XII)[107]:



(XIV)

Since perchloric acid is eliminated in the acylation of organic compounds by acyl perchlorates, the reaction is advantageously carried out with a slight excess of the acid anhydride and very small catalytic quantities of $HClO_4$.[115,116]

Dorofeenko and coworkers made a detailed study of the acylation of a series of reactive aromatic and heterocyclic compounds with carboxylic acid anhydrides in the presence of catalytic quantities of perchloric acid (0.001–0.05 mole of catalyst per mole of compound) and they substantially extended the field of application of this catalyst in the acylation of various organic compounds[115,116,117-127].

When aromatic hydrocarbons are acylated with pure acetyl perchlorate[109,128,129], or with acetic anhydride in the presence of perchloric acid[116,117], the corresponding aliphatic-aromatic ketones are obtained in low yield. Benzene forms only traces of acetophenone[109,116,129], but the yield of substituted alkyl aryl ketones increases considerably as the number of alkyl groups in the benzene nucleus increases[117]. Thus, for example, in the acylation of toluene *p*-methylacetophenone is formed in 5–6% yield[109,116,129], while under the same conditions the yield of ketone from *m*-xylene reaches 22–30%[109,119,128] and the yield of the ketone from mesitylene reaches 45%.[17,119] Naphthalene is also acylated by acetic anhydride, but the yield of α-acetylnaphthalene does not exceed 10–15%.[119]

A slight increase in the nucleophilic properties of the aromatic compounds materially increases the yield of ketone. Good results have been obtained in the acylation of acenaphthene with acid anhydrides in the presence of catalytic quantities of perchloric acid or Anhydrone; the yield of 5-substituted acylacenaphthenes was 50–81%.[119-121] It is interesting that acylation by this method gives mainly ketones substituted in the 5-position; acylation in the presence of aluminium chloride[130] or hydrogen fluoride[131] leads to the formation of a mixture of isomeric ketones.

Cauquil and coworkers found that silver perchlorate is also a good catalyst in the acetylation or aromatic hydrocarbons by acetic anhydride[132,133]. However, this expensive and very light-sensitive compound has no advantages over perchloric acid.

Magnesium perchlorate (Anhydrone)[134,135] and other aprotic or proton-containing derivatives of perchloric acid of the type of inorganic and organic salts, and also aralkyl perchlorates[119], were found to be good catalysts in the acylation of reactive aromatic and heterocyclic compounds by acid anhydrides. In this series of compounds the greatest catalytic activity was shown by magnesium perchlorate, benzyl perchlorate, and triphenylmethyl perchlorate[119].

Magnesium perchlorate has a milder catalytic action than perchloric acid and for this reason its use is preferred in the acylation of acid-labile compounds[134,135]. It may be supposed that the acylating agents in this reaction are acyl perchlorates (XII), i.e. this process proceeds in principle in the same way as the reaction catalysed by perchloric acid.

Detailed studies of the acetylation of anisole by acetic anhydride in the presence of perchloric acid enabled a convenient preparative method to be worked out for the preparation of *p*-methoxyacetophenone in 60–72% yield[106,107,116]. The use of pure acetyl perchlorate in this case has no advantages over the procedure described above[107].

The acetylation of anisole and phenetole in the presence of catalytic quantities of Anydrone gives the same yield (60–66%) as when perchloric acid is employed, but purer ketones are formed[134-136].

Kuhn and Daxner, using the method of Burton and Praill for the acylation of phenyl ethers with the anhydrides of acetic, propionic, and n-butyric acids in solution in the corresponding acid, obtained alkoxyacetophenones in good yield[137].

When anisole and phenetole are acylated with carboxylic acid anhydrides (propionic, n- and iso-butyric, n- and iso-pentanoic, and hexanoic) in the presence of small quantities of perchloric acid, the corresponding *p*-alkoxyphenyl alkyl ketones are obtained in 70–90% yield[138].

Aromatic hydrocarbons (*m*-xylene, mesitylene), phenol ethers (anisole and phenetole), and some heterocyclic compounds (thiophen) may be successfully acylated by carboxylic acid chlorides in the presence of small quantities of perchloric acid or Anhydrone[118,122,125]. However in acylation with aliphatic acid chlorides (from acetic to hexanoic) the yield of the corresponding ketones is as a rule much lower (20–55%) than when acid anhydrides are used. Good

results were also obtained with other acylating agents; mixed anhydrides, silicon anhydrides† and boron anhydrides† of the acids were used[119].

Investigation of the benzoylation of a series of aromatic hydrocarbons and phenol ethers with benzoyl chloride in the presence of small quantities of perchloric acid or Anhydrone enabled a convenient preparative procedure to be developed for the synthesis of *p*-alkyl- and *p*-alkoxy-substituted benzophenones[125,127].

Good results have been obtained in the benzoylation of anisole and thiophen with benzoic anhydride in the presence of catalytic quantities of perchloric acid[139].

The benzoylation of anisole with aromatic acid chlorides (benzoyl, 2,4,6-trimethylbenzoyl, *p*-nitrobenzoyl, and anisoyl) in the presence of equimolar amounts of silver perchlorate in nitromethane solution has been studied; *p*-methoxybenzophenone and its derivatives were obtained in 50–84% yield[108]. Benzoylation of anisole with benzoic anhydride in nitromethane solution gives a lower (27%) yield.

When toluene and anisole are acylated with aralkylcarboxylic acid perchlorates of the type $[C_6H_5(CH_2)_nCO]^+ClO_4^-$ ($n$ = 1–4) [obtained from $C_6H_5(CH_2)_nCOCl$ and $AgClO_4$ in nitromethane solution], ketones of the general formula $C_6H_5(CH_2)_nCOC_6H_4R$ are obtained in good yield[140]. *p*-Allyloxyacetophenone was obtained in 32% yield from allyl phenyl ether[29].

When ethers of mono- and poly-hydric phenols are acylated with a complex acylating agent consisting of molar quantities of acetyl chloride, acetic anhydride, and sodium perchlorate in glacial acetic acid, the corresponding alkoxy-substituted ketones are obtained in 30–50% yield[141]. However, these and other similar ketones are obtained in a higher yield (40–65%) in the acylation of phenol ethers with acetic anhydride in the presence of catalytic quantities of 60% perchloric acid[117].

Acylation of anisole and xylenes with tosyl perchlorate (from $p$-$CH_3C_6H_4SO_2Cl$ and $AgClO_4$ in nitromethane) led to the formation of substituted *p*-tolylphenylsulphones[142].

As already mentioned, in the acylation of phenols *O*-acyl derivatives are obtained in good yield, but hydroxyketones are not formed[106,116,135]. Under the same conditions aromatic amines undergo *N*-acylation[105]; acetylation of dimethylaniline in the presence of Anhydrone gave *p*-dimethylaminoacetophenone[135].

The acylation of azulene and its derivatives with acid anhydrides in the presence of perchloric acid has recently been studied[143].

Good results have been obtained by the acylation of various heterocylic compounds by this method[115,116,122,124,126,134–136,139]. Magnesium perchlorate is more convenient than perchloric acid as a catalyst in the acylation of heterocyclic compounds, because it does not destroy heterocyclic compounds and for this reason only quite small amounts of resinous products and by-products are obtained. Furan and $\alpha$-methylfuran are easily acylated in the presence of traces of perchloric acid or Anhydrone to form 2-acetylfuran, 5-acetyl-2-methyl furan, and other furyl $\alpha$-alkyl ketones in yields of 68–75%.[116,121,126,135,139]. When 2-halogenofurans were acetylated by this method, 5-acetyl-2-halogenofurans were obtained in 85–90% yield[144]. Acylation of thiophen with acid anhydrides proceeds with the same high yield (92–95%) as in the presence of stannic chloride[145], but the method of preparing ketones with perchloric acid is simpler and more convenient[116,126,135,138]. Thiophen is also easily acylated by aliphatic acid chlorides in the presence of Anhydrone to give thienyl $\alpha$-alkyl ketones in 55–65% yield[125].

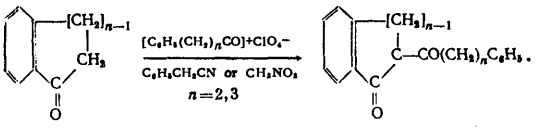
In the acylation of pyrrole by carboxylic acid anhydrides (from acetic to hexanoic) in the presence of small quantities of $HClO_4$ or $Mg(ClO_4)_2$ alkyl 2-pyrrolyl ketones are formed in 35–55% yield[124]. Even when pyrrole is acylated in the cold, 2-acylpyrrole, which is easily separated after neutralisation of the reaction mixture, is the main product; in the majority of experiments, 1-acylpyrroles have not been found in significant quantities. These results indicate that the conclusion of Berlin on the primary *N*-acylation of pyrrole is erroneous[105].

In the same way, in the acetylation or propionylation of pyrrole derivatives(1-methylpyrrole, 1-phenylpyrrole, and 2,4-dimethylpyrrole) substituted 2-acylpyrroles are obtained in high yield (50–72%)[124]. Indole is also easily acetylated in the presence of perchloric acid[116] or Anhydrone[134] to give 3-acetylindole in 32–50% yield together with some 1-acetylindole.

Alkyl aryl ketones(acetophenone and methylacetophenone) are acetylated by acetyl perchlorate on the methyl group to give the corresponding $\beta$-diketones in up to 20% yield[109].

$$ArCOCH_3 \xrightarrow[CH_3NO_2]{CH_3COCl+AgClO_4} ArCOCH_2COCH_3.$$

Burton and Munday[146] extended this reaction to cyclic ketones (cyclopentanone, cyclohexanone, 1-indanone, and 1-tetralone); acylating with acetyl perchlorate and phenylalkanoyl perchlorates, they obtained cyclic $\beta$-diketones in low yield:




Recently it was shown that it was in principle possible to obtain $\alpha\beta$-unsaturated ketones by acylating olefins by Kondakov's method with acid anhydrides in the presence of perchloric acid and its compounds. Acylation of cyclohexene with acetic anhydride in the presence of perchloric acid[147] or with acetyl chloride and silver perchlorate in nitromethane[126,147] leads to the formation of 2-acetylcyclohex-1-ene in yields of 32 and 42% respectively. Hex-1-ene and triisobutylene are also acetylated by acetic anhydride in the presence of catalytic quantities of perchloric acid, unsaturated ketones being formed in 15–20% yield[119]. In the acylation of vinylaromatic compounds (styrene and vinyltoluene) under similar conditions unsaturated ketones were obtained in 15–20% yield, but the formation of considerable amounts of polymeric compounds was also noted[119,123]. Other arylethylenes (acenaphthylene and indene) alone or mixed with styrene only form polymers and copolymers in quantitative yield under the acylation conditions[148]. As shown by Plesh and coworkers the polymerisation of unsaturated compounds is initiated by acetyl perchlorate and proceeds by the usual cationic polymerisation mechanism[149].

Perchloric acid has also proved an effective catalyst in the acylation of a number of high-molecular-weight compounds containing reactive linkages in the polymer chain[123,148].

† Mixed anhydrides with silicic and boric acids ? (Ed. of Translation).

In particular, the *C*-acylation of polyacenaphthylene and of the copolymer of acenaphthylene with styrene have been carried out by this method[148].

The addition of anhydrides of carboxylic acids to vinyl acetate in the presence of catalytic quantities of perchloric acid or silver perchlorate leads to the formation of acylals of β-ketoaldehydes (10–60% yield), which are widely used in organic synthesis for the preparation of heterocyclic compounds[150,151]:

$$R'CH{=}CHOAc \xrightarrow[HClO_4]{(RCO)_2O} RCOCHCH(OAc)OCOR,\ (R' = H,\ CH_3)$$

where R = $CH_3$, $C_2H_5$, $C_3H_7$; R′ = H, $CH_3$.

Of other cases in which perchloric acid is used in an acylation reaction, the cyclisation of benzoylbenzoic acid to anthraquinone should be mentioned; the components are boiled in acetic acid solution[152].

## IV. ACYLATION AND ALKYLATION OF THE HYDROXY--GROUP

Perchloric acid and its salts are widely used for the catalytic acylation of alcohols, phenols, and other hydroxy--compounds, and also for the analytical determination of the hydroxy-group[153]. Alcohols[154] and phenols[106,116] are acylated by acid anhydrides in the presence of traces of perchloric acid or Anhydrone[106,155]. In this way even compounds such as arylnitroalcohols[156] and tertiary alcohols[157], which are sensitive to mineral acids, have been successfully acylated. The acetylation of phenol[116], guaiacol[137], resorcinol[116], hydroquinone[106], and naphthols[114] gives aryl acetates in high yield. Information on the mechanism and kinetics of the *O*-acylation of phenols is given in a paper by Satchell[114].

The catalytic decomposition of 1,3,5-trioxan in acetic anhydride has been described; a mixture of mono-, di-, and (at low temperatures) even tri-oxymethylenediacetates is formed[158].

When $(CH_3CO)_2O$ and $HClO_4$ act on derivatives of 2-phenylcoumarin and tetrahydrofuran, the opening of the heterocyclic ring is accompanied by the formation of *O*-acyl compounds[159].

The use of perchloric acid in the acylation of polyhydric alcohols[160], monosaccharides[160,161], and cellulose[162–164] gives particularly good results. Glucose is acetylated rapidly and easily at ordinary temperatures to the α-pentaacetate[161]. Partial acetylation of cotton cellulose, in a continuous-process apparatus, is effected in a heterogeneous medium by a mixture of 85% $CH_3COOH$ + 15% $(CH_3CO)_2O$ and 0.1–0.2% $HClO_4$, or by 50% $(CH_3CO)_2O$, 50% pentyl acetate, and 0.2% $HClO_4$.[165] When acetylated D-glucosides are heated with acetic anhydride and perchloric acid, D-glucoseheptaacetate is obtained[166].

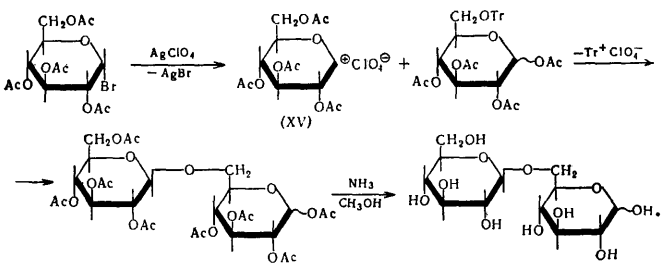
Heating glucose β-pentaacetate with perchloric acid in a solution of $(CH_3CO)_2O$ and $CH_3COOH$ leads to its isomerisation to an equilibrium mixture containing 90% of the α-anomer[113,167].

A convenient preparative method has been developed for acetylating polyhydric alcohols, cyclitols, and some monosaccharides and *O*- and *C*-glycosides in the presence of small amounts of magnesium perchlorate, which is more convenient in this reaction than perchloric acid[154,155,168].

For example, with this method polyhydric alcohol polyacetates are obtained in 85–90% yield, and pure D-glucose α-pentaacetate is obtained in 80% yield.

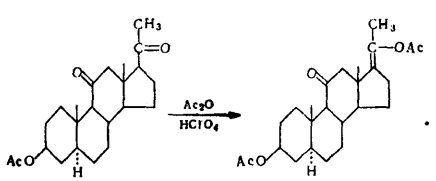
A simple and convenient method has been proposed for deacetylating polyhydric alcohol polyacetates and *C*-glycosides by heating the acetates with small quantities of perchloric acid in methanol solution[168,169]. Hydrolysis of *O*-glycosides with aqueous perchloric acid proceeds through the intermediate glucopyranosylcarbonium cation ("sucronium" cation)[170].

Recently a new method of synthesising oligosaccharides has been proposed[171]. Essentially this method consists in the reaction of acetohalogenose and silver perchlorate in nitromethane to give the sucronium perchlorate, which then reacts with acyl derivatives of 6-tritylmonose. In this way di- and tri-saccharides with 1,1- and 1,6-*O*-glycosidic bonds have been synthesised[172,173] and branching has been introduced into polysaccharide molecules[174]. The synthesis of the disaccharide gentiobiose in 59% yield has been effected according to the following scheme[173,175]:



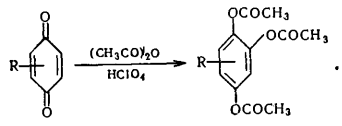

By a similar reaction of (XV) with the trityl derivative of $\Delta^5$-3β-hydroxypregnen-20-one the *O*-glycoside of this steroid has been synthesised[175]. A series of acetylated *O*-glycosides has been synthesised by the interaction of sucronium perchlorates (XV), obtained as unstable colourless syrups from 1-chloro-2,3,4,6-tetra-*O*-acetyl-D-glucose, D-galactose, and D-xylose and $AgClO_4$, with aliphatic and alicyclic alcohols[176].

A method of *O*-acylation previously developed has been applied to the synthesis of fats[171,177]. When mono- and di-trityl ethers of various glycerides react with aliphatic acid chlorides and $AgClO_4$ in nitromethane, homogeneous triglycerides are formed in good yield[177]. There are also reports of the use of perchloric acid in *O*-acylation reactions of some steroids[178,179] and alkaloids[180,181]. Thus when 3-β-acetoxyallopregnane-11,20-dione was treated with acetic anhydride containing traces of perchloric acid in $CCl_4$ solution, the monoenol acetate was obtained in good yield[180]:




Perchloric acid is the most effective catalyst in the acylation of quinones by Thiele's method, since the tri-

acetates of 1,2,4-trihydroxybenzene and its derivatives can be obtained in yields of 90% and more[112,182]:



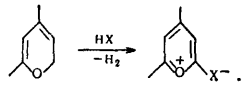
When treated with acetic anhydride and perchloric acid, 1,4-naphthoquinone forms 1,2,4-triacetoxynaphthalene in quantitative yield[183].

## V. SYNTHESIS OF HETEROCYCLIC COMPOUNDS

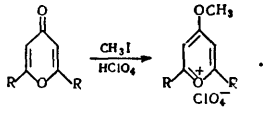
The systematic use of perchloric acid in the synthesis of heterocyclic compounds only began in recent years.

Perchloric acid is an effective catalyst and condensing agent in the synthesis of pyrylium salts, which are easily separated and purified as stable perchlorates. Methods of preparing pyrylium salts associated with the use of the acid may be classified according to three general synthetic routes: (a) synthesis from compounds containing the pyran ring; (b) the alkylation of olefins and other unsaturated compounds; (c) condensation reactions of carbonyl compounds. However, even in the latest reviews and monographs dealing with the chemistry of heterocyclic compounds the methods of synthesis and the properties of pyrylium salts are considered very superficially[184-188].

Under the action of strong mineral acids pyran derivatives eliminate a hydride ion and form pyrylium salts[189]:

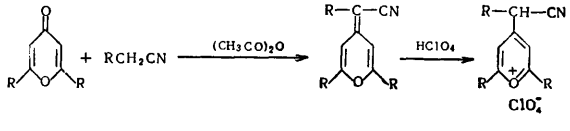


On alkylation with methyl iodide or dimethyl sulphate and subsequent treatment with perchloric acid, the readily accessible 2,6-dimethyl-4-pyrone, 2,6-diphenyl-4-pyrone, and 2,4-dimethyl-2-pyrone form 4(2)-alkoxypyrylium perchlorates[184,185].



2,4,6-Trisubstituted pyrylium salts with different substituents in position 4 of the pyrylium ring may be synthesised by the successive action of organomagnesium compounds and perchloric acid on 2,6-disubstituted 4-pyrones[190,191].

Similarly, in the presence of acetic anhydride or other dehydrating agents disubstituted 4-pyrones react with various nucleophilic compounds (dimethylaniline[192], malonic acid dinitrile, cyanacetic ester[193], etc.) to form substituted pyrylium salts:



Some information on the conversion of pyrones to pyrylium salts is given in a recent review by Dimroth[193].

Data on the second of the aforementioned methods of preparing pyrylium salts, which was discovered almost simultaneously in 1959 by Balaban and Nenitzescu[194,195] and also by Praill and Whitear[157,196], are systematised in a detailed review by the Rumanian workers[197].

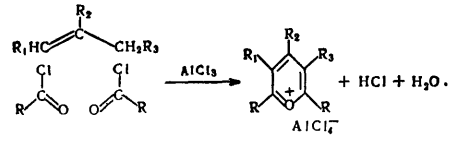
When olefins are acylated by Kondakov's reaction in the presence of the usual catalysts ($AlCl_3$, $SnCl_4$, $ZnCl_2$, $HClO_4$, $BF_3$ complexes, etc.), $\alpha\beta$-unsaturated ketones are formed[198]. However, as has been shown in recent work, pyrylium salts are formed in this reaction in addition to $\alpha\beta$-unsaturated ketones; because of their solubility in water, the pyrylium salts remained unnoticed for a long time[195,199-201].

In their study of the carbonylation of t-butyl chloride by carbon monoxide in the presence of ferric chloride, Balaban and Nenitzescu observed a small quantity of crystalline product (~3%) in addition to trimethylacetic acid and t-butyl isobutenyl ketone; this turned out to be 2,6-di-t-butyl-4-methylpyrylium tetrachloroferrate[194]. From this the correct conclusion was drawn that the pyrylium salt is formed from isobutene produced by the decomposition of t-butyl tetrachloroferrate:

$$(CH_3)_3CCl+FeCl_3 \rightarrow (CH_3)_3C^+FeCl_4^- \rightleftarrows CH_3C(CH_3)=CH_2+HCl+FeCl_3.$$

On bisacylation of an olefin with trimethylacetyl chloride and subsequent cyclisation of the 1,5-diketone formed in the reaction, a pyrylium salt is obtained.

A detailed investigation of the acylation of a series of olefins (isobutene, $\alpha$-methylstyrene, 1,2-diphenylpropene, etc.) with an excess of acid chlorides in the presence of aluminium led to a simple and original method of preparing substituted pyrylium salts in 20–40% yield[195]:



The pyrylium salts formed in the reaction are separated from aqueous solution as slightly soluble perchlorates, chloroplatinates, or derivatives of Reinecke's salt, or they are converted by ammonia to the corresponding pyridine bases.

Tri- and tetra-substituted pyrylium salts may be obtained in 25–50% yield by the acylation of olefins (isobutene, 2-methyl-1-butene, pent-1-ene, $\alpha$-methylstyrene, etc.) with a large excess of acetic or propionic anhydride in the presence of molar quantities of 72% perchloric acid[196]. The structure of the pyrylium salts was established by their conversion into the corresponding pyridine derivatives, which is easily effected by treating the salts with aqueous ammonia or with ammonium acetate in acetic acid solution.

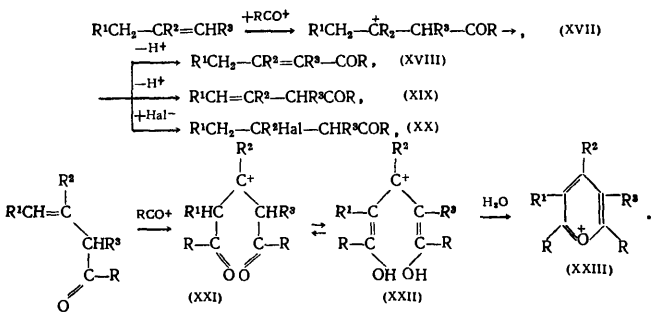
The reaction is obviously a general method of synthesising pyrylium salts from unsaturated compounds, containing the propenyl group, of the general formula (XVI):

$$R_1CH_2-CR_2=CHR_3$$
(XVI)

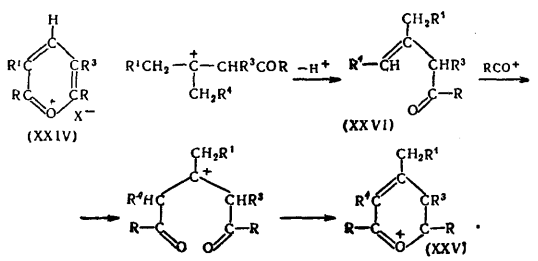
(where $R_1$, $R_2$, and $R_3$ = H, Alk, or Ar).

The mechanism of bisacylation of olefins is discussed

in a series of papers on the synthesis of pyrylium salts and may be represented by the following scheme[197,201,202]:



The first stage of the reaction consists in the addition of an acylium cation to the unsaturated compound (XVI) to form a carbonium ion (XVII), which is stabilised by elimination of a proton, being converted into $\alpha\beta$-(XVIII) or a $\beta\gamma$-unsaturated ketone (XIX), or in the addition of a halide ion to form in the latter case a $\beta$-halogeno-substituted ketone (XX) (if the acylation is carried out by an acid halide). Since the double bond in the $\beta\gamma$-unsaturated ketone (XIX) formed in the reaction is not conjugated with the carbonyl group, it readily reacts with a second molecule of acylium cation to form the dicarbonyl compound (XXI), which is converted into the pyrylium cation (XXIII) by elimination of a molecule of water from the enol form (XXII). The proposed mechanism was further confirmed in work on the bisacetylation of olefins with $CH_3{}^{14}CO^+$.[203] When $R^2 = H$, only one pyrylium salt isomer (XXIV) is formed. When $R^2 = CH_2R^4$, two isomers can be obtained, the pyrylium cation (XXIII) obtained as described above and the isomeric cation (XXV) formed by the following reaction:

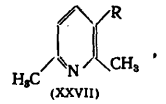


The formation and yield of the isomers (XXIII) and (XXV) is obviously determined by the quantitative ratio of the unsaturated cations (XIX) and (XXVI) and also by thermodynamic and kinetic factors.

As is to be expected, in the acetylation, propionylation and benzoylation of unsubstituted propene (the simplest compound which can be converted into a pyrylium salt by bisacylation), 2,6-disubstituted pyrylium salts are formed in low yield (0.5–5.7%)[204].

Praill and Whitear have made a detailed study of the acylation of a number of olefins (pent-1-ene, pent-2-ene, 3-ethylpent-2-ene, etc.) and other unsaturated compounds by acetic anhydride in the presence of perchloric acid[201].

Dulenko and Dorofeenko studied the bisacylation of higher olefins (the hex-1-ene, hept-1-ene, non-1-ene, and dec-1-ene) but in this case they did not succeed in separating pyrylium salts as perchlorates; these are difficult to crystallise and very soluble in water[205]. However, treatment of the reaction mixture with ammonia gave the corresponding 2,6-dimethyl-3-alkylpyridines (XXVII) (yield 23–42%), which are difficult to obtain

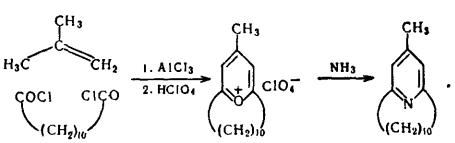


where R = $C_3H_7$, $C_4H_9$, $C_6H_{13}$, and $C_7H_{15}$.

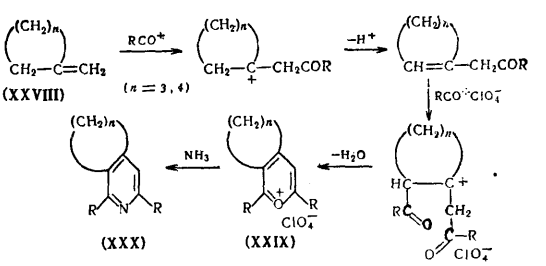
Crystalline pyrylium salts were not obtained when allylbenzene was acetylated in the presence of perchloric acid, but when the final product was treated with ammonia 2,6-dimethyl-3-phenylpyridine and 3-*p*-acetylphenyl-2,6-dimethylpyridine were obtained[206].

Acetylation of 2-methylpropenylbenzene ($CH_3COCl + AlCl_3$) gave a small amount of 2,6-dimethyl-4-benzylpyridine after the usual treatment[207]. The structure of the olefin materially effects the bisacylation reaction and the yield of pyrylium salts. The best results are obtained in the acylation of di- and tri-alkyl-substituted propenes, and also the "middle" members of the $\alpha$-olefin series containing an activated double bond. When one or two aryl residues are introduced into the propene molecule, the yield of pyrylium salts is appreciably reduced. Attempts to synthesise pyrylium salts from olefins with a deactivated double bond (1,2,3-triphenylpropene and methyl methacrylate) have proved unsuccessful[197]. Attempts to synthesise pyrylium salts by acetylation of allyl halides and isoprene, which immediately polymerise under the reaction conditions, were also unsuccessful[208].

An interesting case of intramolecular bisacylation was observed in the action of decane-1,10-dicarboxylic acid chloride and $AlCl_3$ in nitromethane on isobutene[209]: the bicyclic 4-methyl-2,6-decamethylenepyrylium salt was obtained as perchlorate and this was converted into the corresponding pyridine, as isomer of the natural muskopyridine:



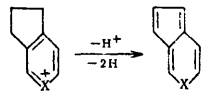
Balaban and Nenitzescu have done interesting work on the bisacylation of methylenecycloalkanes (XXVIII)[200]. Here, too, the pyrylium salts (XXIX) formed in the reaction could not be separated, but when the mixture was treated with ammonia 2,6-disubstituted pyridine, condensed with cycloalkene rings (XXX) were obtained in 18–25% yield



1,3-Dimethyl-5,6,7,8-tetrahydroisochromylium ($n = 4$) perchlorate was obtained in 30% yield by the acetylation of 1-methylcyclohexene, an isomer of (XXVIII) ($n = 4$).[201]

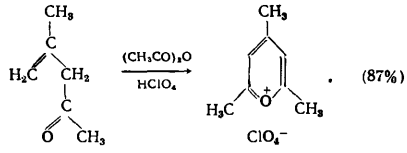
The pyrylium salts condensed with a cyclopentane ring (X = O) are of considerable interest, because they themselves and the quaternary pyridinium (X = NR) salts ob-

tained from them can be used as starting materials in the synthesis of pseudoazulenes:



where X = O or NR.

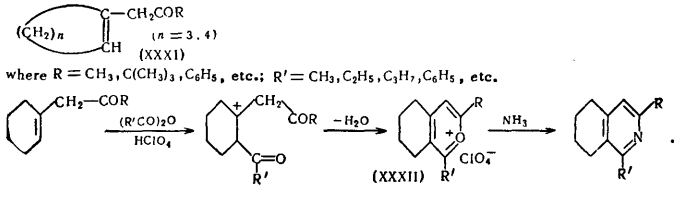
As is to be expected, $\beta\gamma$-unsaturated ketones (for example 4-methylpent-4-en-2-one), which are intermediates in the bisacylation of olefins, form pyrylium salts in excellent yield under the conditions mentioned[201]



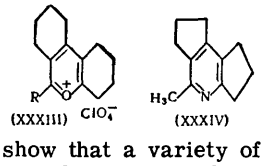
(87%)

The acylation of products of the crotonic condensation of cyclic ketones (cyclopentanone, cyclohexanone, etc.) with aliphatic and alkyl aryl ketones, in one of the isomers of which ($n$ = 4) the double bond is in the $\beta\gamma$-position to the carbonyl group, has been studied with the object of obtaining 5,6,7,8-tetrahydroisochromylium salts[208,211].

$\beta\gamma$-Unsaturated ketones (XXXI) (for example cyclohexenylacetone, cyclohexenylacetophenone, etc.) are acylated very rapidly by anhydrides of carboxylic acids in the presence of perchloric acid, the reaction mixtures becoming hot, and crystalline 5,6,7,8-tetrahydroisochromylium perchlorates (XXXII) can be isolated in good yield (70–90%):



When cyclohexenylcyclohexanone was acylated in the manner described, 2-alkyloctahydrodibenzopyrylium (XXXIII) perchlorates were obtained in high yield (up to 80%)[208]. Attempts to acetylate the product of the autocondensation of cyclopentanone were also successful[208]. Although in this case the crystalline perchlorate was not isolated, treatment of the mixture with ammonia gave 2-methyl-3,4:5,6-biscyclopentadienopyridine (XXXIV) in 30% yield:

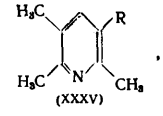


These results show that a variety of 1,3-disubstituted salts of 5,6,7,8-tetrahydroisochromylium can be easily synthesised by this method, and the salts may be used for the preparation of a number of isoquinolines, analogues of isoquinoline alkaloids, and other aromatic compounds difficult to obtain[208,211].

When t-butyl alcohol is acetylated in the presence of molar quantities of perchloric acid[157,199,201,212] or other acid catalysts[199], the final reaction product, obtained in the high yield (55–75%), is 2,4,6-trimethylpyrylium perchlorate. The same product is obtained in 72% yield by acetylating diacetone alcohol, which is evidently converted into a $\beta\gamma$-unsaturated ketone that readily forms a pyrylium salt[201].

Under the same conditions t-pentyl alcohol forms a mixture of pyrylium salts (yield 60%) consisting of 2,3,4,6-tetramethylpyrylium perchlorate (79%) and 2,6-dimethyl-4-ethylpyrylium perchlorate (21%).[157,158,201] Bisacylation of dimethylbenzylmethanol leads to the formation of 2,4,6-trimethyl-3-phenylpyrylium perchlorate[207], and 2,6-dimethyl-4-phenylpyrylium perchlorate is obtained from dimethylphenylmethanol[208]. Studies on the acylation of secondary alcohols in the presence of perchloric acid have shown that the process is accompanied by slow dehydration of the alcohols to the corresponding olefins, which are then diacylated with the formation of pyrylium salts, convertible by ammonia into the corresponding pyridines[208,213]. By this method 2,6-lutidine (11%) has been obtained from isopropanol, and 2,3,6-collidine (15%) has been obtained from butan-2-ol.

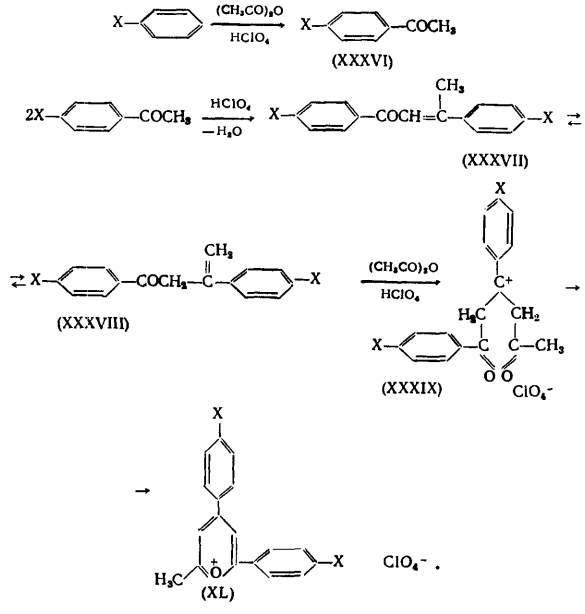
Other secondary alcohols (pentan-2-ol, hexan-2-ol, and octan-2-ol) form 2,3,4,6-tetrasubstituted pyridines (XXXV), which are difficult to obtain, in 27–30% yield:



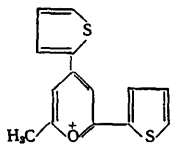
where R = $CH_3$, $C_2H_5$, $C_4H_9$.

However, attempts to extent this reaction to primary alcohols have not been successful[208].

In 1927 Diels and Alder reported on the preparation of pyrylium salts by the acylation of some aromatic compounds (toluene, $o$-xylene) and acetophenone with acetic anhydride in the presence of molar quantities of perchloric acid[104]. Obviously, the first stage in this reaction consists in the acetylation of the aromatic compound to an alkyl aryl ketone (XXXVI). The ketone obtained in this way, or introduced directly, forms a crotonic condensation product (XXXVII). The latter isomerises with a shift of the double bond to form a $\beta\gamma$-unsaturated ketone (XXXVIII), which is acylated again at the double bond with subsequent cyclisation of the diketone (XXXIX) to the pyrylium salt (XL):



2-Methyl-4,6-di(*p*-alkoxyphenyl)pyrylium salts (and from them substituted pyridines) are formed in good yield by acetylating phenol ethers (anisole and phenetole) or the corresponding *p*-alkoxyacetophenones in the presence of perchloric acid[208,214]. When thiophen or methyl-2-thienyl ketone is acetylated in this way, a pyrylium salt with heterocyclic radicals in the ring (XLI) is obtained in good yield (45%).

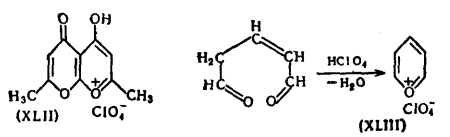


(XLI) $ClO_4^-$

It is interesting that, when dibenzyl ketone is bisacetylated under similar conditions, it forms 2,6-dimethyl-3,5-diphenyl-4-pyrone in low yield, because of the high mobility of its methylene group hydrogen atoms[215].

The schemes given for the formation of pyrylium salts from olefins and ketones are confirmed by the fact that $\alpha\beta$-unsaturated ketones of suitable structure also form pyrylium salts[105,195,201,216]. For example, when mesityl oxide is treated with acetyl perchlorate, it forms 2,4,6-trimethylpyrylium perchlorate in 46% yield[105,201]. Acetylation of acetone in the presence of perchloric acid, which catalyses the crotonic condensation reaction as with mesityl oxide, readily gives a good yield (45–50%) of 2,4,6-trimethylpyrylium[214].

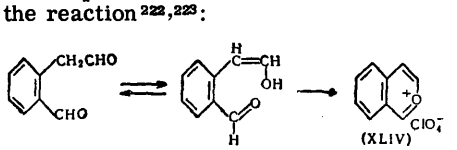
The Diels–Alder method of preparing pyrylium salts is a special case of a general method of synthesising compounds of this class by the bisacylation of olefins and other unsaturated compounds. However, the Diels–Alder method, the synthetic possibilities of which have not been fully elucidated, is very promising since it permits the preparation from readily accessible materials of pyrylium salts that are otherwise difficult to obtain. When a mixture of equimolecular quantities of acetic anhydride and perchloric acid is heated, self-acylation of the anhydride occurs and the acetoacetic acid is subsequently cyclised to the perchlorate of a base to which structure (XLII) has been ascribed[217]; the same compound is obtained when dehydroacetic acid is acetylated:



(XLII) (XLIII)

A third route to the synthesis of pyrylium salts is associated with the condensation of carbonyl compounds and the cyclisation of dicarbonyl compounds in the presence of perchloric acid.

Thus, the unsubstituted pyrylium salt (XLIII) is formed in good yield by the action of perchloric acid on glutaconic dialdehyde[218]. Under the action of dehydrating complexes ($FeCl_3$, $SbCl_5$)[219,220] or trityl perchlorate[221] 1,5-diketones are smoothly converted into 2,4,6-trisubstituted pyrylium salts in 50% yield. Robinson and coworkers obtained salts of the isochromylium cation (XLIV) by treating homophthalic aldehyde with perchloric acid or ferric chloride, which results in the reaction[222,223]:

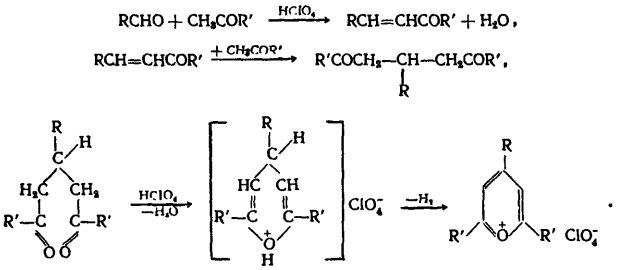


(XLIV)

The salts formed (XLIV) readily react with ammonia or primary amines to form isoquinoline and various *N*-substituted quaternary isoquinolinium salts.

A simple method of preparing 2,4,6-triarylsubstituted pyrylium salts has been developed; these are obtained by the interaction of $\alpha\beta$-unsaturated ketones (chalkones) with alkyl aryl ketones[224–226] or by the direct condensation of aromatic aldehydes with ketones[220,227] in acetic anhydride in the presence of ferric chloride.

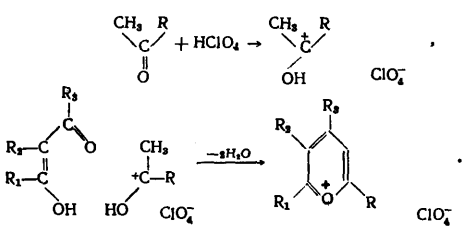
Dorofeenko and Krivun, who studied the condensation of aromatic aldehydes with alkyl aryl ketones in the presence of 70% perchloric acid, have proposed a simple and convenient method for the preparation of pyrylium salts with aryl substituents[228,229]. The synthesis of pyrylium salts appears to proceed through intermediate 1,5-diketones according to the scheme



Pyrylium salts are readily formed by brief heating (1–2 hours) or an aromatic aldehyde and ketone (molar ratio 1 : 2) at 100–110° with or without an inert solvent. In this way 2,4,6-triphenylpyrylium perchlorate (50–60%), 2,6-diphenyl-4-*p*-nitrophenylpyrylium perchlorate (30%), 2,6-diphenyl-4-*p*-dimethylaminophenylpyrylium perchlorate (33–35%), and a number of other pyrylium salts have been obtained[228,229].

The recently described condensation of benzylidenacetophenone and phenacyl acetate to 3-acetoxy-2,4,6-triphenylpyrylium perchlorate is effected in a similar way[230]. When chalkones are condensed with cyclohexanone in the presence of perchloric acid, 2,4-diaryl-5,6,7,8-tetrahydrochromylium perchlorates are formed[231,232].

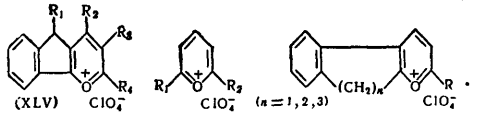
A method has been developed for preparing pyrylium salts in which $\beta$-dicarbonyl compounds are condensed with ketones in the presence of perchloric acid[208,233]:



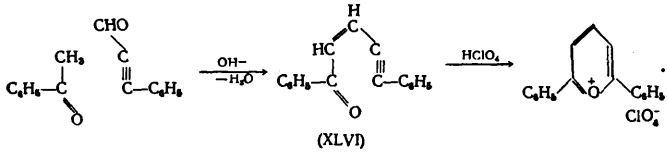
Although the pyrylium salts are obtained in low yield (15–30%) by this method, it appears to have wide possibilities, since it permits the synthesis of pyrylium salts that have not been obtained by other methods.

When 2-indanone and its derivatives are condensed with $\beta$-diketones, indeno[2,3*h*]pyrylium perchlorates (XLV) are obtained[234]; these form dyes when treated with sodium acetate[235]. Condensation of $\beta$-chlorovinyl ketones with

ketones[236] or enamines[237] also leads to pyrylium salts of the following structure:

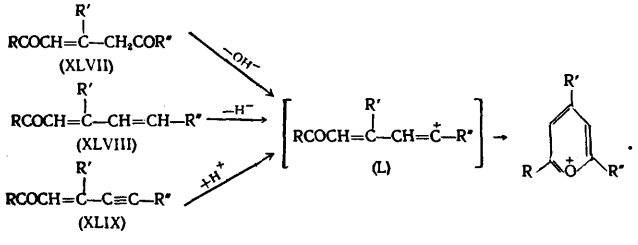


When acetophenone is condensed with phenylpropiolic aldehyde, the chalkone (XLVI) is formed; in the presence of perchloric acid this cyclises to a 2,6-diphenylpyrylium salt in 60% yield[238]:

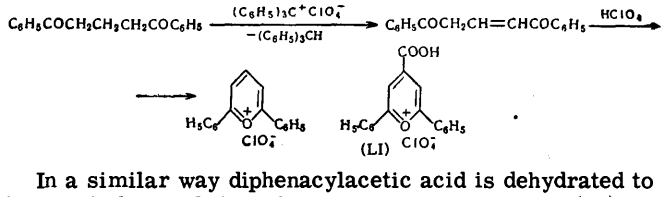


(XLVI)

In a paper by Siemiatycki and Fugnitto a general mechanism is proposed for the formation of pyrylium salts from unsaturated δ-diketones (XLVII) and unsaturated ketones (XLVIII) and (XLIX) containing two double bonds, or a double and a triple bond, conjugated with a carbonyl group[221]. According to this interpretation, the formation of a pyrylium ring from ketones of the structure mentioned proceeds through the same carbonium ion (L), which is converted into a pyrylium cation:



This mechanism is confirmed by results in the paper quoted above[238] and by the studies of Siemiatycki and Fugnitto[221], who, showed that when 1,5-diphenylpenta-2,4-dien-1-one reacts with triphenylmethyl perchlorate, which has considerable dehydrating properties, 2,6-diphenylpyrylium perchlorate is formed (23%).[239,240] The same salt is obtained in good yield (88%) by the dehydration of 1,3-dibenzoylpropane with trityl perchlorate:

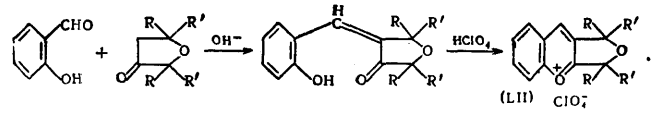


In a similar way diphenacylacetic acid is dehydrated to form 2,6-diphenyl-4-carboxypyrylium perchlorate (LI) in good yield (85%)[221]; this compound has not been otherwise synthesised.

Perchloric acid is frequently used as a condensing agent in the synthesis of benzopyrylium salts[241]. A new method has been proposed for the synthesis of benzopyrylium salts by condensation of various β-chlorovinyl ketones with phenols and naphthols in the presence of ferric chloride or perchloric acid[242-246].

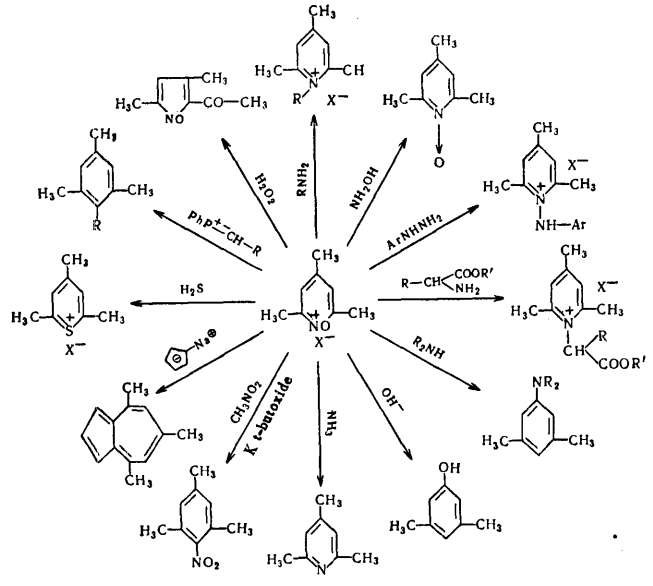
When xanthydrol or its derivatives is treated with perchloric acid in acetic anhydride, xanthylium salts are formed in good yield[247,248]. In this way 9-phenylethynylxanthylium perchlorate was obtained from 9-phenylethynylxanthydrol[249].

Recently it was shown that benzopyrylium perchlorates could be prepared by treating 2-acylcoumarins with perchloric acid in acetic acid[250]. Perchloric acid has also been used as a condensing agent in the Robinson–Kostanetskii reaction for the synthesis of furanidinobenzopyrylium perchlorates (LII), obtained in 30–65% yield[251].



In recent years pyrylium salts have become of very great importance in organic chemistry because they are easily converted in high yield into alkyl- and aryl-pyridines[191,205], which are difficult to prepare; they also form *N*-alkyl(aryl)pyridinium salts[190,191], thiopyrylium salts[252], pyran derivatives[253-255], azulene derivatives[256,257], aromatic hydrocarbons[258,259], nitro-compounds[260], amines[104], phenols[190], and other aromatic compounds[258,261] that are frequently difficult to synthesise by other methods. Recently a new reaction of pyrylium salts was discovered that permits them to be readily converted into substituted alkyl α-furyl ketones[262] by the action of hydrogen peroxide, catalytic hydrogenation of which gives *sym*-trialkyltetrahydropyrans[212].

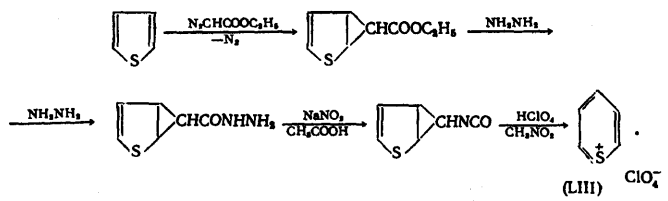
An interesting conversion of pyrylium salts into benzene derivatives by interaction with alkylidenetriphenylphosphoranes was recently discovered by Mark[263]. When pyrylium salts react with esters of α-amino-acids or diamino-acids, quaternary pyridinium salts are formed[264]:



Detailed information on the chemical properties of pyrylium salts and their various reactions is given in an excellent review by Dimroth[193].

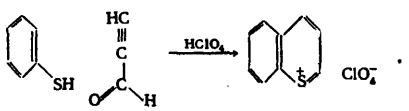
The use of perchloric acid and its compounds in the synthesis of sulphur- and nitrogen-containing heterocycles has also been described.

The preparation of thiopyrylium salts (LIII) by a new and interesting method has recently been described[265]:



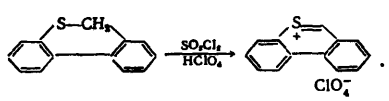
(LIII)

Engelhard and Kolb have proposed a simple single-step synthesis of thionaphththalenium salts; thiophenol or its derivatives is condensed with propargyl aldehyde in the presence of 70% perchloric acid[266].

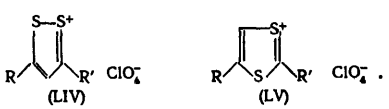


When thioxanthene is dehydrated with trityl perchlorate in acetic acid, thioxanthylium perchlorate is formed in good yield; with the same reagent 1-thiochromanone forms 1-thiochromone, also in good yield[267].

9-Thio-9,10-dihydrophenanthrene is smoothly converted into 9-thiophenanthrenium perchlorate by the action of sulphuryl chloride and perchloric acid in ether solution[268].



Perchlorates of 1,2-dithiolium derivatives (LIV) were obtained in good yield by the interaction of β-diketones with hydrogen sulphide in ether solution saturated with hydrogen chloride, and subsequent treatment with perchloric acid[269].

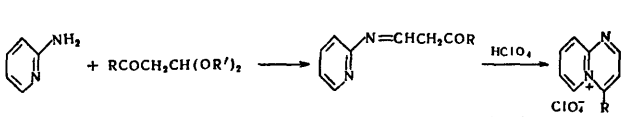


(LIV) (LV)

Similarly, when phenacyl- or acetonyl-carbodithionates were condensed with $H_2S$ in ether solution saturated with HCl, salts of the 1,3-dithiolium cation (LV) were obtained.

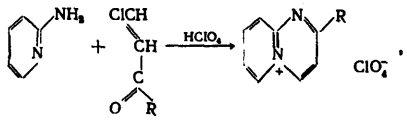
There are reports on the use of perchloric acid in Fischer's indole synthesis. When acetophenone phenylhydrazone was heated to boiling in bromobenzene solution with perchloric acid, 2-phenylindole was obtained[270]. Perchloric acid has been used as a condensing agent in the synthesis of *N*-*p*-tolyl-4,6-dimethylquinolinium perchlorate obtained by Bayer's method by the reaction of *pp*-ditolylamine with acetone and formaldehyde in nitromethane solution[271].

A new method of synthesising salts of 4-alkyl-1-azadehydroquinolizinium cation (LVI) has been developed; this is based on the condensation of α-aminopyridine with acetals of acylacetaldehydes, followed by cyclisation of the condensation products with concentrated acids ($HClO_4$, HBr)[272,273]:



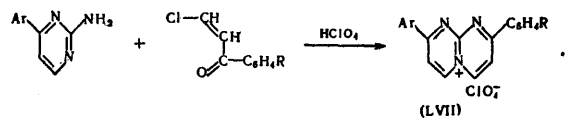
(LVI)

Compounds of this type are obtained easily and in good yield by the reaction of α-aminopyridine with β-chlorovinyl ketones in the presence of 70% perchloric acid[274]:



where R = $CH_3$, $C_3H_7$, $C_6H_5$.

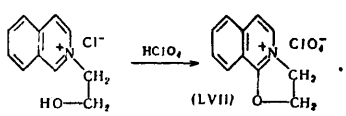
2,8-Diaryl-1,9-diazadehydroquinolizinium{pyrimidino-[1,2-*a*]pyrimidinium} perchlorates (LVII), derivatives of a new heterocyclic system, were synthesised by condensing 4-aryl-2-aminopyrimidines with aryl β-chlorovinyl ketones in the presence of perchloric acid[275]:



(LVII)

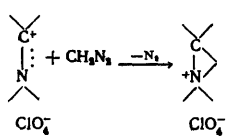
where R = H, *o*-Br, *p*-Br, *p*-$NO_2$.

*N*-(Hydroxy)isoquinolinium chloride is almost quantitatively cyclised to 4,9,5,6,7-hexadehydro-1-oxa-7,8-benzoindolizinium perchlorate (LVII) by boiling with 70% $HClO_4$ in alcoholic solution[276]:



(LVII)

When immonium perchlorates react with diazomethane, aziridinium salts, easily isolated in the crystalline state, are formed in good yield[277]:



We have described the most promising and most developed ways of using perchloric acid and its derivatives in organic synthesis. The scope of this review does not allow us to deal with its use in hydrolysis and solvolysis reactions, addition of carboxylic acids to olefins, polymerisation, dehydration with trityl perchlorate and quinone perchlorates, oxidation, isomerisation, and rearrangements, and also in various condensation reactions.

Although perchloric acid and its compounds began to be used only comparatively recently in organic chemistry, the data presented show that it undoubtedly has a wide and promising range of uses.


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# ION-EXCHANGE CELLULOSES AND THEIR USE IN CHROMATOGRAPHY

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## I. INTRODUCTION

The successful development of sorption technique and chromatography is to a considerable extent dependent on the discovery and utilisation of new types of synthetic sorbents. The production and introduction into sorption technology, particularly chromatography, of a new type of ion-exchange sorbent, the ion-exchange celluloses, is an outstanding achievement of modern chemistry and biochemistry.

The number of papers dealing with the chromatographic use of ion-exchange celluloses has been rapidly growing in recent years, and about 500 have already been published. The use of ion-exchange celluloses in chromatography and other varieties of sorption technology has enabled consider able progress to be made in the resolution of some of the most difficult problems in biochemistry — the separation of proteins, enzymes, nucleic acids, and other high- and low-molecular-weight substances found in living matter.

It is to be expected that ion-exchange celluloses will rapidly find wider application in ever increasing numbers of chemical fields.

The object of this review is to provide an account of current knowledge of the properties and uses of ion--exchange celluloses.

## II. PREPARATION OF ION-EXCHANGE CELLULOSES

We shall not concern ourselves here with the ion--exchange properties of natural and commercial (including chromatographic) celluloses, which may be found in a number of monographs, e.g. those of Rogovin[1] and Hais and Macek[2]. We note only that both natural and the various types of commercial cellulose possess ion-exchange properties mainly because of the presence of carboxyl groups, but their absorption capacity is negligibly small, being only $\sim 0.05$ mg-equiv. $g^{-1}$, which corresponds to about one carboxyl group for 90–130 glucose structural units[3,4].

The use of ion-exchange forms of cellulose for chromatographic purposes already has a history of more than 50 years. Goppelsröder[5] mentioned oxycellulose (a weakly acidic carboxyl-type cation exchanger) as a suitable material for capillary analysis. Oxycellulose is obtained by saponifying the esters present in the initial cellulose and oxidising the primary alcoholic groups present in the 6-position of the glucose structural units[1,2]. Even in this process definite limitations are found in the content of carboxyl groups: there exists a certain critical level for the introduction of these ionogenic groups into cellulose; above this level the cellulose loses the character of an insoluble sorbent. For oxycellulose it was found that the content of carboxyl groups could not exceed 1–4%; with more than 5% (every fifth glucose structural unit then being oxidised in the 6-position) the oxycellulose becomes soluble in water at pH above 9.[2]

The "pioneering" work on the production of different types of ion-exchange cellulose includes that of Lautsch and coworkers[6], Micheel and Albers[7], Sober and Peterson[8,9], and Porath[11]. Lautsch and coworkers obtained a number of ion-exchange cellulose ion exchangers: a carboxyl-type cation exchanger, the ether of glycolic acid containing the $-CH_2OCH_2COOH$ group, by the action of chloroacetic acid in alkaline solution; a strongly acidic cation exchanger containing the $-CH_2OCH_2CH_2CH(SO_3H)CH_3$ group by the action of butane sulphone; and an anion exchange containing $-CH_2\overset{+}{N}R_3X^-$ groups by esterification with *p*-toluenesulphonyl chloride and reaction of the ester with tertiary amines. In each case one ionogenic group could be introduced for each 20–30 glucose structural units; this was the limit of ion-exchange capacity for these ion exchangers, since with more ionogenic groups the cellulose decomposed.

Micheel and Albers[7] obtained a carboxyl-type cation--exchange cellulose in the form of the phthalic acid mono-

ester. This weakly acidic cation exchanger was insoluble in alkalis when containing 5% of carboxyl groups.

Sober, Peterson, and coworkers[8,9] and Porath[11] undertook systematic studies of the production of ion-exchange celluloses for chromatography.

Sober and Peterson[8,9] described the preparation of a series of new cation- and anion-exchange celluloses: CM-cellulose (carboxymethylcellulose); P-cellulose (phosphorylated cellulose); DEAE-cellulose (diethylaminoethylcellulose); and ECTEOLA-cellulose. From DEAE-cellulose, Porath[11] prepared the anion exchanger TEAE--cellulose (triethylaminoethylcellulose), and he also obtained the strongly acidic cation exchangers SE-cellulose (sulphoethylcellulose) and SM-cellulose (sulphomethylcellulose). The abbreviated and full names of some ion--exchange celluloses and their properties are given in Table 1. These are prepared from natural $\alpha$-cellulose.

Sober and Peterson[8,9] used powdered cotton cellulose for the preparation of cation exchangers and powdered wood cellulose for anion exchangers. $\alpha$-Cellulose was found to be the most suitable substrate for the introduction of ionogenic groups.

The absorption capacity of ion-exchange celluloses is limited on the one hand by the need for the sorbent to be insoluble, and on the other by the requirement that the sorbent should have good physical properties suitable for use both in paper and in column chromatography.

The ion-exchange celluloses obtained by the above groups of workers had absorption capacities of less than 1 mg-equiv. $g^{-1}$, which is considerably lower than for ion--exchange resins. However, in most cases this capacity was quite sufficient.

The ion-exchange celluloses are prepared by normal etherification of cellulose; for example, DEAE-cellulose was obtained by heating a mixture of cellulose and $\beta$-diethylaminoethyl chloride in alkaline medium[9], and SM- and SE-celluloses were prepared analogously[11].

TABLE 1. Types of ion-exchange cellulose.

| Abbreviated name | Full name | Ionogenic group | Acidic or basic properties | Total absorption capacity*, mg-equiv. × × $g^{-1}$ |
|---|---|---|---|---|
| Cation exchangers | | | | |
| SE | sulphoethylcellulose | $-C_2H_4SO_3H$ | strong acid | 0.4 |
| P | phosphorylated cellulose | $-PO_3H_2$ | strong acid | 0.8 |
| CE | carboxyethylcellulose | $-C_2H_4COOH$ | moderately strong acid | 0.7 |
| CM | carboxymethylcellulose | $-CH_2COOH$ | weak acid | 0.7 |
| C | carboxycellulose (oxycellulose) | $-COOH$ | weak acid | 0.7 |
| Anion exchangers | | | | |
| PAB | *p*-aminobenzylcellulose | $-CH_2C_6H_4NH_2$ | weak base | 0.6 |
| ECTEOLA | reaction product of cellulose with ethylene chlorohydrin and triethylamine | not known | weak base | 0.5 |
| AE | aminoethylcellulose | $-C_2H_4NH_2$ | weak base | 0.7 |
| TEAE | reaction product of DEAE-cellulose with ethyl bromide | not known | moderately strong base | 1.0 |
| DEAE | diethylaminoethylcellulose | $-C_2H_4N(C_2H_5)_2$ | moderately strong base | 1.0 |
| GE | guanidoethylcellulose | $-C_2H_4NHCNH_2NH_2OH$ | moderately strong base | 0.7 |

* Approximate values are given.

The methods for the production of ion-exchange celluloses have given good reproducibility in the physical properties of the sorbents and in their physicochemical characteristics (absorption capacity, etc.). A considerable part of the work on the uses of ion-exchange celluloses has been carried out on materials produced by the actual investigators. At the present time ion-exchange celluloses are produced by a number of foreign companies, such as Whatman (UK) and Serva (W. Germany), as well as at the Institute of Antibiotics, Academy of Sciences of the USSR (Leningrad) and the Textile Institute (Moscow). Table 1 lists the main known types of ion-exchange cellulose used in chromatography, the cation exchangers in order of decreasing acidity, and the anion exchangers in order of increasing basicity. A whole range of cellulose-based ion exchangers is available, and workers can select those with the required physicochemical properties.

## III. PROPERTIES OF ION-EXCHANGE CELLULOSES

### Structure

In their chemical structure the ion-exchange celluloses are linear polymers comprising long macromolecular chains of $\beta$-glucopyranose units joined by 1–4 $\beta$-glucosidic bonds. At intervals of the order of 50 Å the hydrogen of the cellulose hydroxyls is replaced by the various ionogenic groups. The individual linear macromolecules interact by molecular-type bonds (mainly polar) and by hydrogen bonding[1], the difference in the relative proportions of the two forms of interaction producing the differences in solubility and reactivity between the cellulose and its derivatives. Although the linear cellulose chains are cross--linked, the cross-linking is very weak.

The introduction of groups which cause partial rupture of the hydrogen bonds can increase the solubility. It should also be borne in mind that bonds retained in the ion-exchange celluloses may be broken during chromatography of some materials; thus it has been shown[11] that in chromatography of proteins on ion-exchange celluloses the protein molecules are adsorbed by hydrogen bonding as well as by the formation of ionic and polar bonds. A kind of competition arises for hydrogen bonding between the cellulose macromolecules on the one hand, and between cellulose and protein molecules on the other, which explains the high absorption capacity of ion-exchange celluloses towards proteins and other high-molecular-weight substances. The cellulose macromolecules can also combine with each other by ordinary valence bonds (glucosidic and ester linkages).

### Physical Properties

Because of the irregular thread-like shape of the cellulose particles, it is impossible to obtain an accurate evaluation of their dispersity and dimensions. Direct microscopic measurement of particle lengths has produced distribution curves which show the maximum length to be 350–500 $\mu$m; the maxima on the distribution curves lie in the range 50–100 $\mu$m. The diameter of the particles is 15–20 $\mu$m. The moisture content of air-dried ion-exchange celluloses is 10–15%. The density is 0.1–0.2 g $ml^{-1}$, i.e. like commercial cellulose they are fairly "loose". The

specific volume of ion-exchange celluloses in the swollen state is 10–15 $cm^3 g^{-1}$, and the swelling factor is ~ 2.

Ion-exchange celluloses possess good filtration properties; when they are used in column chromatography, the flow rate of solvent can be controlled within the limits 5–25 ml $cm^{-2} h^{-1}$. No data exist on their combined water content.

## Physicochemical Properties

The extent of dissociation of the ionogenic groups of ion-exchange celluloses and their acidity and basicity can be estimated from their titration curves[19]. Table 1 includes a qualitative indication of the acidic and basic properties of ion-exchange celluloses, and their approximate total absorption capacities.

The total absorption capacity of an ion exchanger, is a sorption constant and is determined by the number of ionogenic groups which have exchangeable ions; in other words, the total absorption capacity as a constant is independent of the composition of the solution in contact with the ion exchanger. However, the utilisation of this total absorption capacity by different ions varies with the energy of the bond produced by the sorbed ions. If the sorption of one ion is studied in the presence of other ions, the distribution follows the ion-exchange isotherm and the law of equivalence of exchange.

The sorbed ions compete for the sorption centres of the ion exchanger in accordance with their bond energies, and of course hydrogen ions (with cation exchangers) or hydroxide ions (with anion exchangers) sorbed by the ion exchangers block part of the total exchange capacity and so also compete; as a result, the real absorption capacity of the ion exchanger depends on the pH of the solution.

The sorption of dissociable high-molecular-weight compounds (polyelectrolytes) and many low-molecular-weight organic compounds by ion exchangers is a complex process, and has been little investigated theoretically or experimentally. Dissociable organic compounds are generally amphoteric substances the ionogenic groups of which differ in their degree of dissociation, and the number of free ionic bonds will vary with the pH of the solution and the presence and concentration of other substances. In addition to polar ionic sorption, organic molecules may also be attached by other types of bond.

In view of what has been said, the laws of ion exchange established for the sorption of inorganic ions will not apply to the sorption of dissociable organic compounds. The absorption capacity of ion-exchange celluloses towards organic compounds cannot be expressed as milliequivalents per gramme of sorbent, nor, in the case of high-molecular-weight compounds of indefinite molecular weight, even as millimoles per gramme of sorbent. In such cases ion-exchange celluloses will have a specific absorption capacity for a specific substance under specific conditions, and this must be expressed as milligrammes of substance per gramme of sorbent. If a more rigorous approach is desired, the universal standard unit of mass of ion exchanger must be taken as 1 g of the ion-exchanger matrix (the mass of the ion-exchanger less the mass of sorbed ions or compounds). At the present time, however, this unit of measurement of the mass of an ion-exchanger has not found widespread use, and the absorption capacity is usually measured per gramme of air-dried (or dry) ion exchanger in the ionic form taken for the experiment.

The sorption properties of ion-exchange celluloses have as yet been very little studied, and there have been no systematic studies of absorption capacity, sorption isotherms, or the kinetics and dynamics of sorption.

Peterson and Sober[9] determined the absorption capacity of some ion-exchange celluloses towards proteins, obtaining the following values:

DEAE 0.498 g of blood serum protein per gramme of sorbent,

ECTEOLA 0.05 g of blood serum protein per gramme of sorbent,

CM 0.98 g of CO-haemoglobin per gramme of sorbent,

P 0.93 g of CO-haemoglobin per gramme of sorbent.

O'Donnell and Thompson[13] investigated the variation of the absorption capacity of ion-exchange celluloses with temperature; for example, a decrease of temperature from 25° to 1° greatly reduces the absorption capacity of DEAE-cellulose towards insulin.

The rate of sorption is known to be determined by the rates of the successive stages of the sorption process, i.e. of diffusion and of actual sorption. The part played by these steps in establishing sorption equilibrium on ion-exchange celluloses has not been investigated. Consideration of the structural features of ion-exchange celluloses suggests that the sorption of various substances on them will be extramicellar in nature; the intradiffusional stage of sorption is practically excluded here.

The extramicellar nature of the sorption and the high degree of dispersion of ion-exchange celluloses (particle diameters of the order of 10–20 μm) should theoretically produce a more rapid sorption than on ion-exchange resins. With inorganic ions and low-molecular-weight organic substances the time required for establishment of sorption equilibrium is probably limited by the time of the extradiffusional stage of sorption. It may well be, however, that with high-molecular-weight substances the time required for the establishment of sorption equilibrium will also depend significantly on the time required for the actual act of sorption.

The literature contains extremely scanty information on the kinetics of sorption of substances on ion-exchange celluloses. When the sorbent is stirred with a solution of calcium ions, the equilibrium for the sorption of $Ca^{2+}$ by SE- and P-celluloses in various ionic forms is attained in 10 s, which corresponds to the time required for the external diffusion of the inorganic ions being exchanged[14]. With DEAE-cellulose equilibrium is established in the exchange of chloride and iodide ions in slightly more than ~ 30 s, i.e. as with ion-exchange resins, sorption by anion exchangers is slower than by cation exchangers. This difference may reflect the influence of the rate of the chemical stage of sorption, which is not always instantaneous. Gusev[15] studied the kinetics of sorption of $Na^+$ and $Fe^{3+}$ ions under somewhat unusual conditions, with sorption of the ions by a dense layer of CM-cellulose, and found the sorption by the surface of the dense cellulose layer to be very rapid, while further sorption inside the layer was very slow, sorption equilibrium being established in 3 h. This result is only comprehensible if, under the conditions indicated, the time required for establishment of the equilibrium is determined by diffusion inside the very dense

layer of sorbent (internal diffusion). However, such conditions do not apply in chromatographic experiments. Gusev also found the rate of sorption to be greater in acid than in neutral media; this effect is also observed with ion-exchange resins, and is associated with the greater swelling of the ion exchangers in acidic media and the greater mobility of the hydrogen ions which participate in the exchange.

Nikolaev[16] has shown that equilibrium is established in 5 min in the sorption of proteins and enzymes on ion-exchange celluloses.

There is very little information available on the sorption isotherms for various compounds on ion-exchange celluloses. Nikolaev[16] investigated the statics of the sorption of asparaginase from 0.08 M NaCl and from buffer solutions of pH 7.0 and 6.5; he obtained a sorption isotherm of convex shape.

There is a little information available on sorption series for some ion-exchange celluloses; for example, Head and coworkers[17] obtained the following sorption series for P-cellulose: $U^{4+} > UO_2^{2+}$; $Th^{4+} > Fe^{3+} > La^{3+} > H^+ > Cu^{2+}$; and $Ca^{2+} > Na^+$. These agree with results obtained for phosphate resins. Veder and coworkers[18] established the following sorption series for anions with ECTEOLA-cellulose:

citrate > formate > $HPO_4^{2-}$ > $SO_4^{2-}$ > phthalate > > salicylate > succinate > glutamate > $NO_3^-$ > > benzoate > $Br^-$ > propionate > tartrate > > caproate > $Cl^-$ > lactate > acetate > $I^-$ > > ascorbate > glycerate.

In investigating the sorption of compounds on ion-exchange celluloses, due account must be taken of the possibility of complex-formation between the ions and the ionogenic groups or other ions in the solution[17,19].

It is evident from this review that the properties of ion-exchange celluloses have been very little studied. Practically no information is available on the mechanisms of the sorption processes or the quantitative laws of sorption of inorganic and organic compounds on cellulose ion exchangers, but this gap in our knowledge will obviously be filled by appropriate studies in the near future.

## IV. TECHNIQUE OF THE APPLICATION OF ION-EXCHANGE CELLULOSES

### Choice of Sorbent

Ion-exchange celluloses are selected on the basis of their properties and the composition of the mixtures to be separated. DEAE-cellulose is usually employed for the separation and analysis of proteins. About 80% of published work on the use of ion-exchange celluloses relates to the chromatographic analysis of proteins, and 75% of this is concerned with the use of DEAE-cellulose, ~ 20% with CM-cellulose, and ~ 3% with TEAE-cellulose; this information is taken from Serva's catalogue[12], and is illustrated in Table 2, which is based on the catalogue but which we have supplemented.

DEAE-cellulose is used for the separation of enzymes and proteins having isoelectric points at a neutral or acid pH, and for the purification of viruses and chromatography of polysaccharides, peptides, and nucleotides; TEAE-cellulose is used similarly, and in some cases gives cleaner separations of proteins and other high-molecular-weight compounds. AE- and GE-celluloses have not yet found wide application. Good separations of nucleic acids and viruses are attained with ECTEOLA-cellulose. CM-cellulose is used for the analysis of neutral and basic proteins.

The strongly acidic celluloses such as SE and P are generally employed for the chromatography of low-molecular-weight substances. PAB-cellulose is in a class of its own. In its primary form it can be used to separate nucleic acids, but it has one important specific property: the amino-group is readily diazotised, and then couples with proteins, enzymes, antigens, and other materials. Because of this, PAB-cellulose can act as a selective sorbent; for example, a PAB-azoantigen selectively absorbs antibodies, PAB-azohistone and PAB-azoguanine selectively absorb nucleotides, and PAB-azotyrosine selectively absorbs tyrosinase. Enzymes attached to PAB-cellulose lose their activity. The discovery of this sorbent opens up new possibilities in chemistry and biochemistry. The production of specific sorbents is extremely important for the development of sorption technology and chromatography.

Ion-exchange celluloses are used in column, paper, and thin-layer chromatography and in drop sorption techniques. The experimental procedure in each of these methods is different, and must be dealt with separately.

### Column Chromatography

Columns of ion-exchange cellulose with a length to diameter ratio of 10 : 1 are usually employed; the size of the column and hence the amount of cellulose are selected in accordance with the amount of mixture to be separated, the separating ability of the column, and the required yields of the separated components of the mixture.

Organic substances are generally separated by displacement or elutive column chromatography, with buffer solutions as eluting solvents. Experience has shown that best results are obtained if the sorbent is first treated with the buffer solution which is to be used as eluent, thus becoming saturated with the ions and other components in equilibrium proportions.

Work with ion-exchange celluloses has shown[20] that in some cases, particularly with concentrated eluate solutions, the chromatography is accompanied by partial dissolution of the cellulose, so that dissolved cellulose fragments. polysaccharides with ionogenic groups, pass into solution; this may lead to errors. This effect can be detected or tested for by analysis of the eluate for polysaccharides[21,22]. The eluate can be readily freed from such impurities, for instance by passage through small columns of ion-exchange resins[23].

Account should also be taken of the possibility of decomposition of the cellulose by the enzyme cellulase[24,25]. Some ion-exchange celluloses are stable towards the action of this enzyme, but some are not[24]; the former group includes P-, SM-, and CM-celluloses, and the latter DEAE-cellulose and the cellulose prepared from Whatman paper.

The cellulose ion exchangers employed in chromatographic analysis can be regenerated by the usual method[26].

Ion-exchange celluloses withstand the not unduly prolonged action of strong acids and alkalis[17].

TABLE 2. Bibliographic index of the applications of ion-exchange celluloses.

| Material | Sorbent | Ref. |
|---|---|---|
| Acetylenemonocarboxylate hydrolase | DEAE | 147 |
| Acetyltrypsin | DEAE | 148 |
| Acetyltrypsinogen | DEAE | 149 |
| Adenosine 5'-phosphate | CM, DEAE | 131 |
| Alanine-activating pH 5 enzymes | DEAE | 132, 133 |
| Albumen (human blood serum) | CM, DEAE | 134–136 |
| Alcohol dehydrogenase | CM, DEAE | 139, 140 |
| Aldehyde dehydrogenase | CM, DEAE | 137 |
| Aldolase | DEAE | 138 |
| L-Amino-acid oxidase | DEAE | 142 |
| Amino-acids | DEAE | 120 |
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In the chromatographic separation of mixtures of substances on ion-exchange celluloses by displacement chromatography with buffer solutions, the distribution constants or sorption factors of the components, the differences in which determine the success of the chromatographic separation, depend on the pH of the solution and the concentration of salts present in it. Optimum conditions for the separation can be found by proper selection and control of the pH and the concentration of salts and other components in the eluent. Experience with various sorbents, including ion exchangers, has shown that the effective separation of mixtures of organic substances by displacement column chromatography requires the use not of a single eluent, but of several eluents in succession, or an eluent of continu-

ously varying composition. This has brought into use such methods of chromatography as single-stage, multistage, and continuous gradient elution.

Several devices exist for setting up concentration gradients [12], differing in how the eluent concentration varies with time.

Elution gradients, their theoretical prerequisites, and practical methods for obtaining them have been actively discussed in the literature, particularly in connection with the use of ion-exchange celluloses [20,27-34].

The choice of eluent and the forms of gradient are greatly dependent on the mechanism of sorption of the dissociable organic substances on the ion exchangers. Unfortunately, this has been very little investigated, either theoretically or practically. In this Review we can only touch upon some of the general theories relating to this type of sorption.

Dissociable organic compounds are usually amphoteric, i.e. according to the pH of the solution they dissociate predominantly by scission of acidic (hydrogen ions) or basic (hydroxide ions) from ionogenic radicals. The organic molecules will exist as neutral molecules and anions in the former case, and as neutral molecules and cations in the latter, the relative amounts of neutral and ionic molecules depending on the degree of ionisation of the ionogenic radicals in the molecule. At a certain pH — the isoelectric point — the dissociation of both types of ionogenic group is equally probable, and the dissociating molecule takes on the properties of a dipolar ion (zwitterion).

The sorption of dissociable organic compounds on ion exchangers is a complex process which may involve all types of bonding.

Since ion exchangers are polar sorbents containing ionogenic groups having ionic bonds, one of the main mechanisms of sorption of dissociable substances on ion exchangers is that of ion-exchange sorption. As in the case of inorganic substances, ion-exchange columns can be used to find the nature of organic compounds, their ionic constitution, etc.; for example, at a given pH "basic" compounds will be firmly sorbed on cation exchangers and loosely held on anion exchangers.

The sorption of dissociable organic compounds is greatly influenced by the nature of other ions present in the solution; these include hydrogen and hydroxide ions, the concentrations of which define the pH of the solution. The ions will combine both with the sorbent and with the dissociating organic ions in the solution.

The distribution of other ions present between the sorbent and the organic molecules in solution depends on the corresponding bond energies and the ionic concentrations. These ions and the ions of the organic compound will compete for the sorption sites in the ion exchanger, and changing the concentration of the former ions will therefore alter the distribution coefficients for the organic material being sorbed. One general feature is observed in this process: the sorption of the dissociating organic compound will decrease as the concentration of other ions is increased, because the latter will utilise more and more of the available ionic bonds in the ion exchanger and in the dissociating organic molecules. The other ions present thus act as a barrier which hinders the sorption of the dissociating organic compound. For this reason, solutions of electrolytes, such as buffer solutions, are used to elute the sorbed organic substances. Experience with the chromatography of organic substances has shown that some are not eluted, after introduction into the column of sorbent (or onto the paper). This means that such organic materials do not dissolve in the eluent employed. However, if the concentration of salts in the eluent is slowly raised, a certain "critical" concentration is reached when the organic material becomes almost completely soluble and begins to move at the flow rate of the eluent. Because each component has its own critical elution concentration, gradient elution can achieve an efficient separation of a mixture of organic substances. This method of chromatographic separation was discovered by Tiselius [35,36] in the chromatographic analysis of proteins, and has sometimes been called the "all or nothing" method or "salting-out" chromatography.

One further application of gradient elution must be mentioned. One of the negative effects in the chromatographic separation of mixtures of substances is the spreading of the fronts of the chromatographic zones, and gradient elution is one of the methods available for overcoming this. In gradient elution the forward and rear boundaries of the chromatographic zones occur at different eluent concentrations, lower at the forward edges and higher at the rear edges, so that at the rear boundary regions the conditions are such that the sorption of the substance is less than at the forward boundary. This means that desorption will be greater at the rear than at the front, and the chromatographic zones will become narrower and form sharp peaks, so improving the efficiency of the chromatographic separation.

## Paper Chromatography

Ion-exchange chromatographic paper is also used analytically. A detailed bibliography and description of working with ion-exchange paper can be found in a Czech monograph [2]. Several firms produce ion-exchange paper for chromatography in addition to powdered ion-exchange cellulose.

Two methods are used for chromatography on ion-exchange paper [37]: with a "dry" and with a "wet" start. In the former, which is generally used in paper chromatography, the eluting solvent is absorbed by the dry paper, and in the latter the paper is first impregnated with the buffer solution and is then used similarly to an ion-exchange column.

Knight has shown that the "dry" start method gives a better separation of amino-acids [38].

## Thin-Layer Chromatography

In recent years much success has been achieved by the use of the so called thin-layer chromatography, first suggested by Izmailov and Shraiber [39] and developed by Stahl [40,41]. Nikolaev [42] has reviewed this field in detail.

The essence of the method is that the sorbent is mixed with some cementing or binding material (such as gypsum), and the resulting paste is then deposited in a thin layer ($\sim 0.5$ mm) on a glass plate. This thin layer is the analogue of the column or sheet of chromatographic paper. One- or two-dimensional chromatograms can be obtained. The main advantage of thin-layer chromatography is that, because of the fine dispersion ($< 25$ $\mu$m) of the sorbing material deposited on the glass plate, there is very rapid

capillary uptake of the solvent, and the chromatography takes very little time. Clean separations of mixtures can be achieved on 10 × 10 $cm^2$ or 15 × 15 $cm^2$ plates. Ion-exchange celluloses can be used as sorbents in thin-layer chromatography, and the Serva company provides prepared mixtures of ion-exchange cellulose powders with cementing material, specially designed for thin-layer chromatography [12].

The following procedure is recommended for the preparation of the plates. 10 g of the sorbent is mixed with 60–80 ml of water, and the paste is spread in a thin even layer on the plate with a special frame or other device. The success of the chromatography depends very much on the preparation of the thin layer, and it is very important to have an even thickness. The glass plate must have a good plane and even surface. The deposited sorbent layer is dried in the air at room temperature. The sample is introduced on to the sorbent layer with a micropipette, and the plate is placed vertically with its edge in the eluting solvent. The eluent front moves at a rate of 10 cm in 15 min.

As in paper chromatography, a very convenient method for developing the chromatograms, in addition to the use of indicator reagents, is to use ultraviolet light; for example, nucleotides show up as dark spots in ultraviolet light ($\lambda$ = 253 m$\mu$m), and proteins can be detected in ultraviolet light after heating the moist chromatogram for several minutes at 150°.

### Fractional Sorption

Hess and Walter have shown [43] that selective separation of individual components from the test material can in some cases be achieved simply by adding the ion-exchange cellulose to the substrate; for example, certain dehydrogenases have been selectively extracted from plasma proteins. This procedure has been called fractional sorption, and has found application as a rapid method in clinical diagnostics, specially standardised DEAE- and CM-cellulose being available for this purpose [12].

## V. USES OF ION-EXCHANGE CELLULOSES

### Chromatography of Proteins

The first systematic studies in the development of the chromatography of proteins on ion-exchange celluloses were made by Sober, Peterson, and their coworkers [8-10,44], who used column chromatography to analyse the proteins of human and horse blood plasma on the anion-exchange DEAE-cellulose, by means of the gradient elution method. The protein content of the individual fractions was found spectroscopically. In addition the fractions were further subjected to electrophoretic separation. It was found that with a decreasing pH gradient and an increasing salt concentration the proteins generally left the column in the order of decreasing isoelectric points. The column of anion exchanger was saturated to the extent of 170 mg of protein per gramme of sorbent. The new method gave a considerably better separation than electrophoresis. The Sober–Peterson method was later applied to the separation of blood serum proteins by many other workers [45-50], using gradient elution with DEAE-cellulose [10,46,49] or CM-cellulose [45,47,50].

Kogent and Broda [46] evolved a chromatographic separation of the high-molecular-weight compounds contained in blood serum and not precipitated by sulphosalicylic acid, using DEAE-cellulose in a phosphate buffer. In their study of normal and pathological blood serum they found these compounds to be mucopolysaccharides.

Morrison and Cook [45] showed that good results in the separation of proteins can be obtained with CM-cellulose. Hess and Walter [43] used ion-exchange celluloses for the analysis of blood proteins in clinical diagnostics. Sober and coworkers [51] used chromatography on ion-exchange celluloses to show that human and horse CO-haemoglobin is less homogeneous in protein composition than dog haemoglobin.

CO-haemoglobin has been analysed chromatographically several times, using CM-cellulose the eluent being 0.01 M phosphate buffer with a "convex" pH gradient from 6 to 8. [52-54] In addition to the chromatographic separation of the proteins, pure globulin was obtained in preparative quantities. Blood haemoglobin has also been analysed by chromatography on ion-exchange celluloses by many other workers [55-58], and the method has been used for the chromatographic analysis of various other proteins: meromyosin [59,60], *l*-myosin [61], insulin [62], $\beta$- and $\gamma$-casein [63], $\gamma$-globulins [64], $\beta$-lactoglobulin [65], and others.

Complex biological materials such as egg protein [66,67] and milk proteins [68,69] have also been analysed chromatographically. Previously unknown proteins have been discovered by chromatography on ion-exchange celluloses, for example in egg protein by Rhodes and coworkers [67] using elutive chromatography on CM-cellulose.

Several papers have been published on the separation of plant proteins [70,72]. As yet unidentified protein fractions have been found in soya bean proteins [71], and six protein fractions have been detected in barley proteins [70].

### Chromatography of Enzymes

Chromatography on ion-exchange celluloses has been successfully used for the separation and isolation of enzymes. Arne [73] used a column of TEAE-cellulose to analyse gastric invertase and maltase; the latter consists of three components, while the former is a single enzyme.

Taborsky [74] separated ribonuclease into four components by chromatography on CM-cellulose.

Ispolatovskaya et al. [75,76] used DEAE- and ECTEOLA-cellulose for the separation and preparative isolation of leucitinase, pologenase, and hyaluronidase of bacterial toxin.

Others have also analysed enzymes by chromatography [77,78].

Many papers have been published on the purification of enzymes by means of ion-exchange celluloses [79-88]; for instance, the dehydrogenase isolated from rat liver was purified with DEAE-cellulose, its activity increasing 250 times [86], and the alkaline phosphatase activity of the enzyme isolated from human intestines and liver was increased 15–140 times [87].

A 50-fold purification of yeast carboxylase on a column of CM-cellulose has been described; the resulting enzyme retained its activity at 5° for a prolonged period. Ion-exchange celluloses have been used to purify hormones [89-91], antigens [92,93], and plasmogen [94].

Brown[95] has developed a procedure for the preparative isolation of pure myoglobin from crude muscle extracts using large columns of ion-exchange cellulose, and Nikolaev has shown that proteins may be concentrated by means of columns of DEAE-cellulose[16].

## Chromatography of Nucleic Acids and Nucleotides

Bendich and coworkers[96] were the first to use ion-exchange celluloses for the separation and analysis of nucleic acids; they tested a number of celluloses, and obtained best results with ECTEOLA-cellulose. They achieved chromatographic fractionation of DNA differing in the composition of the heterocyclic bases. Other workers have also carried out chromatographic fractionation of DNA with ECTEOLA-cellulose[97-99] or DEAE-cellulose[100].

Staehelin and coworkers[101,102] used DEAE-cellulose in their investigation of the nucleotide sequence in RNA. By chromatography of the hydrolysate of yeast RNA treated with pancreatic RNA-ase, they observed a whole range of different mono- and poly-nucleotides: the mononucleotides uridylic and cytidylic acids; the dinucleotides AC, AU, GC, and GU; the trinucleotides AAC, AAU, GAC, AGC, GAU, AGU, GGU, and GGC; and some tetranucleotides. Even the nucleotide isomers GAC and AGC were readily separated.

Mihalyi and coworkers[103] have used ECTEOLA-cellulose for the removal of RNA from muscle myosin; the chromatography separates the RNA from the protein, the RNA/protein ratio being 1.3 before and 0.02 after. In some experiments the protein content of the RNA fraction was reduced by a factor of 50–60. Ward and Putch[104] used ECTEOLA-cellulose to separate a mixture of DNA and RNA.

Reference may also be made to other work in which ion-exchange celluloses have been used for the separation of nucleic acids and nucleotides[105-108].

ECTEOLA- and DEAE-celluloses have also been used for separating and purifying viruses[109-113]. Thus Hayer and Bolton[111] separated and purified certain animal viruses in this way. The prospects of this method for virology and in particular for the production of vaccines are obvious.

Randerath[114] separated a mixture of nucleotides by thin-layer chromatography in 5 minutes using ECTEOLA- and DEAE-cellulose.

## Chromatography of Low-Molecular-Weight Organic Substances

Rouser and coworkers[115] used columns of DEAE-cellulose to separate the lipids isolated from whole beef brain and found the composition to be cholesterol 20.3%, ceramide 0.3%, cerebroside 16.8%, cerebroside sulphate 3.5%, lecithin 11%, phosphatidylethanolamine 17%, and other constituents.

Heri and Neukom[116] carried out a successful separation of the pectins isolated from beet and apples on DEAE-cellulose, obtaining fractions differing in their content of arabinose and galactose and in the degree of etherification and polymerisation. The greater the degree of polymerisation and the lower the degree of etherification, the more firmly were the pectins retained on the DEAE-cellulose.

Elutive chromatography on a column of DEAE-cellulose was used by Muller and coworkers[117] to separate five polysaccharide fractions, differing in their content of uronic acids, from soil. Ion-exchange celluloses have been employed for the isolation of seromucoids from blood serum[118].

Pawelkiewicz[119] used an ion-exchange cellulose for the isolation and purification of vitamin $B_{12}$.

The use of ion-exchange celluloses for the separation of amino-acids has been investigated[38,120,121]. Ion-exchange celluloses have no particular advantages over ion-exchange resins in the column chromatography of amino-acids[120].

Ion-exchange celluloses have been successfully employed for the separation of AMP, ADP, and ATP,[101] peptides[122] and sugarphosphates[17].

## Chromatography of Inorganic Ions

Head's work on the analysis of inorganic substances by chromatography on ion-exchange celluloses has already been mentioned. He found that $Fe^{3+}$, $Ce^{4+}$, $UO_2^{2+}$, $U^{4+}$, $Th^{4+}$, and $ZrO^{2+}$ ions are strongly absorbed from acid solutions by P-cellulose, which is not observed with resins of the sulphonic acid type. These ions can be eluted with reagents which form stable complexes with them, for example $Th^{4+}$ and $UO_2^{2+}$ are quantitatively eluted with 10% $(NH_4)_2CO_3$ solution, $Fe^{3+}$ with chloroacetic acid, $ZrO^{2+}$ with ammonium fluoride, etc.

Head and coworkers also successfully separated mixtures of Bi and Pb, Cu and Pd, Cu and Co, and Cu and Ni; for example, Bi and Pb were separated by eluting Pb with 1 *N* $HNO_3$ and Bi with 1 *N* HCl, in which it forms anionic complexes; and Cu was separated from Cd, Co, and Ni by elution of these with 1 M $MgCl_2$, followed by desorption of the copper remaining on the column by passing HCl.

Cerrai and Testa[19] prepared a new type of anion-exchange cellulose, TOAC (tri-n-octylaminocellulose), with the very high capacity of $\sim 1$ mg-equiv. $g^{-1}$; with this they separated a mixture of $Fe^{3+}$, $Co^{2+}$, and $Ni^{3+}$, using 0.8 M HCl as eluent. Iron and cobalt form anionic complexes in HCl and are sorbed by the anion exchanger, while nickel does not form complexes and moves with the eluent. The Co and Fe are separated by elution with 3 M HCl, which desorbs Co but not Fe. Differences in ion-exchange sorption and complex-forming ability have also been used to separate a mixture of Th, Zr, and U, and such mixtures as La and Th, Zr and La, and Zr and Hf have also been successfully separated.

## Use of Ion-Exchange Paper and Thin-Layer Chromatography

Ion-exchange paper chromatography has been successfully used to separate amino-acids[38], barbiturates[123,124], organic acids[125], proteins[126], inorganic ions[127-129], and other materials.

Curtain[126] separated blood serum proteins on DEAE-cellulose of ion-exchange capacity $\sim 0.003$ mg-equiv. $cm^{-2}$, using gradient elution with pH and ionic strength gradients, established with a programmed photoelectric device. Albumin and $\beta$- and $\gamma$-globulins were separated on a paper strip.

Street [123,124] used DEAE-paper to separate a mixture of 5,5-substituted barbiturates, with t-$C_5H_{11}OH$–0.1 M EDTA disodium salt (1 : 1) as eluent, by circular chromatography. He was able to separate a mixture of phenobarbitone, barbitone, butanobarbitone, and quinobarbitone. The chromatographic zones were inspected in ultraviolet light.

Myhre [125] has described the separation of organic acids on CM-paper, using butanol–ethanol–water (4 : 1 : 5) as the mobile phase. Gluconic and glucuronic acids are better separated on a more acid cellulose.

Kember and coworkers [127] used phosphorylated paper for the separation of cations, and paper treated with 2-aminoethanesulphonic acid for the separation of anions.

Cerrai and Testa [128] have investigated the behaviour of inorganic cations on ICBL1 paper treated with 0.02 *N* tri-n-octylphosphine oxide in cyclohexane. As the mobile phase they employed HCl, $HNO_3$, and $H_2SO_4$ solutions of various concentrations, and they indicated the dependence of the $R_F$ value on the acid concentration for 50 metal cations. Mixtures such as Sr–Y, Bi–Hg–Pt, U–Mo–Y–La, Th–Y–La–Ca, and U–Tl–Fe–Ge were successfully separated.

An anion-exchange paper prepared by treating Whatman paper with tri-n-octylamine has been used to separate the mixtures Fe–Co–Ni and Zn–Co–Mn–Ni, making use of the ability of these metals to form anionic complexes in HCl [22].

By thin-layer chromatography on ion-exchange celluloses, Randerath and Struck [37] were able to separate complex mixtures of heterocyclic bases and nucleotides. They used 10 g of ECTEOLA, CM-, or DEAE-cellulose in a thin-layer on a plate, with ~ 2–5 μg of material taken for the chromatography. Water was used as the mobile phase, the front moving at a rate of 10 cm in 3 min.

The following $R_F$ values were obtained for a number of bases: adenine 0.30, adenosine 0.53, hypoxanthine 0.55, inosine 0.70, guanine 0.37, guanosine 0.58, uracil 0.72, and uridine 0.81. Nucleotides were separated with butanol–acetone–acetic acid–5% $NH_4OH$–water (4.5 : 1.5 : 1 : 1 : 2); the rate of movement of the front was ~ 10 cm in 1 min. The following $R_F$ values were obtained: AMP 0.38, CDP 0.22, UTP 0.13, ADP 0.26, and ATP 0.16.

Randerath has published a fuller review of the uses of thin-layer chromatography on ion-exchange cellulose [130].


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# MONODISPERSE AEROSOLS

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## I. INTRODUCTION

Almost all the properties of aerosols depend to a marked extent on the particle dimensions, and the establishment of these relationships is the chief aim of many aerosol studies. Since all real aerosols are more or less polydisperse, it is necessary, in the experimental study of these relationships, that the quantity to be determined in a polydisperse aerosol with a mean particle radius $\bar{r}$ coincides with the corresponding quantity in a monodisperse aerosol with the same particle radius. The error thus introduced increases with increase in the polydispersity of the aerosol, so that in the last twenty years there has been an ever-increasing tendency in aerosol studies to use aerosols which are as far as possible monodisperse.

In one extremely important case, however, namely in the study of various processes of aerosol deposition, for example in filters, breathing apparatus, etc., it is also possible to use polydisperse aerosols. In this case the total concentration of particles and their distribution with respect to dimensions in the original aerosol and in the aerosol which has passed through the filter or been deposited on it are determined, and the efficiency of the filter for all the particle dimensions of the aerosol is calculated. The precise determination of the total concentration of particles and their distribution with respect to dimensions, even within a fairly narrow range of the latter, is a complex and extremely tedious task, however. This method can thus be recommended only for preliminary measurements, and for accurate studies it is best in most cases to work with an aerosol with the maximum degree of monodispersity attainable by modern methods of preparation. Such aerosols may be described as "practically monodisperse", and it is to these that we shall be referring in the present review.

The degree of monodispersity is conveniently characterised by the magnitude of the coefficient of variation $\alpha$, i.e. the ratio of the standard deviation of the particle radii $\sigma$ to the mean radius $\bar{r}$:

$$\alpha = \frac{\sigma}{\bar{r}} = \left[\frac{\sum_i^N (r_i - \bar{r})^2}{N}\right]^{1/2} \Big/ \bar{r}. \qquad (1)$$

Since the distribution of particles with respect to dimensions in aerosols usually deviates appreciably from the normal gaussian distribution and approximates to a logarithmic-normal distribution, the degree of monodispersity, at values of $\alpha$ which are not too small, is conveniently expressed by the value of the logarithm of the geometric mean square deviation:

$$\sigma_g = \left[\frac{\sum_i^N \left(\ln \frac{r_i}{r_g}\right)^2}{N}\right]^{1/2}, \qquad (2)$$

where $r_g = \left[\prod_i^N (r_i)\right]^{1/N}$ is the geometric mean radius of the particles. For low values of $\alpha$, when $\bar{r} \simeq r_g$, $\ln(r_i/r_g) \simeq (r_i - r_g)/r_g$ and

$$\sigma_g \simeq \left\{\frac{\sum_i^N [(r_i - r_g)/r_g]^2}{N}\right\}^{1/2} \simeq \alpha. \qquad (3)$$

Fig. 1 gives the logarithmic-normal distribution curves for $\sigma_g = 0.1$ and 0.2, and also the normal distribution curves for $\alpha = 0.1$ and 0.2. The choice of criterion for "practical monodispersity" is of course arbitrary. The present review deals with aerosols with $\alpha \leq 0.2$ or $\sigma_g \leq 0.2$. Not all authors have calculated $\alpha$ for the aerosols which they have prepared. Sometimes only the distribution curves or histograms are given, and in some cases only the range of radii containing a certain percentage of the particles. In these cases we calculated $\alpha$ with the accuracy assumed for the data given in the work cited.

Here mention must be made of the methods used to determine the degree of monodispersity of aerosols. The most reliable methods naturally involve the direct determination of the dimensions of a large number of individual particles by means of an optical or electron microscope, ultra-microscope (from the rate of sedimentation of the particles), photoelectric counter, or other methods, followed by statistical treatment of the results of the measurements. Unfortunately, these methods are not always applicable, particularly for aerosols from volatile liquids, whose particles undergo appreciable volatilisation during the removal of the specimens and the actual measurements. It is extremely difficult to eliminate evaporation. Moreover, in the measurement of liquid droplets by means of an optical microscope, it is necessary to make allowance for their spreading over the support, and only preliminary studies of the measurement of droplets with the electron microscope have been made. The measurement of the rate of sedimentation of particles or the rate of movement in an electric field by means of the ultra-microscope is possible[1] only for a particle radius greater than 0.15 $\mu$m, and the errors in the determination of the dimensions of individual particles, associated with brownian movement, lead unavoidably to high values of $\alpha$.

Another method for estimating the monodispersity of aerosols, which has been widely employed, is the optical method based on the fact that the scattering of white light in more or less monodisperse systems of spherical particles produces spectral colours which are purer the higher the degree of monodispersity. If the observer looks through the aerosol towards the light beam, he sees, surrounding the light source, a "halo" consisting of coloured rings whose angular diameter is simply related to the particle dimensions and the length of the corresponding light

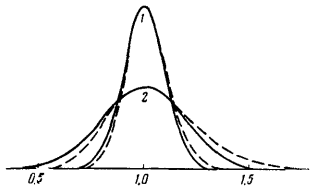



Fig. 1. Normal (solid line) and logarithmic-normal (broken line) distribution curves.

waves. The "halo" method is applicable at $\bar{r} > 1$ μm and is used in the study of fogs formed by the adiabatic expansion of air containing the vapour of water or other volatile liquid and also in the study of natural clouds and fogs. In the latter case the sun or moon is the light source.

When $\bar{r} < 1$ μm, the aerosol is introduced into a vertically-arranged cylindrical vessel with transparent walls and a narrow beam of white light is passed in a direction perpendicular to the axis of the cylinder. In the case of an aerosol which is monodisperse and has a sufficiently high concentration, spectral colours, which show a periodic variation with change in the angle of observation, are visible in the vessel. These diffraction spectra, which were first observed in monodisperse sols of sulphur by Ray[2] and were studied in detail by La Mer and coworkers[3-5], have been called "higher-order Tyndall spectra". A horizontal viewing-tube, focussed on the axis of the vessel and capable of rotating around it, is used to measure $\theta$, the angle of deviation of the red rays, for which $\alpha$ is obtained with the highest accuracy. The spectra are made more distinct by using a polaroid plate, which transmits only the component of the scattered light polarised in a vertical plane. The number of spectra increases with increase in the particle dimensions and is approximately equal to the particle radius in tenths of a micrometer. By means of special tables calculated on the basis of the Mie theory, it is possible to determine $\bar{r}$ from the values of $\theta$ corresponding to spectra of different orders; the position of the spectra depends comparatively little on the refractive index of the particles. This method is applicable for the approximate range $0.15\ \mu m < \bar{r} < 1.2\ \mu m$. The measurement of $\theta$ becomes impossible at lower values of $\bar{r}$, since the spectrum becomes indistinct, and becomes impossible at higher values of $\bar{r}$, because the spectra of different orders are crowded together[6]. The instrument used has been named the Owl.

It is impossible to give a precise answer to the main problem — at what degree of monodispersity do distinct Tyndall spectra appear? It first of all follows from the theory of the phenomenon that with increase in the degree of monodispersity the spectra should appear not immediately but gradually, so that different observers may disagree on the question of whether the spectra are present or absent. Moreover, the clarity of the spectra is influenced by a number of factors: the optical density of the system[7], the mean dimensions of the particles and their refractive index, the conditions of the observation — the thickness of the illuminating beam[8], stray light in the instrument, the shading in the laboratory, the unique features of the observer's vision, etc. The use of a polaroid plate has a marked effect on the clarity of the spectra. For a given value of $\sigma$ and $\bar{r}$, the possibility of observing the spectra also depends on the nature of the distribution curve, since the scattering of the light increases rapidly with increase in the particle dimensions. By using the ultramicroscope method to study the distribution with respect to dimensions for droplets of various non-volatile liquids in fogs produced in a Sinclair–La Mer generator (see below) with $\bar{r} = 0.3$–$0.9$ μm, Kitani[9-11] established that determination of $\theta$ for the red band is possible only for $\sigma \leqslant 0.12$ μm. According to Berner[12], who determined the dimensions of droplets in dioctyl phthalate fogs in the same range of values of $\bar{r}$ using Goetz's Aerosoloscope[13], the first red band can be observed at $\sigma \leqslant 0.14$ μm and the whole spectrum only at $\sigma \geqslant 0.10$ μm. From the data given by Goyer and Pidgeon[14], it follows that in an aqueous fog with $\bar{r} = 0.45$ μm, Tyndall spectra appear only at $\sigma \leqslant 0.09$ μm. In other papers the limiting value of $\sigma$ was not determined, but the quoted values of $\sigma$ at which the Tyndall spectra were or were not observed agree with the above data, with the following two exceptions.

La Mer's report[5] that the spectra disappear when equal volumes of two monodisperse hydrosols of sulphur with $\bar{r} = 0.467$ μm and $0.476$ μm are mixed is undoubtedly based on some major error, since mixing in this way can lead to an increase in $\sigma$ of only $0.004$ μm. In actual fact, according to Maron and Elder's observations[7], the Tyndall spectra are preserved when monodisperse latexes of polystyrene with $\bar{r} = 0.164$ μm and $0.196$ μm are mixed, although in this case the calculated value of $\sigma$ increases by $0.016$ μm. An analogous result was obtained by Petro[15], by mixing monodisperse hydrosols of sulphur with $\bar{r} = 0.310$ μm and $0.385$ μm.

According to Martius[16], who prepared condensation aerosols of dioctyl phthalate with $\bar{r} = 0.34$–$0.67$ μm, Tyndall spectra are observed in these aerosols only at $\sigma \leqslant 0.003$–$0.006$ μm. Such monodisperse aerosols cannot, however, be prepared by a condensation method, and this result is due to the elementary error which Martius made in making allowance for the influence of brownian movement on the scatter of the particle-radius values found by the ultramicroscope method.

Thus the appearance of Tyndall spectra is related to the value of not the relative ($\alpha$) but the absolute ($\sigma$) standard deviation. This is apparently due to the fact that the increase in monodispersity with increase in $\bar{r}$ at constant $\sigma$ is compensated by the simultaneous crowding together of the spectra of different orders.

The qualitative method of estimating monodispersity from the Tyndall spectra can also be developed quantitatively. The most accurate method is the "polarisation ratio" method, based on the measurement of the ratio $k$ of the intensities of the components of the light scattered by the aerosol and polarised in horizontal (parallel to the plane of scattering) and vertical planes. Here it is possible to illuminate the aerosol with monochromatic light of constant wavelength $\lambda$ and measure $k$ as a function of the angle $\theta$ of scattering (Kerker *et al.*[17-19]), or to carry out the measurements at constant $\theta$ (usually 90°) and varying values of $\lambda$ (Heller *et al.*[20,21]). This gives sinusoidal curves, which become flatter (the maximum and minimum values of $k$ approach) with increase in the polydispersity. For a given distribution of the particles with respect to dimensions, for example the logarithmic-normal law, these curves are calculated on the basis of the Mie theory, by means of computers, for different values of $\bar{r}_g$ and $\sigma_g$, and the results are compared with the experimental curves. The distribution parameters can be determined in this way with sufficient accuracy. For a constant value of the product $r_g \sigma_g$, close to the value of $\sigma$ given by formula (3), the nature of the curves changes little with increase in $\sigma_g$.[17] This agrees with the above condition for the production of the Tyndall spectra.

To enable the Tyndall-spectra method to be applied to particles with $\bar{r} < 0.2$ μm, La Mer[5,22,23] suggested that the particle size be increased by using solvent vapour which is in equilibrium with a solution of the aerosol material in the same solvent. The increase in size is determined by the concentration of the solution. The same concentration is also rapidly established in the aerosol droplets (if the Kelvin effect is neglected, see below). In this way La Mer was able to increase the particle size by a factor of 5–10

and to obtain Tyndall spectra in aerosols with an initial value of $\bar{r} \geq 0.02$ μm. In this "cultivation" of the aerosols, the value of $\alpha$, as a first approximation, should not change, but because of the Kelvin effect, it is necessary, in order to maintain equilibrium, that the concentration in the finer droplets be slightly greater than that in the larger droplets, i.e. the latter grow more than the former, so that $\alpha$ should increase slightly during "cultivation"[24]. At the same time the value of $\sigma = \alpha\bar{r}$ increases considerably during the "cultivation", and this possibly explains La Mer's observation[25] that the sulphuric acid fogs with $\bar{r} \geq 0.20$ μm, obtained in his generator, give Tyndall spectra, whereas highly-dispersed fogs with $\bar{r} < 0.1$ μm do not give these spectra on "cultivation".

## II. PREPARATION OF MONODISPERSE AEROSOLS BY CONDENSATION METHODS

A number of conditions must be observed in order to obtain monodisperse aerosols by condensation methods. Since the monodispersity decreases on coalescence, it is necessary to eliminate coalescence as far as possible during the preparation of monodisperse aerosols. From this it follows that the concentration given by the count (the number of particles in unit volume) of the aerosols generated should not be too high, or else they should be diluted considerably immediately after their formation. The maximum permissible concentration naturally depends on the time for which the aerosol being studied should remain unchanged under the conditions of the experiment. Since the aerosol coalescence constant under normal conditions has values of about $3 \times 10^{-10}$ cm$^3$ s$^{-1}$, we find that if the count concentration is to be decreased by not more than 5% after an experimental time $t$, the concentration should not exceed $1.7 \times 10^8$ cm$^{-3}$ for $t = 1$ s, $0.85 \times 10^7$ cm$^{-3}$ for $t = 20$ s, and $3 \times 10^5$ cm$^{-3}$ for $t = 10$ min.

The question of the conditions of formation of monodisperse "primary", i.e. non-coalesced, aerosols during the bulk condensation of a vapour is more complex. In this case it is obviously necessary that formation of all the aerosol particles should take place under exactly identical conditions, and in particular that the supersaturation be the same throughout the whole volume in which the condensation is taking place. This condition can be realised in practice only by producing the supersaturation by the adiabatic expansion of a vapour–gas mixture in a sufficiently large chamber, in which it is possible to neglect the decrease in supersaturation close to the walls, or by a homogeneous gaseous chemical reaction. In ordinary methods of generating condensation aerosols — by cooling a gas–vapour mixture in a heat exchanger or by mixing it with a cold gas — variations in the degree of supersaturation at different points in the gas stream and hence fluctuations in the size of the particles formed are unavoidable.

In spontaneous condensation of vapour, another unfavourable factor is introduced — the nuclei are not formed simultaneously, even when the supersaturation is constant throughout the volume. According to the general theory of new-phase formation, the rate of spontaneous formation of nuclei increases extremely rapidly with increase in supersaturation. Thus if the supersaturation were created instantaneously, the rate of production of new nuclei would decrease extremely rapidly as the supersaturation was eliminated, i.e. all the particles would have approximately the same age. Under real conditions, however, the supersaturation is produced at a finite rate and continues to increase for some time after the start of formation of the nuclei, passing through a maximum. The slower the increase in supersaturation, the less distinct this maximum, and the longer the time interval within which new nuclei may be produced. Thus spontaneous condensation generally leads to the formation of more or less polydisperse aerosols.

As in the case of colloidal solutions, aerosols with a much higher monodispersity are obtained by the "nucleus" method, i.e. by condensation on prepared (extraneous) condensation nuclei, which may be gaseous ions or highly dispersed aerosols of non-volatile substances. If these nuclei exhibit more or less identical activities, i.e. if the condensation of vapour on these nuclei begins at approximately the same supersaturation, an aerosol with an extremely high monodispersity should be formed.

In addition to the above factors which do not favour monodispersity in the formation of aerosols by condensation, there is a factor which effectively increases the monodispersity, namely the equalisation of particle dimensions during condensation growth. The rate of growth (increase in dimensions) of particles with a radius much less than the mean free path of the vapour molecules $l$ is independent of $r$, whereas when $r \gg l$ the rate of growth[26] is inversely proportional to $r$. Thus in the initial stage of the growth of nuclei of different ages the absolute difference in their dimensions remains constant, and later even begins to decrease. As a result, the relative difference in the size of the particles decreases appreciably as they grow. From this it follows, *inter alia*, that the degree of monodispersity of condensation aerosols should, generally speaking, increase with increase in the particle dimensions, as is observed experimentally. In this discussion we have neglected the increase in vapour pressure above very fine particles, but in the initial stage of the growth of the particles the supersaturation is usually fairly high, so that this factor is of no significance.

### 1. Preparation of Monodisperse Aerosols by the Adiabatic Expansion of a Vapour–Gas Mixture

From the above it follows that the most favourable conditions for the formation of monodisperse aerosols are achieved by condensing a vapour on prepared nuclei or by adiabatic expansion of a vapour–gas mixture. Unfortunately, this method has up to the present been used only to prepare fogs of volatile liquids, chiefly water, and the determination of the degree of monodispersity of the resulting fogs by direct measurement of the droplets is extremely difficult. For this purpose, only the optical methods described above can be used.

In the adiabatic expansion of moist atmospheric air containing a large quantity of condensation nuclei with widely differing activities, an extremely polydisperse fog is formed. If, however, this fog is allowed to disappear, partly by deposition of the droplets and partly by evaporation, the largest and most active (hygroscopic) nuclei will be removed, the total number of nuclei will be reduced considerably, and when the expansion is repeated a fog with a larger particle size and hence a higher monodispersity is formed. After several expansions, the purity of the halo colours indicates that extremely monodisperse fogs are produced[27].

2. Preparation of Monodisperse Condensation Aerosols in Generators of the Heat-Exchange Type

The nucleus method for preparing monodisperse aerosols from high-boiling substances was first applied by Sinclair and La Mer [28-31]. The generator which they designed in 1941 rapidly received extensive acceptance in aerosol studies. In this generator (Fig. 2) the liquid is placed in the vaporiser ($A$) — a 2 litre Pyrex flask placed in an air thermostat. Filtered air or nitrogen enters the vaporiser at a rate of not more than 4 litre $min^{-1}$, partly through a generator of condensation nuclei ($B$) and partly through a tube immersed in the liquid. The gas containing the vapour of the liquid, spray, and condensation nuclei passes through two narrow nozzles into a superheater ($C$) — a similar but empty flask placed in another thermostat at a slightly higher temperature. In the superheater the spray is vaporised, the contents of the flask are mixed, and the gas mixture passes into a condenser ($D$), 50 cm long and 2 cm in diameter, with air jacket, where the gas is slowly cooled and the vapour condenses, partly on the walls and partly in the space within the condenser, forming an aerosol. On leaving the condenser, the aerosol is diluted in the mixing vessel ($E$) with 10–100 times its volume of filtered air, to prevent coalescence.

Let us consider what happens in the condenser of the generator. In the vapour–gas mixture entering the condenser, the vapour is unsaturated, so that in the lower section of the condenser, only gradual cooling of the gas takes place under conditions of laminar flow, since the temperature of the gas near the axis of the condenser is higher than that at the walls. At a certain height, the dew point is reached at the walls and the vapour begins to condense there; the concentration of the vapour at the walls becomes less than that at the axis. In the absence of condensation nuclei (or when the rate of flow is too low), it is frequently found that almost all the vapour condenses on the walls, since the supersaturation is insufficient for spontaneous condensation in space. With an increase in the concentration of nuclei $n$, the ratio of the quantity of vapour condensed in space to that on the walls increases. Thus although the mean volume $v$ of the resulting droplets decreases, the product $nv$ increases. The dimensions of the droplets subsequently increase with increase in the concentration of vapour (at constant $n$), i.e. with increase in the temperature of the vaporiser. This makes it possible to control the particle size within certain limits. The temperature of the superheater has comparatively little influence on $\bar{r}$, however.

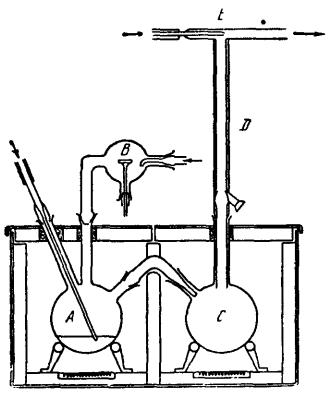


Fig. 2. Sinclair–La Mer generator.

To obtain aerosols with a low degree of dispersion corresponding to $\bar{r} > 1-2$ μm, a low concentration of nuclei and a high concentration of vapour are thus required. Since increase in temperature in the vaporising liquid may lead to its decomposition, it is recommended that the degree of vapour saturation of the gas be increased by bubbling the gas through a porous plate and by decreasing the rate of flow of gas through the nucleus generator [32-34]. Moreover, in the preparation of large droplets it is necessary to increase the duration of their growth, i.e. to use a longer condenser and to direct it not upwards but downwards, so that the rapidly-settling large droplets can leave the condenser. In this way it was possible to obtain monodisperse fogs of tetralin with $\bar{r}$ up to 27 μm. [33] On the other hand, La Mer used the generator to prepare an aerosol with $\bar{r} = 0.006$ μm; [35] but he was able to verify the monodispersity (by "cultivation") only for $\bar{r} > 0.02$ μm.

To obtain monodisperse aerosols with mean particle dimensions which do not change with time, a number of conditions must be satisfied in the Sinclair–La Mer generator. The temperature of the vaporiser should be constant to within 0.2 deg, otherwise, as we have seen above, the dimensions of the aerosol particles will change continuously. Because of the high heat capacity of the generator, the establishment of constant operating conditions requires about 6 h.

The purity of the vaporising liquid is extremely important — volatile impurities are particularly undesirable, since the dimensions of the particles decrease continuously as these are removed from the liquid. Since the liquid undergoes prolonged heating in the generator, it gradually decomposes, particularly when air is passed through; the walls of the vaporiser and superheater become covered with a deposit of decomposition products and the aerosol is no longer monodisperse [24]. It is therefore necessary to change the liquid and wash the generator at intervals. The decomposition is inhibited considerably in an inert gas atmosphere.

Thus the monodispersity of aerosols, generally speaking, increases with increase in $\bar{r}$, but it sometimes decreases sharply when a definite value of $\bar{r}$ has been reached [36]. This is probably due to the fact that spontaneous condensation of the vapour begins when the concentration of nuclei becomes too low. The same is observed when the vapour–gas mixture is cooled too rapidly in the condenser, for example when the flow rate in the condenser is too high [31].

It is also extremely important to have a constant concentration of condensation nuclei. Thus in the usual method of generating the nuclei, by the sublimation of sodium chloride or other substances, it is necessary to maintain the sublimation temperature and the rate of gas flow through the generator constant, since this affects the conditions of both the volatilisation and the condensation.

In agreement with theory, almost all authors report that aerosols obtained in the absence of nuclei are polydisperse (except for sulphuric acid aerosols, see below). The observations of Matijevich *et al.* [37] that in the production of AgCl aerosols the introduction of AgCl nuclei has no influence on the polydispersity of the aerosols ($\alpha$ = 0.20–0.25) are simply explained by the fact that these nuclei

were able to volatilise before condensation of the vapour on the nuclei had begun.

In most cases the nuclei are provided by highly-dispersed sodium chloride aerosols obtained by sublimation of the salt or, less frequently, by atomisation of dilute NaCl solutions followed by drying of the resulting fog [35,38]. Sometimes other salts, for example AgCl, [39] or metals [10] are sublimed; in the latter case a spark or arc discharge between metallic electrodes is frequently used [10,35,38]. In one method widely employed — sublimation of NaCl deposited on the surface of a nichrome wire which is made incandescent — allowance must be made for the fact that the salt recrystallises with the passage of time, so that the rate of its volatilisation and hence the concentration and dimensions of the nuclei decrease considerably [40]. It is therefore necessary either to "condition" the NaCl deposit for a prolonged period or to sublime the salt under conditions where the gas is saturated with its vapour [41].

Polydisperse aerosols containing large particles should not be used to provide nuclei. The use of an AgCl aerosol of this type gave polydisperse linolenic acid fogs [39], but when aerosols containing no large AgCl particles were used the monodispersity of the fogs increased considerably. Particularly unfavourable conditions are created when the condensation nuclei dissolve in the droplets of the fog being generated, decreasing the vapour pressure above the droplets. Petro [15] prepared a fog from aqueous NaCl solution by passing the NaCl aerosol through the vaporiser of a Sinclair–La Mer generator filled with water at room temperature. Since the walls of the condenser were very wet with water, the growth of the solution droplets took place in an atmosphere saturated with water vapour. Thus in the case of polydisperse NaCl aerosols containing large particles, a fairly polydisperse fog was obtained, but when an NaCl aerosol in which the radii of all the particles were less than 0.1 $\mu$m was used, it was possible to obtain fogs which gave Tyndall spectra.

It has not been possible to find condensation nuclei for all vapours. Thus mercury vapour does not condense on the nuclei usually employed [42]. Some gases, for example $NO_2$, bring about the condensation of mercury vapour, but monodisperse aerosols are not obtained in this way. Indigo vapour shows analogous behaviour [43].

On the other hand, $H_2SO_4$ vapour obtained from the 98–99% acid not only does not require the presence of nuclei for condensation but even condenses spontaneously in the presence of condensation nuclei [25]. The spontaneous condensation of these vapours makes it possible to obtain aerosols with $\overline{r}$ = 0.1–0.4 $\mu$m, giving Tyndall spectra [25,44].

Until recently, the Sinclair–La Mer generator was used to obtain monodisperse aerosols only from organic substances, sulphur, and sulphuric acid. Recently, Movillat [36] used a slightly modified generator to prepare a cadmium aerosol with $\overline{r}$ = 0.28 $\mu$m and $\alpha < 0.17$.

A considerably simplified generator is used in Kerker's laboratory [17,45]. The substance to be volatilised is placed in a boat in a long tubular furnace through which helium is passed. The gas, saturated with the vapour of the substance, leaves the furnace and passes through a tube, which apparently acts as an air condenser, into the chamber for examination. Since condensation nuclei are not used, aerosols with a fairly high polydispersity are obtained.

Rapaport and Weinstock [46] developed a fundamentally different design of heat-exchange generator (Fig. 3).

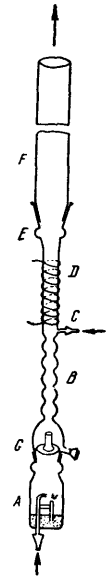



Fig.3. Rapaport and Weinstock's generator.

Filtered air passes at a rate of ~ 4 litre $min^{-1}$ into a pneumatic atomiser ($A$), which gives an extremely polydisperse fog. Large particles are deposited on the walls of the vaporiser, which acts as a screen. When the fog is passed through the column ($B$), further deposition of the large droplets takes place, and only droplets with $\overline{r} \leqslant$ $\leqslant$ 1 $\mu$m remain in the fog. Where necessary, the fog is diluted with air supplied through the side arm ($C$). The fog then passes into the volatiliser ($D$) (2.0 cm in diameter and 25 cm long), heated with a nichrome spiral, and the temperature is raised to a value at which all the drops volatilise. This is verified by the absence of a Tyndall cone at the point $E$. The gas–vapour mixture then enters the condenser ($F$) (2.5 cm in diameter and 120 cm long), where the vapour condenses on the nuclei which remain after volatilisation of the droplets and consist of the non-volatile impurities present in the liquid. The liquid which has not volatilised flows downwards over the walls into the ring ($G$) and leaves the generator.

This generator gives the same degree of monodispersity as the Sinclair–La Mer apparatus, but it has a number of important advantages: steady-state operating conditions are attained in times of the order of 10 min instead of several hours; the cost of the generator is much lower; decomposition of the substance has no effect, since the spent liquid is removed and fresh liquid is supplied continuously to the generator; and the quantity of liquid used is very small.

Another characteristic feature of this generator is that the temperature of the vaporiser need not be strictly constant, since under the condition that volatilisation of the primary drops is complete the concentration of the vapour is independent of temperature. Moreover, since the concentrations of both the vapour and the condensation nuclei are proportional to the concentration of primary drops, change in the latter again has no significant effect on the

particle dimensions of the aerosol generated. In order to decrease $\bar{r}$, air is introduced as diluent through the side arm (C), but this permits a change in $\bar{r}$ only within comparatively narrow limits.

As shown by Lassen[47], it is possible, by varying the distance from the atomiser to a special screen, to alter considerably the dimensions and number of primary droplets and hence $\bar{r}$. In this way Lassen was able to change $\bar{r}$ in a dioctyl phthalate aerosol from 0.15 μm to 0.7 μm at constant vaporiser temperature and constant rate of flow of air.

According to Berner's experiments[12], the purity of the liquid used is of considerable importance in the production of monodisperse aerosols in a Rapaport–Weinstock generator. Very pure liquids or liquids appreciably contaminated with high-boiling impurities give fogs with a greater polydispersity than those given by liquids with a low concentration of these impurities: in the first case, the nuclei remaining after the evaporation of the primary droplets are so fine that their growth requires a high supersaturation, at which spontaneous condensation is possible; in the second case, large polydisperse nuclei are formed.

Martius' generator[48], which is intermediate between the two assemblies described above, consists of a glass tube, 30 mm in diameter and 2 m long, arranged at an angle of 30° to the horizontal. The lower half of the tube is heated with a nichrome spiral and the upper part is fitted with a jacket and acts as condenser. Dry filtered air is passed into the tube at a rate of 0.3–3 litre $min^{-1}$. In the centre of the heated section of the tube there is a side arm containing a syringe, which is operated from a servo-motor and passes the fog-forming liquid to the lower wall of the tube at a controlled rate within the range $10^{-3}$–$10^{-2}$ ml × × $min^{-1}$. The air–vapour mixture is then superheated and passes to the condenser, in the jacket of which water at a controlled temperature is circulated (for dioctyl phthalate a temperature of 17° is recommended).

In this generator the products of the thermal decomposition of the liquid being vaporised are not removed from the heated zone. It is thus hardly possible to maintain steady-state generating conditions over more or less prolonged periods. Martius does not mention this, and the data which he gives[16] do not indicate the monodispersity of the fog generated.

The generator of Fuks and Sutugin[49] is a modification of Kogan and Burnasheva's mixer-generator[50] (see below). The gas containing the condensation nuclei, before being mixed with the hot gas containing the vapour of the liquid, is heated to the temperature of the hot gas, after which the mixture is passed to the condenser. In the ultramicroscope study of dibutyl phthalate fogs with $\bar{r}$ = 0.61–1.3 μm and $\alpha$ = 0.02–0.12, obtained in this generator, it was found that the distribution of the droplets with respect to dimensions approximates more or less satisfactorily to the normal distribution. It was later found that, with decrease in the concentration of nuclei $n$, the mean radius of the particles increases only to a certain limit and then remains constant. Thus, at a vaporiser temperature of 95° and a flow rate of gas equal to 2.8 litre $min^{-1}$, the maximum value of $\bar{r}$ is 0.9 μm (at $n = 1.5 \times 10^3$ $cm^{-3}$). Calculation showed that for this value of $n$, only ~ 2% of the total vapour condensed on the nuclei, while the rest condensed on the walls of the condenser. Thus under these conditions, the supersaturation of the vapour inside the condenser is determined almost entirely by the rate of condensation of the vapour on the walls and is independent of the concentration of nuclei.

## 3. Preparation of Monodisperse Condensation Aerosols in Generators of the Mixer Type

A generator of the mixer type was designed by Kogan and Burnasheva[50]. Filtered gas passes at a rate of ~ 1 litre $min^{-1}$ through a vaporiser (A) (Fig. 4), which is placed in a thermostat and is filled with large-pore silica gel impregnated with the liquid to be evaporated; the gas then passes in a narrow stream into the conical nozzle (B) of the mixer. Cold gas containing condensation nuclei passes at a rate of ~ 4 litre $min^{-1}$ through the tube (C) and a narrow annular gap (whose width can be varied) into the same nozzle. The degree of supersaturation in the mixture depends on the nature of the liquid, the velocity of the two gas streams, the temperature of the mixer, the concentration of nuclei, and the width of the annular gap; it is controlled in such a way that the supersaturation is not so high that spontaneous condensation begins, or so low that all the vapour condenses on the walls of the mixer. For liquids with a high boiling point (dioctyl sebacate), it was possible to use gaseous ions as condensation nuclei. In this generator the mean dimensions of the particles cease to depend on the concentration of nuclei $n$ at high values of $n$, of the order of $10^4$ $cm^{-3}$, probably because the ratio of the quantities of vapour condensing on the nuclei and on the walls is even lower than that in heat-exchange generators. At a higher concentration of nuclei ($n > 10^6$ $cm^{-3}$) the volume of the particles is approximately inversely proportional to $n$. The methods used to vary $\bar{r}$ are the same as those for the Sinclair–La Mer generator. The degree of monodispersity and the shape of the curves giving the distribution of the particles with respect to dimensions in the aerosols obtained in this generator and in the Fuks–Sutugin generator are approximately the same.

Fig. 5 shows a typical distribution of droplets with respect to dimensions (on a probability graph) in dibutyl phthalate fogs which we prepared in a Kogan–Burnasheva generator[49]. The distribution approximates to the normal distribution given by the straight line.

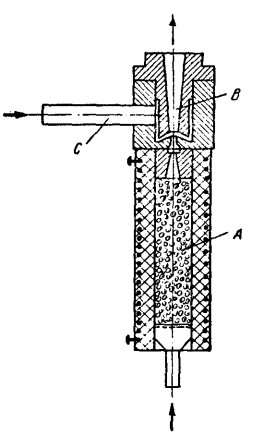



Fig. 4. Kogan and Burnasheva's generator.

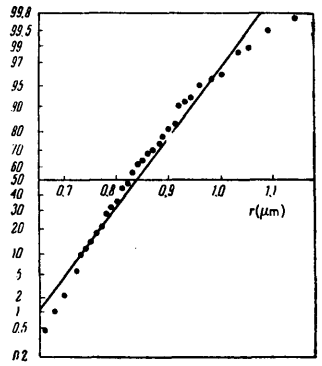



Fig.5. Distribution of particles with respect to dimensions in dibutyl phthalate fog.

In some cases, mixer-generators give fairly monodisperse aerosols even without extraneous condensation nuclei, for example from sulphuric acid (see above). In some cases atmospheric condensation nuclei appear to have been used, although no reference was made to these. Nuclei of this type are probably responsible for the production of dioctyl phthalate aerosols with $\overline{r}$ = 0.1–0.2 μm, giving Tyndall spectra, in mixer-generators [51,52].

### 4. Formation of Monodisperse Condensation Aerosols as a Result of a Chemical Process

There are very few data on this subject. An extremely promising method involves the preparation of monodisperse aerosols by photochemical or radiochemical gas reactions. When nitrogen containing methyl acrylate or methyl methacrylate vapour but no condensation nuclei was passed through a quartz tube illuminated with ultraviolet light, polymer aerosols with $\overline{r}$ = 0.05–1 μm, giving Tyndall spectra, were obtained [53]. When sufficiently fine condensation nuclei were introduced, it was possible in this way to obtain an aerosol with an extremely high monodispersity, since in this case it is possible to achieve constant supersaturation of the polymer vapour throughout the whole period of growth of the particles.

Fogs of aqueous ammonium chloride solution, with $\overline{r}$ = 0.15–0.40 μm and $\alpha \simeq 0.10$, were prepared by mixing $NH_3$ and HCl, in a long vertical tube, with air which had been saturated with water vapour and freed from gaseous-ion condensation nuclei [54].

In concluding this section we would point out that the particles of condensation aerosols obtained at low temperatures, at which no thermoelectronic emission takes place, are uncharged or very weakly charged (as a result of capture of atmospheric ions).

## III. PREPARATION OF MONODISPERSE AEROSOLS BY DISPERSION METHODS

The extremely varied dispersion methods for preparing monodisperse aerosols can be divided into three groups: (1) atomisation of liquids; (2) atomisation of monodisperse suspensions; and (3) atomisation of monodisperse powders.

### 1. Preparation of Monodisperse Aerosols by Atomising Liquids

The mechanical atomisation of liquids in jets, nozzles, etc. is used in many branches of technology and generally produces extremely polydisperse fogs. The mechanism of atomisation in all cases involves the action of hydraulic pressure or centrifugal or aerodynamic forces which draw the liquid out into a fine stream or film [55] which then breaks down to form droplets under the influence of surface tension. The finer the liquid stream or film, the smaller the resulting droplets, but the degree of polydispersity is always high.

On the other hand, it is known that, when a liquid is drawn slowly from a capillary tip, drops with constant dimensions are formed, although these are accompanied by very fine droplets or satellites. The latter are formed from the fine thread of liquid joining the droplet to the rest of the liquid before the actual rupture. The radius $r$ of the main drops is determined from the condition that the force of gravity on the drop $G$ and the capillary force $H$ are equal at the moment when the neck of the drop begins to narrow

$$G = \frac{4}{3}\pi r^3 \gamma g = H = 2\pi\rho s k, \qquad (4)$$

where $s$ is the surface tension, $\gamma$ the density of the liquid, $\rho$ the radius of the neck when it begins to narrow, approximately equal to the radius of the capillary from which the liquid is flowing, and $k$ is a numerical constant of the order of unity. It can readily be shown that only droplets of the order of 1 mm can be obtained in this way, even from very fine capillaries.

To obtain finer droplets, it is necessary to increase considerably the force causing the drop to break away. Lane [56] suggested that this be done by blowing a fine stream of air downwards against the capillary (syringe needle with an internal diameter of 0.45 mm). When the needle was placed exactly along the axis of a short tube (diameter 2.5 mm) through which the air was blown, it was possible to obtain water droplets with values of $r$ in the range 0.15–0.50 mm, depending on the velocity of the air and the rate of supply of liquid $V$. The value of $\alpha$ decreased from 0.012 to 0.005 with increase in $\overline{r}$, i.e. the degree of monodispersity was very high. Finer droplets could be obtained by using finer needles or by placing wires inside the needles, and by decreasing $V$.

Other workers [57], unlike Lane, did not allow the liquid to flow spontaneously [under the action of gravity (Ed. of Translation)] into the needle but forced the liquid into the needle by means of a micro-plunger. In spite of this, the degree of monodispersity was slightly lower than that obtained by Lane: the value of $\alpha$ varied in the range 0.11–0.05 for values of $\overline{r}$ in the range 22–220 μm.

Lane's generator has a very low output. When an attempt was made to increase the output by means of a battery of 169 needles with an internal diameter of 0.22 mm, the degree of monodispersity decreased sharply, the decrease being greater, the smaller the droplets [58]. For $\overline{r}$ = 0.45 mm, $\alpha$ = 0.22. The reason for the polydispersity was the small difference between the internal and

external diameters of the needles, the latter determining the flow-rate profile in the surrounding stream; moreover, the drops obtained in the middle of the battery were larger than those obtained at the edges. The output of the battery was 200 g of water per minute for $\overline{r}$ = 0.5 mm and 20 g per minute for $\overline{r}$ = 0.1 mm. The monodispersity of the fog generated in the battery could probably be increased considerably if it were constructed with greater precision.

Much finer droplets can be obtained by centrifugal force in the so-called disc atomisers consisting of a horizontal disc rotating around a vertical axis passing through its centre. The liquid supplied to the disc flows to the tapered edge of the disc. At a high flow rate of liquid the latter forms a thick ring on the edge of the disc from which streams or films are drawn out to give a polydisperse fog.

Walton and Prewett[59] discovered, however, that when the flow rate of liquid is sufficiently low, so that it forms a very thin layer on the surface of the disc and a narrow ring at the edges, individual droplets are torn from the latter. If the liquid is supplied to the exact centre of the disc and its surface is effectively wetted by the liquid, the thickness of the ring is constant over the whole perimeter and droplets with equal dimensions are formed (together with much finer satellite droplets).

From the theory of the breaking away of drops from a wall which they are wetting, it follows that in this case the quantity $\rho$ in Eqn. (4) should be replaced by a quantity close to the radius $\overline{r}$ of the actual drop. Further replacement of $g$ by $\omega^2 D/2$, where $\omega$ is the angular velocity of the disc and $D$ its diameter, and of $r$ by $d/2$, where $d$ is the diameter of the drops, gives

$$d\omega (D\gamma/s)^{1/2} = C. \qquad (5)$$

The value of the constant $C$ is $\sqrt{12} = 3.47$.

In Walton and Prewett's experiments at low rates of rotation the values of $C$ were in fact close to 3.47 for organic liquids which effectively wetted the surface of the disc; the value was slightly lower for water, which did not wet the disc effectively. At very high values of $\omega$, equal to several hundred rev $s^{-1}$, the liquid is unable to acquire the tangential velocity of the disc, the drop dimensions are greater than the theoretical, and the values of $C$ reach 5.

Water droplets with $\overline{r}$ = 0.1–1.5 mm were obtained on a disc rotating at 10–50 rev $s^{-1}$, and droplets of non-volatile liquids with $\overline{r}$ down to 8 $\mu$m were obtained at 1500 rev $s^{-1}$. Methyl salicylate droplets with $\overline{r}$ = 0.9 mm were obtained with a disc diameter of 4 cm and a velocity of 15 rev $s^{-1}$. At a flow rate of liquid $V \leq 0.4$ ml $s^{-1}$, the mass of the main droplets is greater by several orders of magnitude than the mass of the satellite droplets, but increase in $V$ leads to an increase in both the relative number and dimensions of the satellite droplets, and at $V$ = 2.8 ml $s^{-1}$ an obviously polydisperse fog is formed. The greater the rate of rotation and the smaller the diameter of the disc, the smaller should be the value of $V$ necessary to obtain a monodisperse fog. Since the droplets fly further from the disc the greater their dimensions, it is possible, when the satellite droplets are much smaller than the main droplets, to separate the two by surrounding the disc with a jacket sectioned to allow the passage of the main droplets.

In May's experiments[60], the flow rate of liquid was very low ($\leq$ 1 ml $min^{-1}$) and more attention was paid to the application of the liquid exactly in the centre of the disc and to the determination of the degree of monodispersity of the fog generated. For dibutyl phthalate fog with $\overline{r}$ = 32 $\mu$m, $\alpha$ = 0.014, and for a water fog with $\overline{r}$ = 22 $\mu$m, $\alpha$ = 0.031, i.e. in the second case the monodispersity was slightly lower, in agreement with what was said above. The value of $\alpha$ changes little with the mean dimensions of the droplets, but increases appreciably as $\overline{r}$ approaches the height of the irregularities on the disc surface. It is therefore recommended that the disc be polished and treated with wetting agents to improve its wettability with water.

Boshoff[61], working with a large disc ($D$ = 35 cm) at 2.7–27 rev $s^{-1}$, found that monodisperse fogs with $\overline{r}$ = = 0.35–1.15 mm are formed only at $6 < V < 22$ ml $s^{-1}$. The existence of the lower limit for $V$ is undoubtedly due to rupture of the layer of liquid when it becomes very fine (the actual thickness is not stated) on the surface of the disc. Ryley[62], working at $D$ = 5 cm, $V$ = 0.4–0.8 ml $s^{-1}$ and a velocity of 1000 rev $s^{-1}$, obtained water droplets with $\overline{r}$ = 11 $\mu$m, but no data on the degree of monodispersity are given. Monodisperse fogs can also be obtained on conical dishes with tapered edges, rotating about a horizontal axis[55].

The output of disc atomisers is higher than that of other monodisperse-fog generators; a slight inconvenience associated with their use is that the drops fly in all directions.

The mechanism of operation of a generator with a vibrating capillary, proposed by Dimmock[63], is not quite clear. A glass tube is drawn out at one end to form a 20 cm long capillary with an external diameter of 0.6 mm. A piece of steel needle from a syringe is fixed to the capillary at a distance of 2–5 cm from its base. An electromagnet supplied with alternating current is used to vibrate the capillary and the liquid fed to the latter is atomised to give drops of identical dimensions. The dimensions of the capillary are chosen in such a way that it is brought into resonance with the forced vibrations. From the diagram published in the paper, it is evident that the liquid is thrown not from the tip of the capillary, as stated in the text, but from the side opening, and individual droplets are torn away. Since 100 drops per second were torn from the capillary, the frequency $\nu$ of the vibrations was evidently 50 c $s^{-1}$. The maximum acceleration of the capillary tip is $(2\pi\nu)^2 a$, where $a$ is the amplitude of the vibrations, with an order of magnitude in any case not more than 1 cm. Thus according to Eqn. (4), only water drops with $\overline{r}$ = 0.5 mm could be obtained in these experiments. In actual fact, Dimmock obtained drops with $\overline{r}$ = 5–150 $\mu$m, and this is extremely difficult to explain. All other workers[64–66] working with a generator of this type obtained drops with $\overline{r} \geq 150$ $\mu$m. Ryley[62] pointed out that a quite different mechanism of drop formation is possible. By using a syringe needle with an internal diameter of 0.14–0.61 mm and a tip polished at right angles to the axis, and by making this needle vibrate at a frequency of 200–3000 c $s^{-1}$, Ryley obtained a fine sinusoidal stream of liquid, which broke down to form droplets at a certain distance from the capillary. In order to obtain a monodisperse fog with $\overline{r}$ = = 0.15–0.68 mm, the stream had to be broken down into fragments with a length equal to the total period of the sinusoid $\lambda$. In agreement with Rayleigh's theory, breakdown in this way is favoured when the ratio of $\lambda$ to the thickness of the stream has the value 4.5 or a multiple of this figure. In this case the volume of the drops formed is directly proportional to the linear velocity of the stream. The capillary may be vibrated extremely simply by directing over it a narrow stream of compressed air[67].

In Mason's laboratory[68] needles with an internal diameter of 0.1 mm and a frequency of vibration equal to 1000 c $s^{-1}$ were used to obtain water drops with $\overline{r}$ = 15 $\mu$m.

In the same laboratory use was made of the phenomenon of reflection of water droplets falling on the surface of water at a definite velocity and at a definite angle. When an electric potential is applied to the vibrating needle, the drops which are torn away are charged, and lose some of their mass when reflected from water, the quantity lost being greater, the higher the potential. Thus the drops leaving the water are identical and smaller than the primary drops; moreover, their dimensions can be controlled within certain limits. When the potential is sufficiently high, the drops falling on the water surface are completely absorbed, but by applying an additional pulsating voltage to the needle it is possible to vary at will the frequency of formation of the secondary droplets and the distance between them, and this is very convenient in certain studies [69].

In the work cited transverse vibrations of the capillary were used; analogous results are obtained with longitudinal vibrations. If pressure pulsations are applied to a liquid in a vessel with a narrow side-tube, large drops with a high degree of monodispersity are ejected from the tube [66], and in this case, unlike the case of the vibrating-capillary generators, no satellite droplets are formed. Drops with $\overline{r}$ = 1–4 mm were prepared in this way; with increase in $\overline{r}$, $\alpha$ decreased from 0.005 to 0.002.

A similar method is based on the following principle. When a point is rapidly immersed in a liquid and then removed, a connection is formed between the point and the liquid surface and is drawn into a fine thread. This thread breaks away first from the liquid and then from the point, and forms a drop which flies in the direction of movement of the point. This process is repeated periodically by using a vibrating point. The size of the drops is determined by the nature of the liquid, the shape and dimensions of the point, the frequency and amplitude of the vibrations, the wettability of the point, and, more particularly, the depth of its immersion in the liquid. It is extremely convenient to work with a liquid which flows slowly from a capillary. In this case the depth of immersion of the point and the dimensions of the droplets generated increase with increase in the dimensions of the drop hanging from the capillary. As a result, the rates of flow and atomisation (ml $s^{-1}$) are equalised automatically and the dimensions of the droplets are determined only by the flow rate. Drops with $\overline{r}$ = 25–200 μm can be obtained in this way, at 100 vibrations $s^{-1}$. [70,71]

In Wolf's experiments [72] the point (a rod with a diameter of 10–50 μm) was immersed not in a hanging drop but in the meniscus of a liquid filling a horizontal slit cut in a piece of porous glass, through which the liquid was passed. At a frequency of 120 c $s^{-1}$, drops of water and aqueous solutions with $\overline{r}$ = 5–100 μm, and drops of molten wax and paraffin with $\overline{r}$ = 2–20 μm, were obtained. In the latter case the rod was immersed vertically in the free surface of a melt, held accurately at a constant level.

The vibrating rod may be replaced by a 3 mm broad, 0.5 mm thick plate with a tapered end, cut from a safety razor blade and rotating at 10–20 rev $s^{-1}$. [73] Drops with $\overline{r}$ = 40–350 μm were obtained in this way from aqueous solutions and Diesel fuel flowing from a capillary. To obtain monodisperse drops, it is important that the capillary and blade be effectively wet by the liquid. In contrast to the work with a vibrating point, where the monodispersity was estimated visually from photomicrographs of the droplets, the work cited gave numerical data: $\alpha$ = 0.012–0.22 for $\overline{r}$ = 50–60 μm.

The electrostatic atomisation of liquids, now used for painting manufactured articles, depends on the repulsion forces between the electric charges on the liquid surface. These forces decrease the surface tension of the liquid, and when they are sufficiently high the surface of the liquid becomes unstable. In small protuberances formed randomly on the surface, the charge density increases, the repulsion forces become greater than the surface tension, and the raised section is drawn out into a thread, rupture of which produces a drop.

In accordance with the foregoing, the immersion of an electrode into a vessel containing a liquid flowing through a capillary, and the application of a voltage of constant sign and increasing magnitude to the electrode lead to a decrease in the surface tension, and the dimensions of the droplets decrease, in accordance with Eqn. (4), while the frequency of their formation increases. In this way it is possible to obtain several hundred drops (accompanied by satellite drops) of identical dimensions per second, with $\overline{r}$ varying from 50 μm to several hundred μm. [74,75]

At a certain critical voltage the nature of the process changes sharply; in addition to a stream of comparatively large drops, a broad beam of highly-dispersed fog giving Tyndall spectra begins to be formed. At the critical voltage, the above-mentioned process of liquid-thread formation evidently begins. It cannot yet be stated with certainty why the threads give a monodisperse fog.

In most work using this method glass apparatus was employed, and it was found that a highly-dispersed fog can be obtained only when the sign of the voltage applied to the electrode is positive and when the conductivity of the liquid lies between $10^{-13}$ $\Omega^{-1}$ $cm^{-1}$ and $10^{-5}$–$10^{-6}$ $\Omega^{-1}$ $cm^{-1}$. Distilled water, alcohol, and other polar liquids lie in this range [76]. When the conductivity is very low (non-polar liquids) the charges evidently accumulate too slowly on the liquid surface. When the conductivity is high (electrolyte solutions), atomisation is apparently accompanied by a corona discharge from the regions of the surface with high curvature, and this prevents the formation of threads.

When a metal capillary — a syringe needle connected to a voltage source, with tip polished at right angles [77,78] — is used and an earthed metallic plate is set up parallel to the needle at a short distance from it, the atomisation becomes much easier; fairly highly-dispersed fogs of any liquid, including non-polar liquids and dilute electrolyte solutions, could be obtained, irrespective of the sign of the potential. The dimensions of the droplets decreased with increase in the voltage, and drops with $\overline{r}$ = 1 μm could be obtained.

Unfortunately, there are very few data on the degree of monodispersity of the fogs obtained by means of an electric field: it is known only that in highly-dispersed fogs obtained in this way, Tyndall spectra are observed, and there are no data for larger drops. The drops have high charges, with the same sign as the electrode, and in a number of cases this limits their application.

Mention must be made of some less important methods. When air is bubbled from narrow capillaries through distilled water or sea water, a polydisperse fogs forms from the bursting bubbles, but segregation of the droplets according to size takes place in the ascending current of air and collection of the droplets at a definite height makes it possible to obtain monodisperse drops with $\overline{r}$ = 1–250 μm. [79]

Ultrasonic atomisation appears to give fogs with fairly high polydispersity [80].

## 2. Preparation of Monodisperse Aerosols by Atomising Suspensions

When non-aggregated monodisperse suspensions in water or other volatile solvent are atomised under conditions where not more than one particle is present in each drop, drying of the resulting fog should obviously produce monodisperse aerosols. This method of generating aerosols was first used by microbiologists, who prepared bacterial aerosols in this way. The atomisation of suspensions acquired practical importance as a method for generating monodisperse aerosols with the introduction of monodisperse polystyrene latexes with accurately spherical particle shape, developed by the Dow company. In these latexes, $\alpha$ is equal to $\sim 0.09$ at $\bar{r} = 0.044$ μm, $\sim 0.04$ at $\bar{r} = 0.07$–$0.09$ μm, 0.015–0.023 at $\bar{r} = 0.13$–$0.28$ μm, and $\sim 0.012$ at $\bar{r} = 0.4$–$0.6$ μm.[81]

The latexes contain $\sim 7\%$ of polymer and before atomisation are diluted extensively with distilled water. The resulting fog is dried by mixing with dry filtered air. In the first experiments on the preparation of monodisperse aerosols with $\bar{r} = 0.17$–$0.49$ μm by this method it was found that the degree of monodispersity is much lower than that of the latexes themselves[82], and in most cases $\alpha$ varied from 0.11 to 0.16 (the dimensions of the particles were determined with a photoelectric counter). This phenomenon may be due to the presence of more than one particle in the drops, leading to the formation of twins, etc., when the drops are dried, and to the presence of the water-soluble non-volatile emulsifier in the latexes ($\sim 30\%$ of the weight of polymer). Thanks to the emulsifier, the latex particles do not aggregate even on extensive dilution of the suspension, but with complete removal of the emulsifier, coagulation of the suspensions is unavoidable. The probability that the drop contains more than one particle depends on the concentration of the suspension and on the dimensions of the drops and particles. If it is assumed that a concentration of 5% of twins in the aerosol is permissible (in this case the number of triplets, etc. will be negligible), we find from Poisson's formula that, for the mean drop radius of $\sim 1$ μm attainable in practice by means of special atomisers, the concentration of the suspension should not exceed 1% for a particle radius $\bar{r} = 0.5$ μm, $\sim 0.1\%$ for $\bar{r} = 0.25$ μm, and $\sim 0.01\%$ for $\bar{r} = 0.1$ μm. These conditions have obtained in most work.

The greatest difficulty is due to the presence of emulsifiers in the suspension; we have already seen that its complete elimination is impossible. The emulsifier is apparently extremely hygroscopic, and when the above method is used to dry drops containing polymer particles, a coating of concentrated emulsifier solution is deposited on the particles; when drops containing no particles are evaporated, "blanks" of the same solution are left. Moreover, it follows from Poisson's formula that when the number of twins is low, the number of "blanks" should be much greater than the number of droplets with polymer particles.

This was observed particularly clearly in work by Langer and Lieberman[83]. In the atomisation of a suspension prepared by tenfold dilution of a latex with $\bar{r} = 0.407$ μm, into a chamber containing air with a moisture content of 4%, study of the resulting aerosol by means of a photoelectric counter showed that the concentration of particles was 25 times the calculated value, because of the presence of the "blanks". The radius of the "blanks" varied from the limit of sensitivity of the counter ($\bar{r} \simeq 0.25$ μm) to 1.5 μm, the mean radius of the aerosol particles was 0.7 μm, and the value of $\alpha$ was 0.39.

When the fog was heated to 165°, the number of particles recorded by the counter decreased by a factor of 10–100; the radius of most of the completely dried "blanks" was evidently less than 0.25 μm and was not recorded by the counter. The maximum particle radius decreased to approximately 0.5 μm, approaching the true radius of the polymeric granules. An analogous effect was observed for hundredfold dilution of the latex: in the aerosol dried at room temperature, $\bar{r}$ decreased to 0.55 μm and $\alpha$ to 0.22; the number of "blanks" recorded decreased considerably, because of their smaller size.

It must be emphasised that in the microscopic measurement of the particles the emulsifier solution, which effectively wets the support, flows over the latter in a very thin film and cannot be seen. Thus the authors who studied these aerosols only by the microscope method concluded that the aerosols had a high monodispersity[84,85]. However, the presence of a large number of "blanks" could also be detected under the microscope in the deposit from an aerosol with $\bar{r} = 0.407$ μm, obtained in an electrostatic sorter, in which the particle dimensions are determined from their position in the deposit[86]. In other work[87] with an aerosol prepared from the same latex and deposited in a centrifugal sorter (conifuge) in which the particle dimensions are determined in analogous fashion, the value found for $\bar{r}$ corresponded to the dimensions of the particles in the latex, and the influence of the emulsifier was revealed only in the increase in the value of $\alpha$ from $\sim 0.012$ to 0.11. In the second case the degree of dilution was probably greater and the drop dimensions smaller, than in the first case.

Aerosols have also been prepared by atomising extremely highly monodisperse AgI suspensions[88]. Since coagulation took place during purification of the suspensions from the salts present, the monodispersity of the aerosols was probably low.

A monodisperse aerosol with very fine particles was prepared by atomising suspensions, thoroughly freed from all impurities, of *E. coli* bacteriophage T3 with $\bar{r} = 17.5$ mμ and $\alpha = 0.07$. Electron-microscope study of the suspension and the aerosol prepared from it showed that the particle distribution with respect to dimensions was the same in each[89].

## 3. Preparation of Monodisperse Aerosols by Atomising Powders

The chief disadvantage of the above method for generating monodisperse aerosols, associated with the presence of dissolved substances in the suspensions, is obviously eliminated in the atomisation of dry monodisperse powders, but in this case other difficulties arise. Powders with $\bar{r} > 5$ μm are comparatively readily atomised by compressed air, with the formation of aerosols containing completely disaggregated particles, but with decrease in the particle size the atomisation becomes more difficult and for powders with $\bar{r} < 0.5$ μm, complete atomisation has not yet been achieved. Important factors, in addition to particle size, are the shape, elastic properties, and moisture content of the particles. Lamellar or acicular particles are more difficult to atomise than spherical particles. Powders of hard materials are more readily atomised than those from soft materials. Increase in the moisture content of the particles leads to a sharp decrease in the ease of atomisation, but powders which have been

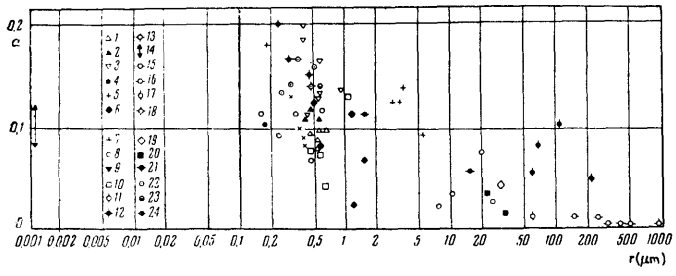



Fig. 6. Characteristics of monodisperse aerosols prepared by different methods, from published data.
Condensation method: aerosols from:
1) dioctyl phthalate[46]; 2) dioctyl phthalate[120]; 3) dioctyl phthalate[10,11]; 4) dioctyl phthalate[138]; 5) dioctyl phthalate[119]; 6) dibutyl phthalate[49]; 7) glycerol[125]; 8) tetralin[33]; 9) stearic acid[36]; 10) stearic acid[143]; 11) linolenic acid[39]; 12) linoleric acid[19]; 13) sodium chloride[45]; 14) sodium chloride[41]; 15) cadmium[36].
Atomisation of liquids:
16) blow capillary, water[56]; 17) rotating blade, mineral oil[73]; 18) pulsating pressure, water[66]; 19) rotating disc, water[126]; 20) dibutyl phthalate[60]; 21) electrostatic atomisation, butyl benzoate[78].
Atomisation of suspensions:
22) latex[82]; 23) spores of *B. globulis*[144].
Atomisation of powders:
24) lycopodium[105].

over-dried are also difficult to atomise, because of the high triboelectric charges.

Elutriation under the influence of gravity or in a centrifuge can be used to obtain powders with any degree of monodispersity, but the method is time-consuming. The well-fractionated glass powders consisting of spherical particles, supplied by some Non-Soviet firms, are very convenient. Powders with extremely high monodispersity are also found in nature. Thus in lycoperdon spores $\bar{r}$ = = 2.09 μm and $\alpha$ = 0.08;[90] in maize-rust spores $\bar{r}$ = 3.9 μm and $\alpha$ = 0.038;[91] and in clover pollen $\bar{r}$ = 26 μm and $\alpha$ = = 0.04.[92] Because of its availability, lycopodium spores with $\bar{r}$ = 15 μm and $\alpha$ = 0.10 have been most widely used[93].

In concluding this section we would point out that in all aerosols obtained by dispersion methods, with the exception of fogs formed by non-polar liquids, the particles have fairly high charges of either sign. In some studies this property is extremely undesirable.

Fig. 6 gives data on the particle size and degree of monodispersity of aerosols obtained by condensation and dispersion methods.

## IV. APPLICATIONS OF MONODISPERSE AEROSOLS

The titles of most papers describing the use of monodisperse aerosols for different purposes do not mention the application. In many cases the application is mentioned only in a few lines in the text of a paper. Moreover, monodisperse aerosols are used in the solution of an extremely varied range of problems, and the appropriate papers may be found in specialised journals of the widest range. All this makes a search of the literature on this subject extremely difficult, and cannot but be reflected in the completeness with which it is covered in a review.

Monodisperse aerosols have been used in the study of various optical properties of aerosols (condensation aerosols[24,31,39,94-96] prepared from latexes[85,97] or lycopodium[98]); the absorption of sound in aerosols (lycoperdon[99]); the vibrations of particles in a sonic field (condensation[100]); deposition of aerosols on obstacles from a stream (condensation[101-103], latex[104], and lycopodium[105]), on the walls of tubes from a turbulent stream (lycopodium[106]), in impactors (condensation[101], lycopodium[107], and latex[142]), in thermal precipitators (condensation[108], disc atomiser[109]), in electrostatic precipitators (latex[84]), and in breathing apparatus (condensation[110], atomisation of bacterial suspensions[111]); methods for sampling aerosols (condensation[112], fractionated powders[113]); diffusion deposition during flow in narrow channels (condensation[114]); sedimentation and diffusion in a cell (condensation[115]); filtration of aerosols through fibrous filters (condensation[24,31,115-122], latex[123], bacterial and virus suspensions[124,144]) and granular filters (condensation[121]); the efficiency of collisions between drops and solid walls (condensation[125], vibration atomiser[70]), liquid surfaces, and one another (vibration[64,65] and disc[126] atomisers); the charges of particles in condensation aerosols during their formation[127] and during charging by an ion beam[119,128]; the elution of aerosols by rain (lycopodium[129]); the dependence of the efficiency of insecticides and herbicides on drop dimensions (condensation[32], disc atomiser[130,131]); the supercooling of droplets[132] and their vapour pressure (condensation[38]); the ice-forming power of AgI particles (atomisation of a suspension[88]); the movement of coarse dust in tubes (glass spheres[133]); the activation of aerosols by radioactive gases (condensation[134], latex[134]); the chemical reaction of aerosols with gases (condensation[44]); and the lubrication of ball bearings with oil fogs (disc atomiser[135]). They have also been used to verify Stokes' law (lycoperdon[90]) and Kelvin's law (condensation[22,23]), to prepare monodisperse emulsions (condensation[136], electrostatic atomisation[78]); for the calibration of instruments used for the dispersion analysis of aerosols — photometers (latex[137]), photographic[138], photoelectric (condensation[139]), and thermoelectric (vibration atomiser[67]) counters (sorters), and electrostatic (condensation[128]) and centrifugal (condensation[140], latex[87,141]) sorters.

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# THE PRESENT STATE OF THE ANALYTICAL CHEMISTRY OF TECHNETIUM

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## I. INTRODUCTION

Interesting properties of technetium have been discovered in recent years. Unlike its nearest analogue, the perrhenate ion, the pertechnate ion exhibits exceptional anti-corrosion properties[1], greatly superior to those of $CrO_4^{2-}$ ions. For example, iron which has been immersed in ammonium pertechnate solution with a technetium concentration of only 5 $\mu g\ ml^{-1}$ undergoes no rusting over a period of several years. This reveals promising possible applications of technetium compounds as effective inhibitors of the corrosion of iron and steel. These compounds may prove particularly useful for preventing the corrosion of homogeneous boiling reactors[2], certain submarine parts, etc.

Metallic technetium and its alloys (for example an alloy containing 50% Tc and 50% Mo) are superconductors at low temperature[3,4] and can be used to replace super-purity niobium in inertial control systems in rocket technology[2], as memory elements in electronic machines[5,6], and in thermonuclear-synthesis assemblies for the production of magnetic fields of high intensity[6]. Many fundamental properties of this element have not been studied, since large quantities are not available. When larger quantities are produced, new properties of technetium and extensive possibilities for its use in industry may be revealed.

Thus the problems of preparing large (kilogramme) quantities of technetium and separating it from the neighbouring elements rhenium, molybdenum, and ruthenium are now of pressing importance. It is therefore of interest to examine the latest achievements in the analytical chemistry of technetium, since recent reviews on the chemistry of technetium[6-12] devote little space to this topic, and there are no special reviews on the subject.

## II. METHODS OF ISOLATING AND CONCENTRATING TECHNETIUM

A large number of technetium isotopes with mass numbers from 92 to 107 and half-lives from several seconds to $2 \times 10^6$ years are now known. The most important isotopes of technetium, their radioactive characteristics, and methods of preparation are given in Table 1.[13]

Four of the isotopes given in Table 1: $^{95m}Tc$, $^{96}Tc$, $^{97m}Tc$, and $^{99m}Tc$, are used as tracer atoms in the study of the chemical properties of technetium. The most readily available for this purpose is the nuclear isomer $^{99m}Tc$, which is formed with high specific activity from molybdenum irradiated with neutrons. The other three isotopes: $^{97}Tc$, $^{98}Tc$, and $^{99}Tc$ are long-lived, with half-lives $>10^5$ years, and can be used for the study of the chemistry of technetium in ponderable quantities. The last of these isotopes is the most readily available, since it is formed by the fission of uranium and plutonium nuclei or by the prolonged irradiation of molybdenum in a reactor.

TABLE 1. Most important isotopes of technetium.

| Isotope | Half-life | Decay type | Energy of radiation, MeV | | Method of preparation |
|---|---|---|---|---|---|
| $^{95m}Tc$ | 60 days | e.c. ~96%<br>i.t. ~3%<br>$\beta^+$ ~0.4% | $\beta^+$<br>$\gamma$ | 0.4<br>0.201 | $^{95}Mo(p,n)^{95m}Tc$ |
| $^{96}Tc$ | 4.2 days | e.c | $\gamma$ | 0.77–0.84 | $^{96}Mo(p,n)^{96}Tc$ |
| $^{97m}Tc$ | 91 days | i.t. | $\gamma$ | 0.096 | $^{97}Mo(p,n)^{97m}Tc$ |
| $^{97}Tc$ | $2.6 \times \times 10^6$ years | e.c. | $\gamma$ | | $^{97}Mo(d,2n)^{97}Tc$ $^{97m}Tc \rightarrow {}^{97}Tc$ |
| $^{98}Tc$ | $1.5 \times \times 10^6$ years | $\beta^-$ | $\beta^-$<br>$\gamma$ | 0.30<br>0.66; 0.75 | $^{98}Mo(p,n)^{98}Tc$ |
| $^{99m}Tc$ | 6.04 h | i.t. | $\gamma$ | 0.14 | $^{98}Mo(n,\gamma)^{99}Mo \xrightarrow{\beta} {}^{99m}Tc$ |
| $^{99}Tc$ | $2.12 \times \times 10^5$ years | $\beta^-$, no $\gamma$ | $\beta^-$ | 0.296 | fission products from uranium and plutonium; daughter $^{99m}Tc$ |

1. Isolation of Technetium from Irradiated Molybdenum

The best method for obtaining relatively large quantities of technetium is by isolating it from the mixture of uranium fission products or from the waste products of the atomic [energy] industry. Because of the high level of radiation, however, all operations involved in the isolation of technetium from these materials must be carried out in special radiochemical laboratories using apparatus with remote control. When small (milligramme) quantities are required, technetium can also be obtained by the prolonged neutron irradiation of very pure molybdenum in a nuclear reactor, according to the reaction

$$^{98}Mo(n,\gamma)^{99}Mo \xrightarrow[67\ h]{\beta^-} {}^{99m}Tc \xrightarrow[6.1\ h]{i.t.} {}^{99}Tc\ (\text{long-lived, } 2.12\times10^5 \text{ years}).$$

When the $^{99}Mo$ has decayed, the technetium can be isolated in ordinary radiochemical laboratories.

The first ponderable quantities of technetium were obtained by irradiating 5.7 kg of pure metallic molybdenum powder in a nuclear reactor for 130 h with a neutron beam at $5\times10^{11}$ neutrons $cm^{-2}\ s^{-1}$.[14,15] In this case, according to calculations, 2.8 mg of technetium, i.e. only $5\times10^{-5}$%, was formed.

A variety of methods have been described for extracting small quantities of technetium from molybdenum irradiated with neutrons, protons, or deuterons. After dissolution, the main bulk of the molybdenum was removed by precipitating silver molybdate[16] or lead molybdate[17] or by precipitation with 8-hydroxyquinoline from ammonium acetate solution[18]. Technetium can be extracted from an ammoniacal solution of molybdenum by coprecipitating the pertechnate ion with sparingly-soluble crystalline $MgNH_4PO_4$ and $MgHPO_4$ [19] After dissolution of the precipitate in 6 M HCl, the technetium was reduced to a lower valency by passing $H_2S$, after which $MgNH_4PO_4$ or $MgHPO_4$ was again precipitated from ammoniacal solution. Under these conditions, technetium remained in solution. Further concentration and purification was achieved by coprecipitation with certain sulphides ($Re_2S_7$, $PtS_2$, CuS, etc.[15]) or by ion-exchange[15,20] or electrochemical[15,16,21,22] methods. A chromatographic method for the isolation of technetium using strongly-basic anion-exchange resins (Dowex I-X8, IRA-400, etc.)[23] has also been developed. The metallic molybdenum which had been irradiated with neutrons was dissolved in a 10% NaOH + 30% $H_2O_2$ mixture, the solution was boiled to remove $H_2O_2$, and passed through a chromatographic column containing the resin. Molybdenum was weakly absorbed by the resin and eluted with 3 M NaOH solution, after which the technetium was eluted with 1 M $HClO_4$ or $NH_4ClO_4$ solution. When technetium is being isolated from kilogramme quantities of molybdenum, however, precipitation methods are unsuitable, because of the large volumes of solution and precipitate involved. Ion-exchange chromatography is also inapplicable, so that methods have been developed for isolating technetium by extraction and distillation.

Extraction methods are based on the extraction of pertechnate ions from alkaline media by means of chloroform in the presence of tetraphenylarsonium chloride[24,25] or with pyridine or methyl derivatives of pyridine[26-28]. Another effective method involves the extraction of technetium by ketones from 3–5 *N* solutions of alkalis or alkali metal carbonates[28-32]. The last method is used fairly frequently to isolate the nuclear isomer $^{99m}Tc$ for analytical purposes from molybdenum trioxide irradiated with neutrons. The molybdenum trioxide $MoO_3$ is dissolved with heating in 3–4 *N* KOH or NaOH solution in the presence of small quantities of hydrogen peroxide, after which the technetium is extracted from the solution by ethyl methyl ketone, by treatment for 5–10 min. The organic phase is washed 2–3 times with small volumes of 3–4 M $K_2CO_3$ solution to remove traces of molybdenum and radioactive impurities. The technetium is then re-extracted into the aqueous phase using chloroform or other non-polar solvents.

To isolate the short-lived isomer $^{99m}Tc$, use is made not only of the above extraction methods but also of chromatographic methods with synthetic anion-exchange resins[33] or inorganic sorbents such as alumina[34,35] and zirconium hydroxide[36]. As the $^{99m}Tc$ from the molybdenum, adsorbed on the inorganic sorbents, accumulates on the column, the technetium is eluted at intervals with 0.1 M $HNO_3$ or $H_2SO_4$ in the case of alumina or 2 M $HNO_3$ in the case of zirconium hydroxide. Methods based on the electrochemical separation of $^{99m}Tc$ from non-aqueous media[37,38] and on the irradiation of certain carbonyl compounds of molybdenum[39-41] have also been proposed. These methods have not been widely used in analytical chemistry, however, because of the time required for the electrochemical separation and the complexity of preparation and low stability to irradiation shown by the carbonyl compounds of molybdenum.

The most effective methods for separating technetium from very large quantities of molybdenum are the distillation methods. A method based on the codistillation of technetium and perchloric acid has been described[22]. To prevent the distillation of molybdenum dissolved in the $HClO_4$, phosphoric acid was added to form the non-volatile molybdophosphate complex.

Boyd and coworkers[15] showed that the distillation of technetium with concentrated sulphuric acid provides a fairly effective method for separating technetium from molybdenum. Thus when 6 ml of acid were taken per gramme of metallic molybdenum, 75% of the technetium passed into the distillate, and this figure increased to 90% when the quantity of acid was doubled. After two distillations, more than 98% of the technetium is extracted. This method was used to isolate milligramme quantities of technetium from 5.7 kg of molybdenum. As an example, we can describe a method developed[15] for the isolation and concentration of technetium from molybdenum. The molybdenum, irradiated with neutrons, was left for 6 weeks until the $^{99}Mo$ had decayed, after which it was dissolved in concentrated $H_2SO_4$. The sulphuric acid was then distilled from solutions containing approximately 190 g of the metal. The resulting distillate was diluted to a concentration of 4 M with respect to sulphuric acid, heated to boiling, and treated with bromine water. Platinum was then added to the solution (1 mg per 200 ml) and platinum sulphides were precipitated. The precipitate was filtered off, dissolved in an $NH_4OH + H_2O_2$ mixture, the solution was evaporated to dryness, the residue was treated with concentrated $H_2SO_4$ or $HClO_4$, and the technetium was distilled into a flask cooled with ice. After 4-fold dilution, the sulphides were precipitated from the solution. Spectroscopic analysis of the resulting concentrate showed the presence of technetium, together with fairly large quantities of molybdenum. The methods used to purify technetium from molybdenum and also from rhenium, which is present in traces in molybdenum and is concentrated with the technetium, will be described below.

The milligramme quantities of technetium isolated from molybdenum irradiated with neutrons have played an important part in the study of the chemical and physical properties of this element. The further development of research and the practical application of technetium require large quantities (tenths of a kilogramme) of the element, however, and these cannot be obtained from molybdenum. At the present time, therefore, increasing attention is being paid to the isolation of technetium from uranium fission products.

## 2. Isolation of Technetium from Uranium Fission Products

The nuclear reactor gives, in addition to other fission products, one of the most long-lived isotopes of technetium — $^{99}$Tc. The yield of this isotope in the fission of $^{235}$U with thermal neutrons amounts to ~6.2%. When the reactor has operated for a prolonged period, however, considerable quantities of $^{239}$Pu and $^{241}$Pu accumulate, and the fission of these isotopes provides an additional source of technetium. According to calculations[42], considerable quantities of $^{99}$Tc accumulate in the fuel elements of the first atomic power-station. Thus the consumption of 50% of the $^{235}$U gives 600 mg of $^{99}$Tc per kg of $^{235}$U. According to other data[43], the production of 10 kg of Pu in the nuclear reactor leads to the accumulation of 150 g of $^{99}$Tc. Thus the development of atomic power provides an opportunity for the production of technetium in large quantities. Particularly suitable materials for this purpose are the waste solutions from atomic plants. Treatment of these solutions makes it possible, for example, to obtain 400 g of technetium per month[3].

Ponderable (milligramme) quantities of technetium were first isolated from uranium fission products by Parker *et al.*[44] A rod of metallic uranium which had been irradiated in a nuclear reactor was dissolved in 37% HCl and the $UCl_4$ formed on dissolution was oxidised with $H_2O_2$ and bromine water to $UO_2Cl_2$. The technetium was then coprecipitated with $PtS_2$ using hydrogen sulphide, the precipitate was dissolved in a mixture of $H_2O_2$ and $NH_4OH$, and the solution was evaporated to dryness. The subsequent purification of the technetium was carried out by distilling $Tc_2O_7$ from 18 *N* $H_2SO_4$.

The first gramme of technetium was obtained in 1952 from the waste products from plutonium production[45]. Because of the high concentration of nitrate ion in the solution used, it was impossible to concentrate the technetium in the form of sulphides. Use was therefore made of the organic base tetraphenylarsonium chloride, which forms sparingly soluble precipitates with perchlorate ions added to the waste solutions and coprecipitates the structurally-similar pertechnate ion. The precipitate was dissolved in concentrated $H_2SO_4$ and the technetium was deposited electrolytically on platinum electrodes. The resulting black deposit of $TcO_2$ was dissolved in 18 M $H_2SO_4$, the technetium was distilled off, and technetium sulphide was precipitated from the distillate. The use of electrolysis in this procedure makes it impossible to regenerate the expensive tetraphenylarsonium chloride. A method was therefore developed[46] to avoid the decomposition of this reagent. The mixture of tetraphenylarsonium perchlorate and pertechnate was dissolved in alcohol and the solution was passed through a column of anion-exchange resin in the $Cl^-$ form. The perchlorate and pertechnate were absorbed on the resin and the tetraphenylarsonium cation passed through the column. The technetium was then eluted with 2 *N* NaOH solution.

Technetium has also been concentrated and isolated by precipitation and coprecipitation methods from the waste products from the processing of atomic fuel[47,48]. Technetium and ruthenium were coprecipitated on iron hydroxide in the presence of hydrazine hydrate at a controlled pH of 2–3, the precipitate was dissolved in $HNO_3$, and tetraphenylarsonium pertechnate was precipitated and reprecipitated several times. $Tc_2S_7$ was then precipitated from 2 *N* HCl. The precipitate was dissolved in an $NH_4OH$ + + $H_2O_2$ mixture and pure $KTcO_4$ was isolated. Technetium can also be isolated from alkaline solutions of uranium fission products by coprecipitating $Tc^{IV}$ with $Fe_3O_4$.[49]

The chromatographic and extraction methods for isolating and concentrating technetium from fission products appear to be the most effective. One of the earliest extraction experiments was carried out by Tribalat and Beydon[24,50], who extracted technetium with a solution of tetraphenylarsonium chloride in chloroform. The equilibrium constant for the extraction reaction

$$(C_6H_5)_4As^+(aq.) + TcO_4^- \rightleftarrows (C_6H_5)_4AsTcO_4(org.),$$

is $\sim 3 \times 10^6$. The isolation was carried out as follows. Irradiated uranium trioxide $UO_3$ was dissolved in $H_2SO_4$ and the solution was treated with ammonium persulphate to oxidise $I^-$ ions to elementary iodine, which was extracted with toluene. The aqueous solution was boiled to remove traces of iodine, neutralised with $(NH_4)_2CO_3$, and treated again with ammonium persulphate. $TcO_4^-$ was then extracted with a solution of tetraphenylarsonium chloride in chloroform.

In the isolation of technetium from industrial solutions, extensive use has recently been made of extracting agents such as amines and ketones, which give high distribution constants for $TcO_4^-$.[28,51-55] For example, the extraction of technetium with pyridine from alkaline media makes possible selective and almost quantitative separation of technetium from nitrate and other solutions. This can be seen from Tables 2 and 3,[28] which give the distribution constants for technetium and certain other elements obtained by the fission of uranium, for extraction with pyridine from alkaline $NaNO_3$ and $Na_2CO_3$ solutions.

High distribution constants for technetium are given by methyl derivatives of pyridine. For example, the distribution constants for technetium in extraction from 2 M $(NH_4)_2CO_3$ solution using pyridine and 2-methylpyridine are 7.5 and 242 respectively. 3-Methyl- and 4-methyl-pyridines give even higher values of *E* than 2-methylpyridine. 2,4-Dimethylpyridine has proved particularly effective for the isolation of technetium from solutions with high nitrate ion concentration (for extraction from 4 *N* $NaNO_3$–0.5 *N* NaOH, *E* = 50). The technetium is usually recovered by distillation of the pyridine and its methyl derivatives, which can be used again. Another convenient method involves the re-extraction of technetium with non-polar solvents: chloroform, hexane, kerosene, and petrol, which also purify the technetium solution from organic impurities.

Amines have recently been used[3] to isolate kilogramme quantities of technetium from industrial wastes remaining after the fluorination of uranium irradiated in reactors. The technetium was recovered by repeated extraction with 2,4-dimethylpyridine, followed by purification by extraction with trioctylamine in petrol and repeated crystallisation as ammonium pertechnate from $NH_4NO_3$ solution.

TABLE 2. Distribution constants ($E$) for technetium in extraction with pyridine from alkaline $NaNO_3$ solutions of different concentration.

| $NaNO_3$, M | $E$ | |
|---|---|---|
| | 2 $N$ NaOH | 0.25 $N$ NaOH–2.0 M $Na_2CO_3$ |
| 0 | 54 | 740 |
| 0.25 | — | 110 |
| 0.50 | 19 | 89 |
| 0.75 | — | 71 |
| 1.0 | 16 | 58 |
| 1.5 | 12 | 52 |
| 2.0 | — | 42 |

TABLE 3. Distribution constants ($E$) for various uranium fission products in extraction with pyridine from 0.25 $N$ NaOH–2.0 M $Na_2CO_3$ solution.

| Fission product | $E$ |
|---|---|
| $^{99}Tc$ | 740 |
| $^{137}Cs$ | $2.87 \cdot 10^{-3}$ |
| $^{106}Ru$ | $1.27 \cdot 10^{-1}$ |
| $^{95}Zr$, $^{95}Nb$ | $6 \cdot 10^{-4}$ |
| $^{152-155}Eu$ | $6 \cdot 10^{-3}$ |
| $^{90}Sr$ | $3.48 \cdot 10^{-3}$ |

Another effective method[52,54] for the isolation of technetium in this case is by extraction with a 0.3 M solution of trilaurylamine in an organic solvent. After the removal of uranium with 0.5 $N$ $HNO_3$ and of neptunium with 0.1 $N$ $H_2SO_4$, the technetium was re-extracted with 1 $N$ $NH_4OH$ or 4 $N$ NaOH.

An extraction method using tributyl phosphate in kerosene has been developed for isolating technetium from sulphuric acid solutions[56]. Tributyl phosphate has not found wide application, however, because of the poor extraction of technetium from nitrate solutions by this solvent (the distribution constants for extraction from 0.5 M and 4 M $HNO_3$ are 1.36 and 0.04 respectively).

Chromatographic methods are based on the extensive sorption of pertechnate ion from weakly acidic, neutral, and alkaline media by strongly basic anion-exchange resins; most other fission elements ($^{137}Cs$, $^{90}Sr$, $^{152-155}Eu$, etc.) are not absorbed by anion-exchange resins. Appreciable sorption of $TcO_4^-$ takes place even from solutions with high concentrations of nitrate ion, which is usually present in the waste solutions from the atomic industry. Table 4 [28] gives the distribution constants for technetium between Dowex-1 resin and $NaNO_3$ solutions of different concentration.

According to data obtained by other workers[57], who carried out experiments under factory conditions and in plant assemblies, $TcO_4^-$ is readily absorbed by strongly basic anion-exchange resins from solutions with nitrate ion concentrations up to 7.5 $N$. This has made it possible to develop an effective and economic chromatographic method for isolating technetium from neutral industrial solutions ("Purex wastes")[57]. The solution was passed through a chromatographic column containing 5 litres of anion-exchange resin, and after desorption the technetium was separated from traces of ruthenium by oxidising the latter to $RuO_4$ and sorption on a cation-exchange resin. The technetium was then precipitated as the sulphides.

TABLE 4. Distribution constants ($E$) for technetium between Dowex-1 anion exchange resin and alkaline (0.25 $N$ NaOH) $NaNO_3$ solutions of different concentration.

| $NaNO_3$, M | $E$ |
|---|---|
| 0 | 4500 |
| 0.5 | 575 |
| 1.0 | 340 |
| 2.0 | 190 |
| 3.0 | 142 |
| 4.0 | 125 |
| 5.0 | 121 |
| 6.0 | 122 |

The method makes it possible to obtain in one stage a high yield (> 80%) of technetium with a chemical and radiochemical purity >99%.

In one of the latest improved chromatographic methods[58] acidic nitrate solutions of uranium fission products were treated with NaOH and the alkaline solutions were passed through a column of strongly basic anion-exchange resin. The technetium was then eluted with $HNO_3$, alkali was added to the solution, and the technetium was extracted with ethyl methyl ketone.

A new method for the production of technetium was recently developed in the USA[2,59]. In the processing of atomic fuel from gas-diffusion plants, technetium is separated from uranium hexafluoride by passing their heated mixture through a column packed with magnesium fluoride, in which the technetium is retained. The mechanism of the absorption of the technetium has not been studied in detail, but data which have been obtained suggest that the phenomenon is based on physical adsorption.

## 3. Methods of Isolating Technetium from Minerals in the Search for the Element in Nature

The detailed study of the chemical and physicochemical properties of technetium and its production in ponderable quantities have made it possible to undertake intensive searches for technetium in nature, and these have led to the detection of technetium in the sun's atmosphere and in young stars[60]. The question of the possible discovery of technetium in terrestrial materials is important in the geochemistry of this element[61-66]. Boyd and coworkers' searches[62] for technetium in various minerals showed that some of the minerals contained extremely small traces of the element.

Recently, Kenna and Kuroda[64-66] isolated appreciable quantities of technetium ($10^{-9}$ g) from pitchblende obtained in the Congo. Like Boyd, Kenna and Kuroda considered that the presence of technetium in the minerals results from the spontaneous fission of uranium or the activation of molybdenum, ruthenium, and niobium by powerful cosmic radiation.

A variety of methods, depending on the mineral studied, are available for the isolation and determination of technetium in natural materials. Chromatography, distillation, and coprecipitation have been used[62] in the analysis of minerals such as $MoS_2$ and yttrotantalite. The mineral was fused with five times its weight of $Na_2O_2$ in a zirconium or iron crucible. To control the chemical process, radioactive technetium (usually $^{96}Tc + {}^{95m}Tc$) was added

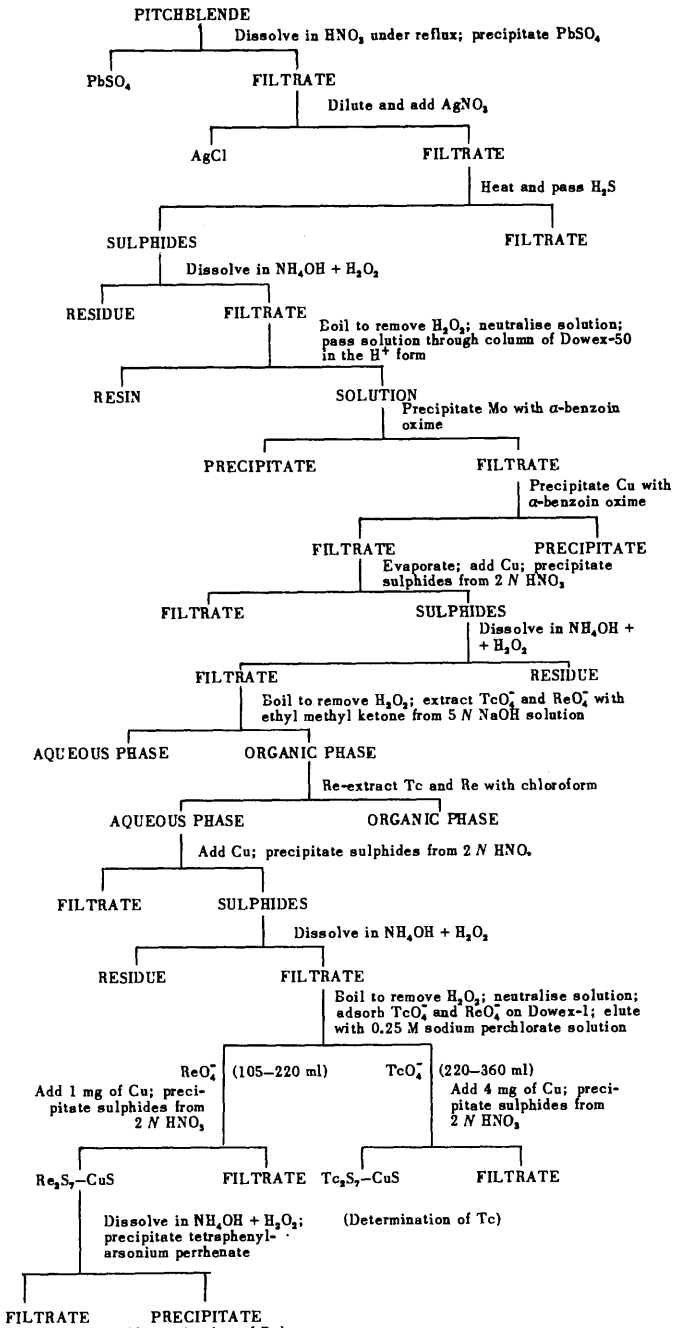



Fig. 1. Scheme for separating technetium from pitchblende.

at each stage to the material being studied. The melt was dissolved in water, the solution was boiled and cooled, and iron was precipitated as the hydroxide, 1–45 litres of the filtrate was passed through a 22 cm × 9.6 cm column of strongly basic anion-exchange resin (Dowex-2 or Amberlite IRA-410). The anion-exchange resin absorbed all the technetium, rhenium, and a small proportion of molybdenum, ruthenium, sulphate, etc. Sodium, copper, nickel, etc. cations passed through the column. Molybdates and other anions were then eluted with 1 M $NaNO_3$ at pH 10 or with 2 N NaOH, after the column had been washed with distilled water. Technetium and rhenium were eluted with 2 N $HClO_4$ or $NaClO_4$. The solution was acidified, heated, and treated with bromine water, after which rhenium and technetium sulphides were precipitated. The precipitate was dissolved in an $NH_4OH + H_2O_2$ mixture, the solution was evaporated to dryness, and the residue was dissolved in 10 M HCl. The main bulk of the rhenium was separated from technetium by precipitating rhenium sulphide with hydrogen sulphide in this medium. Further separation of technetium from rhenium was achieved by the methods of ion-exchange chromatography described below. Finally, technetium was coprecipitated with copper sulphide (1–1.5 mg Cu) and this "technetium concentrate" was treated by one of a number of methods for quantitative determination of technetium.

In addition to the above methods, methods involving the extraction of technetium have been used in the analysis of pitchblende[66]. A scheme illustrating the analytical operations involved in the isolation and purification of technetium from this mineral is shown in Fig. 1.

## III. METHODS OF SEPARATING TECHNETIUM FROM RHENIUM, MOLYBDENUM, AND RUTHENIUM

The most difficult task in the isolation of technetium from irradiated products is its separation from the neighbouring elements rhenium, ruthenium, and molybdenum. In the isolation of technetium from irradiated molybdenum it is necessary to separate it quantitatively not only from molybdenum, but also from rhenium, which is usually present in traces in the molybdenum and is concentrated with the technetium. In the extraction of technetium from fission products it is necessary to separate it from ruthenium isotopes, which, although formed in approximately the same yield as $^{99}Tc$, exhibit a very much higher specific activity.

Technetium is separated from these elements by methods involving distillation, extraction, precipitation and crystallisation, anion-exchange chromatography, etc.

### 1. Distillation Methods

Since the oxide $Tc_2O_7$ is volatile, heptavalent technetium can be codistilled with certain strong acids. Acids can be divided into three groups according to the extent to which codistillation of technetium with the acid takes place (Fig. 2 [15]): (1) with acids such as $HClO_4$ codistillation is quantitative, up to 75% of the technetium codistilling with the first 20% of distillate; (2) with $HNO_3$, aqua regia, $H_2SO_4$, and fuming $H_2SO_4$, codistillation is incomplete, appreciable quantities of technetium beginning to codistil only when more than half of the acid has been transferred to the distillate; (3) with acids such as HCl, HBr, and HI, technetium is not codistilled, since these acids reduce technetium to non-volatile compounds.

The degree of codistillation of technetium is influenced chiefly by the oxidising power of the acid, temperature, and the stability of the volatile oxide. The addition of oxidising agents to acids such as $H_2SO_4$ and $H_3PO_4$ increases appreciably the degree of codistillation of technetium, as can be seen from the curves in Fig. 2. The lower extent of the codistillation of this element with $H_2SO_4$ is due to the possible presence of reducing impurities.

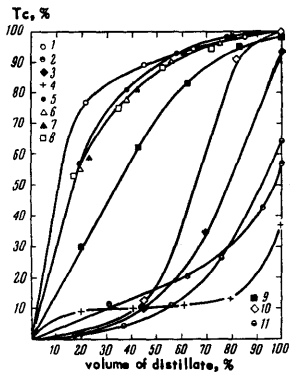



Fig.2. Codistillation of technetium with various acids.
1) $HClO_4$; 2) $H_2SO_4$; 3) fuming $H_2SO_4$; 4) $HNO_3$; 5) $H_2SO_4 + KIO_4$; 6) $H_2SO_4 + K_2Cr_2O_7$; 7) $H_2SO_4 + Na_2S_2O_8 + AgNO_3$; 8) $H_2SO_4 + KBrO_3$; 9) $H_2SO_4 + Na_2S_2O_8$; 10) $H_3PO_4 + KMnO_4$; 11) aqua regia.

The ability of technetium to undergo ready reduction in hydrochloric acid solutions has been used to develop a distillation method for separating technetium from rhenium[9,15,67]. The distillation is carried out at 180–200° from a mixture of sulphuric and hydrochloric acids. In this case an appreciable proportion of the rhenium (~95%) enters the distillate, whereas almost all the technetium is reduced to the tetravalent state by the hydrochloric acid and remains in the solution. The separation factor is equal to 50. This process was recently made the basis of another method[68] involving the reduction of pertechnate ion with hydroxylamine (the perrhenate ion is not reduced in the process). The rhenium is distilled from sulphuric acid containing hydroxylamine. The method can be used to separate 10 mg of rhenium from microquantities of technetium.

A method has been described for separating technetium and rhenium by distillation of the elements as the chlorides[69]. The distillation is carried out from a mixture of metallic technetium and rhenium or their sulphides, in a current of chlorine. Rhenium is then distilled from the distillate at 300° *in vacuo*; the technetium chloride decomposes, leaving metallic technetium.

Partial separation of these two elements can be achieved by codistillation with perchloric acid[9], but in this case ruthenium distils with the technetium.

Codistillation of technetium with sulphuric acid has been used to separate technetium and ruthenium[9]. In this case separation factors of the order of $10^5$ and above are obtained. In the absence of oxidising agents, however, the degree of codistillation of technetium is often very low, because of its reduction by impurities present in the acid[9,15]. (A detailed study[70] of the distillation of technetium with $H_2SO_4$ showed that technetium can be distilled quantitatively with $H_2SO_4$ if highly pure acid and scrupulously clean distillation apparatus are used.) In practice, therefore, complete distillation of technetium is best achieved by adding oxidising agents, which should moreover be non-volatile, stable in boiling sulphuric acid, sufficiently powerful to retain technetium in the heptavalent state, but incapable of oxidising lower valency states of ruthenium to the volatile $RuO_4$. It is very difficult to select oxidising agents satisfying these requirements, and $Ce^{IV}$ and $CrO_3$ are usually employed. In the distillation of technetium in the presence of oxidising agents some ruthenium distils as $RuO_4$, so that for the quantitative separation of technetium from ruthenium, the $RuO_4$ is reduced to insoluble $RuO_2$ by boiling the distillate with alcohol for 1–2 min.

Technetium and ruthenium can be separated from alkaline solutions by distillation of the $RuO_4$ in a current of chlorine[71].

## 2. Methods of Separation Based on Precipitation and Crystallisation

A convenient method for separating large quantities of rhenium from technetium involves the fractional precipitation of rhenium sulphide from concentrated hydrochloric acid solutions. Under these conditions technetium is not precipitated and remains in solution. Curves illustrating the dependence of the coprecipitation of microquantities of technetium and rhenium with platinum sulphide on the hydrochloric acid concentration at 90° are shown in Fig. 3.[15] Almost no technetium is coprecipitated at an HCl concentration 9 M and above, whereas rhenium is coprecipitated up to 10 M HCl. This difference in coprecipitation is due to the reduction of the pertechnate ions by hydrochloric acid to a lower valency state in which technetium is not coprecipitated with metal sulphides. An interesting feature is that complete coprecipitation of technetium with sulphides is observed from other acidic media (for example 24 *N* $H_2SO_4$) exhibiting no reducing properties. The separation by the above method is not quantitative, however (some Re remains in the solution), and the complete purification of Tc from Re requires the use of more refined methods (for example chromatography).

Satisfactory separation of Tc from Re can be achieved by reducing $Tc^{VII}$ with HCl and coprecipitating $Tc^{IV}$ with $Fe(OH)_3$.[29,72] The technetium can then be oxidised to the heptavalent state by oxidising the precipitate in concentrated $HNO_3$ or dilute $H_2SO_4$ in the presence of $H_2O_2$, and precipitating the iron from solution with ammonia.

The separation of ponderable quantities of Tc and Re can be achieved by fractional crystallisation of potassium pertechnate and perrhenate (Fig. 4)[15], and small quantities of ruthenium can be separated by recrystallising $KTcO_4$.[8]

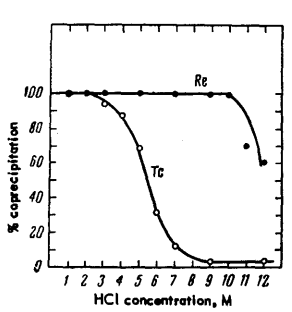



Fig.3. Coprecipitation of technetium and rhenium with $PtS_2$ at different HCl concentrations (90°).

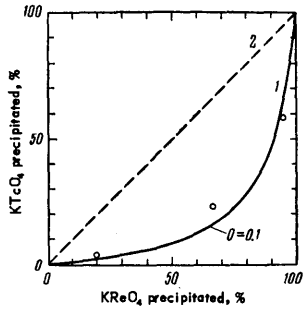



Fig. 4. Separation of $KTcO_4$ from $KReO_4$ by fractional crystallisation:
1) experimental data; 2) calculated data.

Precipitation methods for separating technetium and molybdenum have been described above. These involve the precipitation of molybdenum with 8-hydroxyquinoline or $\alpha$-benzoin oxime or as silver or lead molybdate. On the other hand, the pertechnate ion can be separated from an alkaline solution containing molybdenum or ruthenium, by coprecipitation with tetraphenylarsonium perrhenate or perchlorate. The latter is more convenient, since the technetium is subsequently more readily separated.

### 3. Extraction Methods

Extraction methods are very effective for the recovery of technetium from various materials and its separation from most elements of the Periodic System, but they generally do not give quantitative separation of this element from its analogue rhenium. Some extraction methods are fairly effective for the separation of technetium from molybdenum and ruthenium, however. As noted above, appreciable separation of technetium from molybdenum and ruthenium can be achieved by extraction with pyridine[26-28] from alkaline media and by ketones[28-32] from 3–5 $N$ solutions of alkalis or alkali metal carbonates. In this case the technetium can be re-extracted in the aqueous phase with chloroform or other non-polar solvents. Another effective method for the separation of technetium and molybdenum is that based on the extraction of tetraphenylarsonium pertechnate with chloroform[24,25,50]. Before extraction it is best to add small quantities of oxidising agent such as $H_2O_2$ to prevent the reduction of $TcO_4^-$ by impurities in the organic reagents. During washing, the solution should contain a sufficient concentration of tetraphenylarsonium ion ($\sim 5 \times 10^{-5}$ M) to prevent the premature re-extraction of $TcO_4^-$ into the aqueous phase. The technetium is re-extracted with 0.2 $N$ $HClO_4$ or 12 $N$ $H_2SO_4$. Finally, technetium and molybdenum can be separated by extracting the molybdenum with ether from hydrochloric acid solutions[8,67,73]. In this case the best results are obtained[73] by extracting the molybdenum with ethyl ether from 1 M HCl–1 M $NH_4NCS$ solution. Radiochemically pure technetium is left in the aqueous phase in ~80% yield.

An effective extraction method for the separation of technetium and ruthenium was developed in the Geochemical Institute of the USSR Academy of Sciences[74]. It is based on the extraction of technetium as triphenylguanidinium pertechnate from sulphuric acid by means of chlorex ($\beta$-chloroethyl ether). The technetium can be re-extracted with 3 $N$ $NH_4OH$ solution.

It has been suggested[75] that in the separation of a mixture of technetium and ruthenium in uranium fission products the extraction be first carried out with pyridine from 4 $N$ NaOH in the absence of oxidising agent. In this case only technetium, which is present in solution as $TcO_4^-$, is extracted. NaOCl is then added to the aqueous phase, the Ru is oxidised to $RuO_4^{2-}$, and extracted with pyridine.

Partial separation of technetium from rhenium can be achieved by extraction of the cupferron complex of technetium after reducing the latter to a lower valency state[76]. In this connection, mention may be made of the need for study of the extraction separation of technetium and rhenium using ethyl methyl ketone, from alkaline solutions containing reducing agents, such as hydrazine or hydroxylamine.

Extraction methods are widely used in the analytical chemistry of technetium for separation, isolation, and determination. Table 5 gives data on the extraction of technetium compounds with different organic solvents and the fields in which they are used.

TABLE 5. Extraction of technetium compounds by various organic solvents.

| Technetium compound | Extracting agent | Applications | References |
|---|---|---|---|
| Salts with organic cations or bases: tetraphenylarsonium triphenylguanidinium methyltricaprylammonium quinolinium trilaurylammonium nitron | benzene, chloroform, nitrobenzene, chlorex ($\beta$-chloroethyl ether) | separation of Tc from fission products and irradiated molybdenum separation from Ru, Mo, and other elements | 24,25,45 74 77 78 52 29 |
| Technetic* acid and its salts | | | |
| $HTcO_4$ | isopentanol, isobutyl methyl ketone, tributyl phosphate in kerosene | separation of Tc for its determination in fission products | 6,56,78 |
| Pertechnate ion: | | | |
| from acidic media | alcohols, ketones, trioctylamine in chloroform, hexane, or ether | isolation from waste solutions from the atomic industry and irradiated Mo. Separation from isotopes of Mo, Ru, Cs, Sr, Nb, and other elements | 7,26–32, 51–56, 75,80, 81 |
| from alkaline media | ketones, cyclic amines | | |
| Complexes of technetium reduced to a lower valency state: | | | |
| thiocyanato-complexes | alcohols, ethers, ketones, solution of trioctylphosphine oxide and trioctylamine hydrochloride in cyclohexane and dichloroethane | extraction–spectrophotometric determination, separation from Mo and other elements | 8,29,73, 82,83 |
| $p$-Thiocresolate | chloroform, ether, benzene, $CCl_4$, toluene | ditto | 84 |
| 1,5-Diphenylcarbohydrazide | $CCl_4$ | » | 85 |
| Hexachlorotechnate | trioctylamine in cyclohexane and tetraphenylarsonium [chloride] in chloroform | » | 7,11 |
| Xanthate | chloroform, $CCl_4$ | » | 86 |
| Toluene-3,4-dithiol | $CCl_4$ | » | 87 |
| Compounds with $\alpha$-picolinic and sulphosalicylic acids | chloroform | » | 89 |
| Cupferronate | ether, chloroform | partial separation from Re | 76 |

* Presumably pertechnic acid is meant here (Ed. of Translation).

### 4. Chromatographic Methods of Separation

The most effective method for the quantitative separation of technetium from rhenium and molybdenum is ion-exchange chromatography. In the isolation of technetium this method is generally used in the last stage of the purification of technetium from these elements, when the main bulk of the impurities have been removed by other methods, such as distillation, extraction, precipitation, etc. As already noted, the chromatographic method is based on the extremely strong sorption of the pertechnate ion by strongly basic anion-exchange resins, from which it can be eluted only by ions with a high affinity for the resin. The nature of the eluent thus plays an extremely important part in methods for the chromatographic separation of technetium, rhenium, and molybdenum. The eluents used in analytical practice are solutions containing the anions $SCN^-$,[90,91] $NO_3^-$,[91] and $ClO_4^-$.[62,92]

Atteberry and Boyd[90] separated $TcO_4^-$ and $ReO_4^-$ on Dowex-2 resin in the $SO_4^{2-}$ form, using as eluent a mixture of ammonium sulphate and thiocyanate, with pH 8.3–8.5. Rhenium was first eluted with a 0.1 M solution of these salts, after which technetium was extracted by increasing the concentration of the salts in the eluent to 1 M. Technetium and rhenium were also separated by successive elution from a column of Amberlite IRA-400 resin in the $Cl^-$ form using $NH_4CNS$ and $HNO_3$ solution[91]. Rhenium was eluted with 5% $NH_4CNS$ solution and technetium with 4 M $HNO_3$.

A more effective separation of $TcO_4^-$ and $ReO_4^-$ was achieved by using perchloric acid or ammonium perchlorate as eluent[62,92]. The separation was carried out[92] on a 23 cm × 0.204 cm column filled with Dowex-1-X4 anion-exchange resin in the $ClO_4^-$ form (200–400 mesh); 0.2 M $HClO_4$ was used as eluent. The elution of rhenium required 23.6 free column volumes and the elution of technetium 47.7 free column volumes (Fig. 5). The same quantities of eluents are used when ammonium perchlorate solution is taken for this purpose. The volumes of eluents used to extract rhenium and technetium are inversely proportional to the perchlorate ion concentration.

In the development of a method for the chromatographic separation of $TcO_4^-$ and $ReO_4^-$, it was found[92] that the efficiency of separation of the anions is influenced considerably by effects such as the possible partial reduction of technetium by the anion-exchange resin or the formation of radio-colloids; this often leads to indistinct peaks and less effective separation. To eliminate these effects, it would be useful to study the anion-exchange separation of technetium and rhenium by means of concentrated solutions of hydrochloric acid, which selectively reduces $Tc^{VII}$ to $Tc^{IV}$ with the formation of the complex anions $TcCl_6^{2-}$. Some anion-exchange resins, particularly the AV-17 resin produced in the Soviet Union, have a high absorbing power for complex anions from acidic media[93]. This can apparently be used for the effective separation of technetium and rhenium.

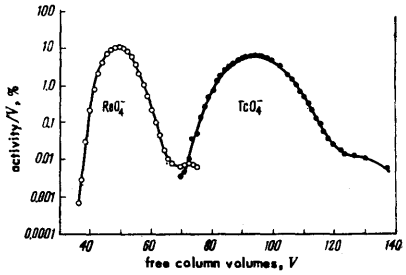



Fig. 5. Chromatographic separation of technetium and rhenium on Dowex-1-X4 anion-exchange resin. Rate 0.75 cm $min^{-1}$.

Chromatographic methods for the separation of Tc and Mo have been based on the successive elution of $MoO_4^{2-}$ with 1 M HCl [94] or 3 M NaOH [23] and $TcO_4^-$ with 4 M $HNO_3$ or 1 M $HClO_4$ respectively.

Lederer and coworkers[95-97] developed a method for separating technetium and molybdenum by paper chromatography, and Garvalho[98] developed a method using electrophoresis. The separation of Tc and Re by these methods was not efficient, but more effective separation was achieved by the selective reduction of $TcO_4^-$ with HCl,[99] HI, or $NH_2NH_2$.[98]

### 5. Electrochemical and Other Methods

Electrochemical methods are based on the selective electrolytic reduction of Tc to $TcO_2$ under definite conditions and its deposition on electrodes, while Re and Mo remain in solution. Rogers[21] developed a method for the electrolytic deposition of Tc on a Pt cathode from 2 M NaOH solution at a controlled cathode potential of 1.1 V.

Boyd *et al.*[15] studied the electrodeposition of technetium under different conditions and showed that the optimum deposition is achieved from neutral media containing $10^{-3}$ M $F^-$ ion. The small quantity of $F^-$ ions apparently increases the hydrogen overvoltage and improves the electrodeposition of Tc. The deposition is also improved by replacing the Pt cathode with polished Ni or Cu electrodes.

A method based on complex formation by technetium with phthalocyanine has also been developed for separating small quantities of technetium and rhenium[61]. Rhenium does not form these complexes. In the separation it is best to use copper phthalocyanine as carrier.

## IV. METHODS OF DETERMINING TECHNETIUM

### 1. Gravimetric Methods

Large quantities of technetium are readily and conveniently determined by gravimetric methods. Two methods for the determination of technetium are known: (1) precipitation of technetium(VII) sulphide and weighing as $Tc_2S_7$;[15,100] (2) precipitation and weighing as tetraphenylarsonium or nitron pertechnates[46].

Technetium sulphide is often the final product in general schemes for the purification of technetium. The concentration process is usually completed by the precipitation of $Tc_2S_7$. The precipitation is carried out from 2–4 M HCl or $H_2SO_4$ using hydrogen sulphide. The precipitate is washed carefully several times with carbon disulphide to remove the sulphur formed. A necessary condition for maximum precipitation of technetium is that the element be in the heptavalent state. This method can be used to determine technetium concentrations down to 3 $\mu g$ $ml^{-1}$.

In the precipitation of tetraphenylarsonium pertechnate, the sensitivity of the determination is reduced to 5 $\mu g\ ml^{-1}$. The precipitation is usually carried out from hot alkaline solution at pH 8–9 by adding 0.05 M $(C_6H_5)_4AsCl$ solution. The resulting precipitate is washed several times with cold distilled water, dried at 110°, and weighed as tetraphenylarsonium pertechnate $(C_6H_5)_4AsTcO_4$. Permanganate, perrhenate, perchlorate, iodide, and bromide ions interfere.

## 2. Spectrophotometric Methods

Aqueous solutions of the pertechnate ion absorb strongly in the ultraviolet range (Fig. 6). Careful measurement of the absorption spectra reveals characteristic peaks with maxima at 247 mμm and 285 mμm.[8,101-104]. It was also found that for these wavelengths Beer's law is obeyed to a pertechnate ion concentration $10^{-3}$ M. This makes it possible to determine 1 μg of technetium spectrophotometrically[62,108]. This method is particularly convenient for the simultaneous determination of technetium and rhenium (Fig. 6).

Spectrophotometric methods based on the measurement of the absorption of technetium complexes are more sensitive. In Crouthamel's method[82], the absorption of the red complex formed by technetium(V) with thiocyanate ions was measured at 510 mμm. The method is very sensitive but certain elements such as uranium and iron interfere. Moreover, the complete development of the colour, which is produced by the slow reduction of $Tc^{VII}$ to $Tc^{V}$ by thiocyanate, requires a considerable time (~3 h), and this is a disadvantage.

In Howard and Weber's work[83] on the development of a rapid method for determining technetium in uranium materials, particular attention was paid to increasing the rate of the reduction process. The use of ascorbic acid for the reduction of $Tc^{VII}$ to $Tc^{V}$ was recommended for rapid development of the colour. Iron(III) was added to the solution to prevent further reduction to $Tc^{IV}$. The red thiocyanato-complex of technetium(V) was extracted from 3 *N* HCl with butyl acetate, and the extract was washed twice with 30% $NaH_2PO_4$ solution to remove iron. The spectrophotometry was then carried out at 585 mμm ($\epsilon$ = 16 500) in the presence of molybdenum or at 510 mμm ($\epsilon$ = 50 000) when molybdenum was absent. This method can be used to determine 0.3 μg of technetium in 5 g of uranium. The accuracy of the method is ±0.07 μg in the determination of 0.5 μg and ±0.2 μg in the determination of 30 μg of technetium. The determination requires 15 min.

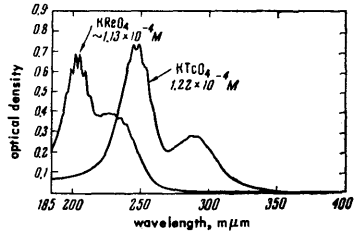



Fig. 6. Absorption spectra of aqueous $KTcO_4$ and $KReO_4$ solutions.

Miller and Thomason[105] developed a method for the spectrophotometric determination of technetium using thioglycollic acid as the complex-forming reagent. The absorption of the coloured solution was measured at 655 mμm. The method is rapid, but insufficiently sensitive. Moreover, many elements such as uranium, iron, etc. interfere in the determination. Later, the same authors developed another method[87], in which the complex formed by technetium with toluene-3,4-dithiol was extracted with carbon tetrachloride and the absorption was measured at 450 mμm. This method is more sensitive than that in which thioglycollic acid is used, but many elements again interfere in the determination and the extraction equilibrium is established only slowly.

Miller and Zittel[86] recently proposed a new method for the spectrophotometric determination of microgramme quantities of technetium using diphenylcarbazide (1,5-diphenylcarbohydrazide). The determination was carried out in 1.5 M $H_2SO_4$, in which diphenylcarbazide reduces $Tc^{VII}$ to $Tc^{IV}$ and forms a stable complex with the latter. The molar extinction coefficient of solutions of this compound is 48 600. Complete development of the colour requires 35–40 min, after which the absorption of the solution is measured at 520 mμm. $VO_3^-$, $MoO_4^{2-}$, $ReO_4^-$, and $Hg^{2+}$ cause little interference in the determination, but $Fe^{3+}$, $Ce^{4+}$, and $CrO_4^{2-}$ should be removed from the solution. Thus in the determination of technetium in the presence of $Cr^{VI}$, technetium diphenylcarbazide was extracted with chloroform (the corresponding $Cr^{VI}$ compound is not extracted) and the optical absorption of the extract was measured.

A convenient method for the determination of microgramme quantities of technetium in the presence of rhenium using *p*-thiocresol has been described[84]. *p*-Thiocresol does not react with $Tc^{VII}$ and and $Re^{VII}$, but reacts with these elements in lower valency states to form coloured complexes which are readily soluble in $CCl_4$, benzene, and ether. In acetic acid solutions, *p*-thiocresol reduces technetium to the tetravalent state with the formation of a complex with absorption maxima at 320–325 mμm and 410 mμm. The maximum at 410 mμm is used for the determination of technetium. The molar extinction coefficient of the solutions of the compound at this wavelength is 7350. $Re^{VII}$ is not reduced under these conditions and does not interfere in the determination. $WO_4^{2-}$, $Sn^{2+}$, $Cd^{2+}$, $Bi^{3+}$, $Pb^{2+}$, $Ni^{2+}$, $Cr^{3+}$, $VO_3^-$, $UO_2^{2+}$, $S^{2-}$, and $MoO_4^{2-}$ do not interfere but ions of elements of the platinum group react with the reagent to form coloured complexes which are readily extracted by chloroform.

The ability of technetium to undergo comparatively ready reduction by concentrated HCl with heating, and to form the anionic complexes $TcCl_6^{2-}$, was used by the author of the present review to develop a new method for the spectrophotometric determination of technetium in the presence of microgramme quantities of molybdenum and rhenium[106]. The molar extinction coefficient of solutions of the chloro-complex of technetium(IV) is 32 000. The method is simple, has a high sensitivity (0.2 μg), and low experimental error (~ 2%).

α-Furyl dioxime can also be used for the spectrophotometric determination of technetium[88,107]. The determination is carried out in the presence of $SnCl_2$ in 1 M HCl. The light absorption is measured at 520 mμm ($\epsilon$ = 13 181). The presence of a 10-fold excess of molybdenum ($10^{-4}$ M) relative to technetium ($10^{-5}$ M) does not interfere in the determination. The sensitivity of the determination is not high, however (~1 μg), and the time required is fairly long (~2 h).

Methods have also been proposed for the determination of technetium with thiourea and dimethylglyoxime[86], potassium hexacyanoferrate(II), and sulphosalicylic and α-picolinic acids[89].

### 3. Radiometric Method

The simplest and earliest method for determining $^{99}Tc$ is the radiometric method, based on the measurement of the β-activity of this isotope on a proportional β-counter[108]. The specific activity of technetium is fairly high (37 800 counts $min^{-1}$ $\mu g^{-1}$), so that this method can be used to estimate 0.1 μg of technetium. The low energy of the β-particles from $^{99}Tc$ (~0.3 MeV) introduces a number of difficulties into the measurement, associated with self-absorption in the specimen, back β-scattering, etc. Despite these disadvantages, the radiometric method in some cases makes possible more accurate determination of the technetium content than chemical methods.

Geiger–Muller counters are often used for the identification and determination of the activity of the nuclear isomer emitting soft γ-quanta (~0.3 MeV), but it is better to carry out the measurements on a γ-scintillation counter or spectrometer[9,109].

### 4. Spectroscopic Method

The spectrochemical method provides a sensitive method for the determination of technetium. It is based on the use of the resonance lines in technetium at 4297.06, 4262.26, and 4238.19 Å and Tc-1 at 4031.63 Å. The method can be used to determine 0.1 μg of technetium[62].

Milligramme quantities of technetium and rhenium can be determined by infrared spectroscopy[110]. Tetraphenylarsonium pertechnate is pressed with sodium bromide into a disc and the infrared absorption is measured at 11.09 mμm. $MoO_4^{2-}$, $WO_4^{2-}$, $SO_4^{2-}$, $PO_4^{3-}$, $Br^-$, $NO_3^-$, $NCS^-$, $IO_3^-$, $UO_2^{2+}$ ions and the ions of organic acids do not interfere, but $ReO_4^-$ and $MnO_4^-$ ions absorb infrared radiation in an adjacent region and should be removed before the determination of technetium.

### 5. Polarographic Method

Traces of technetium can also be determined polarographically[111-113] from the waves produced in the polarographic reduction of $Tc^{VII}$ at at dropping mercury electrode (Fig. 7)[113]. The first wave at pH 2, corresponding to the four-electron reduction of technetium, together with the first and second waves at pH 13, due to the three- and one-electron reductions respectively, can be used for the determination of technetium in the presence of rhenium. Measurement of the third catalytic wave gives maximum sensitivity and has been used[113] for the determination of very small quantities of technetium.

In neutral solutions with 1 M $NaClO_4$ as the supporting electrolyte a distinct diffusion wave with a half-wave potential $E_{1/2}$ = -0.8 V is observed[114], corresponding to the three-electron reduction. This has made it possible to determine technetium fairly accurately. In the range $5 \times 10^{-3}$–$8 \times 10^{-2}$ M, the technetium concentration is directly proportional to the magnitude of the limiting current.

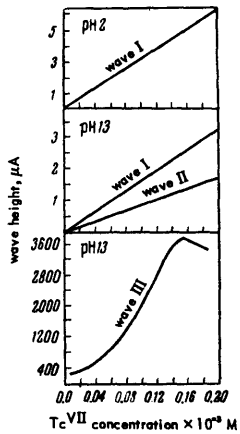



Fig. 7. Dependence of the height of the polarographic wave on the $Tc^{VII}$ concentration.

Miller *et al.*[111] developed methods for determining technetium in buffer solution at pH 7, and White and Thomason[115] determined milligramme quantities of this element by potentiometric titration with chromium sulphate.

A recent paper[112] described a simple rapid method for determining technetium by coulometric titration at controlled potential (-0.70 V) in an acetate-buffer tripolyphosphate solution. The relative error in the determination of 0.5–5 mg of technetium is ±1%. Many ions, for example $ReO_4^-$, $MnO_4^-$, $CrO_4^{2-}$, $Ce^{4+}$, $Cu^{2+}$, $Zn^{2+}$, $Cl^-$, $ClO_4^-$, and $SO_4^{2-}$, do not interfere, but ions such as $Fe^{3+}$, $MoO_4^{2-}$, $Ru^{4+}$, $UO_2^{2+}$, $VO^{2+}$, $F^-$, and $NO_3^-$ cause interference. Technetium can be separated from interfering elements by codistillation with sulphuric acid.

For the rapid determination of $^{99m}Tc$ in a mixture of uranium fission products, Love and Greendale[116] used the method of amalgam polarography. Technetium was concentrated in the mercury drop, after which its activity was measured. The coefficient of purification was $10^5$ and the accuracy of the determination was ~1%.

### 6. Mass-Spectrometric Method

The mass-spectrometric method has been used for the identification of technetium in the isolation of the latter from the fuel elements of the reactor in the first atomic power-station[117] and, in conjunction with isotopic dilution methods, for quantitative determination[62].

The determinations were made on mass-spectrometers with a 60° magnetic field and chamber radius 15–20 cm. Technetium was deposited on the iridium emitter in the form of aqueous ammonium pertechnate solution from a micropipette[117], or electrolytically[62]. After the emitter had been heated at 400° in an atmosphere of hydrogen to reduce the technetium to the metal, the ion source of the specimen was placed in the mass-spectrometer, in which $Tc^+$ ions were produced at 1600–1800°.

In the quantitative determination of $^{97}Tc$ and $^{98}Tc$ in minerals[69] by this method a known quantity of $^{99}Tc$ was

TABLE 6. Sensitivity of methods for determining microgramme quantities of technetium.

| Method | Sensitivity, g |
|---|---|
| Gravimetric | $(3—5)\cdot10^{-6}$ |
| Spectrophotometric | $3\cdot10^{-7}$—$10^{-6}$ |
| Radiometric | $10^{-7}$ |
| Spectroscopic | $10^{-7}$ |
| Polarographic | $5\cdot10^{-6}$ |
| Mass-spectrometric (using isotopic dilution method) | $5\cdot10^{-9}$ |
| Neutron-activation | $2\cdot10^{-11}$ |

introduced into the solutions containing the technetium to be determined, before deposition on the emitter; the $^{99}$Tc served as isotopic diluent. The quantitative determination was made by the isotopic dilution method from the change in the isotopic composition on mixing[118]. The sensitivity of the determination is $5 \times 10^{-9}$ g, which is much higher than the methods previously described.

### 7. Neutron-Activation Method

The most sensitive method for the determination of traces of technetium is neutron-activation analysis, which has been used successfully by Boyd and Larson[62] in the search for technetium in natural materials. The determination of the $^{99}$Tc content by the neutron-activation method is based on irradiation of the specimen with slow neutrons and the formation, as a result of an $(n,\gamma)$-reaction, of the radioactive $^{100}$Tc, with a half-life of 15.8 s. $^{99}$Tc has a fairly high thermal-neutron capture cross-section (20 barn), and this makes it possible to determine down to $10^{-11}$ g of technetium by this method. Because of the fairly short half-life of $^{100}$Tc, however, this method has not been widely applied.

The sensitivities of all the above methods of determination are compared in Table 6.

## V. FUTURE DEVELOPMENTS

One of the main tasks in the analytical chemistry of technetium is the development of new, effective, and economic methods for concentrating technetium from its extremely dilute solutions containing high concentrations of various salts. A promising method in this connection is ion-exchange chromatography with strongly basic anion-exchange resins, which make it possible, for example, to extract and purify technetium from concentrated nitrate solutions. Study of the sorption capacity and selectivity of a variety of synthetic anion-exchange resins and inorganic sorbents for technetium ions in various media is therefore of interest.

The development of extraction methods for concentrating technetium from various materials is desirable. Of particular promise are extraction methods for isolating and purifying technetium from fairly concentrated technetium solutions, and also for the preliminary concentration of the element for subsequent spectrophotometric, spectroscopic, or polarographic determination.

Studies of the lower valency states (less than seven) of technetium with a view to their utilisation in analytical chemistry are necessary. In these valency states, technetium forms a variety of complexes which may be used for the selective concentration, separation, and determination of technetium in extraction, chromatographic, spectrophotometric, and other methods of analysis. The study of the varied analytical properties of this element, which exhibits both metallic and non-metallic character, and also the investigation of new possible applications in science and technology, are of interest.


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# STRUCTURE AND PROPERTIES OF MOLTEN SALTS

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## 1. INTRODUCTION

Molten salts form a large class of the liquids which exhibit electrolytic conductivity. The principal structural units in molten salts are ions, they are therefore also terms ionic liquids.

The practical importance of molten salts has increased considerably in recent years in connection with the development of new branches of metallurgy and energetics. Molten salts are widely used for the electrolytic production of various light and rare metals[1,2], used in nuclear technology as heat transfer media or reactor fuels[2,3], employed as electrolytes in fuel cells[4], etc. Recently there has been a sharp increase in the number of publications — both research papers and review articles. Reviews and monographs on various aspects of the physics and chemistry of molten salts have been published by Belyaev *et al.*[5], Voskresenskaya[6], Delimarskii and Markov[7], Morachevskii[8-10], and many other authors[2,3,11-20]. The earlier investigations have been critically discussed and reviewed[1,21].

Electrolytic conductivity and other properties of molten salts are explained if the salts are considered to be composed of charged structural units — ions. In characterising the properties of molten salts and comparing them with the properties of ionic crystals, reference is sometimes made to dissociation on melting. However, here the term "dissociation" has only conventional significance, since during fusion there is no decomposition of neutral molecules into ions. The fusion of a salt is essentially the destruction of the crystal lattice, usually accompanied by an increase in volume. The extra volume produced ensures freer movement of ions, so that it is more logical to speak of the disordering or disintegration of the crystal lattices than of dissociation. The condensation of salt vapours, which consist of neutral molecules, is accompanied by self-dissociation, as a result of which ions, earlier bound in pairs, are socialised, are collectivised, to form an ionic liquid. In this respect there is a definite analogy between salts and metals, since in the condensation of metal vapours there is the collectivisation of the electrons[22].

It is natural for properties of molten salts such as electrical conductivity, viscosity, diffusion, surface tension, heats of phase transformations, and so forth to depend on the characteristics of the ions forming the melt — their dimensions, masses, polarisability, and charge. However, in considering this dependence it is necessary to take into account that the ions in the melt form a single collective, exhibiting a definite structure. Just as the properties of ionic crystals are determined not only by the properties of the individual ions, but also by the properties of their set, that is, the crystal lattice, the properties of molten salts can be understood only by studying their structure. In turn, a study of the properties of salt melts permits assessment of their structure and makes possible their quantitative characterisation.

The development of the theory of the liquid state as applied to molten salts shows that their principal properties are due to the structural peculiarities more than to

the properties and interaction of the individual ions. This is shown especially clearly by the example of electrical conductivity of molten salts. Most of the ions in a melt are vibrating at each moment of time at definite equilibrium positions analogous to the nodes of a crystal lattice; these ions cannot participate in forward motion even in very strong fields, and consequently cannot take part in the transport of electricity. Forward motion becomes possible for a given ion only when a neighbouring equilibrium position becomes vacant, that is, as a result of fluctuations in the structure.

In the present review an attempt is made to consider the experimental data available about the properties of pure molten salts in the light of contemporary theoretical views about their structure and molecular constitution.

Until recently the ionic–molecular composition of molten salts had been studied solely by cryoscopic methods. Not long ago spectroscopy and X-ray diffraction became widely used for this purpose. The essence of the cryoscopic method lay in the use of the Raoult–van't Hoff law, according to which the freezing point depression $\Delta T$ on dissolution of a foreign salt in a given melt is

$$\Delta T_f = \nu \frac{RT_f}{L_f} \times \frac{M}{1000} \times m = \nu m k_f, \qquad (1)$$

where $M$ is the molecular weight of the solvent, $L_f$ its heat of fusion, $m$ the molarity of the solution, $k_f$ a cryoscopic constant, and $\nu$ the number of particles, foreign with respect to the solvent, which are formed from one molecule of the solute salt. Naturally, study of the freezing point depression not only permits confirmation of the ionic structure of the salt but also provides concrete information about the ionic composition of the melt.

The number of cryoscopic investigations is very large. The older works on the cryometry of molten salts were discussed by Hoenen[23] and contemporary investigations in the review of Janz *et al.*[11] The earlier works on cryometry (Zakura and others[21,23]) were not distinguished by exceptional accuracy. In later years Janz and coworkers[24,25], Kordes and coworkers[26–28], and others[29–52] made careful measurements of freezing point depressions. As an example Fig. 1 gives $\Delta T_f = f(m)$ curves for molten $AgNO_3$, and shows that Eqn. (1) is obeyed satisfactorily. Some deviations can be related to the formation of solid solutions or with the non-ideality of the system[29].

The scheme of "dissociation" of salts, as follows from the cryometric results, usually corresponds with the ionic structure of the crystals. The particles bound in the crystal, mainly by electrostatic forces, form relatively free ions in the melt, for example, $Na^+$, $Cl^-$, $NO_3^-$, etc. Complex ions, between the structural constituents of which covalent forces act ($NO_3^-$, $CO_3^{2-}$, $SO_4^{2-}$) behave as integral units and there are no signs of their decomposition into their individual constituents. In certain cases the fusion of ionic crystals leads to the formation of new, more complex ions. Thus it follows from cryoscopic measurements that in the dissolution of NaF in $PbF_2$ $\nu = \frac{1}{2}$, and in the dissolution of NaF in NaCl $\nu = 1$.[16] These results can be explained by assuming that a complex ion is formed during the fusion of sodium fluoride:

$$2NaF \rightleftarrows Na_2F^+ + F^-.$$

The formation of such autocomplexes during fusion is also possible in several other instances.

## 2. OPTICAL PROPERTIES OF MELTS

More complete information about the ionic composition of molten salts can be obtained by the study of optical properties.

Many authors have studied the absorption spectra of molten salts[53–65], and it has been shown that they usually absorb in the ultraviolet region. Their absorption spectra are essentially different from those of salt vapours. The latter usually exhibit absorption bands spaced over a rather wide range of frequencies and which consist of many closely spaced spectral lines. The molecular absorption spectra of melts consist of wide bands with one or two maxima. This diffuseness is linked with the small distance between the ions and the strong excitation of the electron clouds of the absorbing particles by the neighbour ions.

The absorption band of a molten salt is connected with the excitation of the outer electron in the anion and its transfer to an orbital in the field of neighbouring cations. Ionic crystals give similar spectra (Fig. 2).

The energy corresponding to maximum absorption is

$$\varepsilon_{max} = \varepsilon_i - h^2/8mr_0, \qquad (2)$$

where $\epsilon_i$ is the ionisation potential of the anion, $m$ the mass of an electron, and $r_0$ the radius of the excited orbital, equal to the inter-ionic distance less the radius of the cation[63–65]. In the absorption band the optical density is usually very

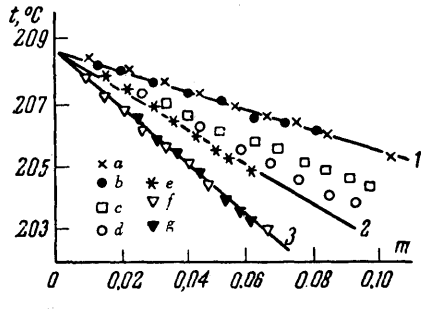



Fig. 1. Depression of the freezing point of $AgNO_3$ [26] on dissolution of: *a*) $Ag_2SO_4$; *b*) $KNO_3$; *c*) $ZnSO_4$; *d*) $PbSO_4$; *e*) $KClO_4$; *f*) $PbCl_2$; *g*) $K_2Cr_2O_7$. 1), 2), and 3) calculated curves for $\nu = 1$, 2, and 3 respectively.

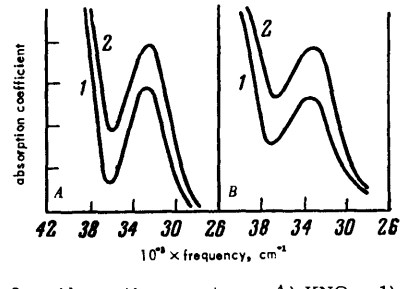



Fig. 2. Absorption spectra. *A*) $KNO_3$: 1) 338°, melt; 2) 333°, crystal. *B*) $NaNO_3$: 1) 308°, melt; 2) 304°, crystal.

great[59,60], so that the structure of the spectrum cannot always be established. Therefore some authors characterise the spectra by the parameters of the absorption edge ($\epsilon_{edge}$, $\lambda_{edge}$) and not by the energy or wavelength at the absorption maximum ($\epsilon_{max}$, $\lambda_{max}$).

There is little information about the dependence of the absorption spectrum on the nature of the salt. For the alkali metal halides, on going from Cs to Li there is a displacement of the absorption band into the violet, and on going from Cl to I, into the red side. The absorption limit of the alkali metal halides near their melting points lies at about 250–350 mμm and that of the halides of the metals of the auxiliary subgroups in the 500–600 mμm region[53,60]. A quantitative relation has been found for the alkali metal nitrates between the spectra and the cation radius:

$$\varepsilon_{max} = 3.81 + 0.33/r_+, \text{ eV}. \quad (3)$$

Probably, analogous relations exist for other salts.

A temperature dependence of the absorption spectra is predicted by Eqn. (2) and is expressed by the formula:

$$\varepsilon_{max} = \varepsilon_0 - \kappa t, \quad (4)$$

in which the coefficient $\kappa$ is proportional to the coefficient of thermal expansion of the salt[55,58,60,63]. It is also noted, that for many salts the $\epsilon_{max}(t)$ curves do not have inflections near the melting point, showing that there is no complex formation[54-58,63].

There is another important parameter of molten salts — their refractive indices. Both the old work[66-68] and the more recent investigations of Bloom[13,14,69,70], Thurmond[58], and Murgulescu[71] show that the refractive indices of melts decrease linearly with rise in temperature:

$$n_t = n_0 - bt. \quad (5)$$

The dependence of the refractive indices on the nature of the salt is shown in Table 1.

It is more convenient to characterise a melt by its molecular refraction:

$$R = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{\rho}, \quad (6)$$

TABLE 1. Refractive indices of molten salts for the sodium D line[13,14].

| Salt | $n_0$ | $10^4 b$ | $\Delta t$, °C |
|---|---|---|---|
| LiCl | 1.590 | 1.60 | 620—750 |
| KCl | 1.667 | 3.50 | 780—810 |
| AgCl | 2.148 | 2.10 | 480—656 |
| $CdCl_2$ | 1.735 | 0.35 | 590—700 |
| $PbCl_2$ | 2.244 | 3.67 | 515—620 |

TABLE 2. Molecular refractions of salt melts ($cm^3$) for the sodium D line[13,70,72]

| Salt | $t$, °C | $R_{melt}$ | $R_{crystal}$ | $R$ for infinitely dilute solution |
|---|---|---|---|---|
| LiCl | 650 | 8.20 | 7.59 | 8.42 |
| NaCl | 850 | 9.48 | 8.52 | 8.88 |
| KCl | 800 | 11.68 | 10.85 | 10.93 |

which for most salts is almost independent of temperature and is, to a known degree of approximation, the sum of the refractions of the individual ions. This follows, in particular, from the fact that the molecular refractions of molten salts, crystals, and infinitely dilute aqueous solutions are close to one another (Table 2).

## 3. RAMAN SPECTRA AND INFRARED SPECTRA OF MOLTEN SALTS

An investigation of Raman spectra and infrared spectra provides a possibility of obtaining important information about the structure of molten salts. As is well-known, in the molecular spectra produced by transitions between vibrational or rotational energy levels, there are lines which correspond to these transitions. These frequencies, which correspond to the molecular vibrational levels, determine the value of the Raman frequencies, which are equal to the sums $\nu_0 \pm \nu_i$, where $\nu_0$ is the frequency of the exciting radiation and $\nu_i$ is that of a natural vibration of the molecule, which can be excited in scattering a beam of frequency $\nu_0$.

Raman and infrared spectra of molten salts have been investigated only in recent years[73-81]. Bues[73-75] and Walfaren *et al.*[80] obtained Raman spectra for alkali metal nitrates, phosphates, pyrophosphates, and hydrogen sulphates, and also for zinc and cadmium chlorides, and Janz and McIntire[81] obtained those for mercury halides. Wilmshurst[76-78] and Bradbury[79] studied the vibrational spectra of various nitrates, chlorates, phosphates, and other salts with complex anions.

As an example let us consider work devoted to alkali metal nitrates. The $NO_3^-$ ion forms a planar equilateral triangle of oxygen atoms with a nitrogen atom at the centre. Here, symmetric and antisymmetric vibrations along the bonds, giving Raman frequencies $\nu_1$ and $\nu_3$, two-dimensional vibrations leading to destruction of the symmetry, with frequency $\nu_4$, and out-of-plane Raman-inactive vibrations of frequency $\nu_2$, are possible (Fig. 3). Table 3 gives the Raman frequencies of the $NO_3^-$ ion for crystals, aqueous solutions, and molten salts.

The values of frequencies $\nu_1$, $\nu_3$, and $\nu_4$ are always very close. The spectra of melts do not contain any new frequencies. The line $\nu_3$ for $LiNO_3$ (and $AgNO_3$) is split, which is due to the marked deformation of the $NO_3^-$ ion. Bues[73] established that the frequency $\nu_1$ is directly determined by

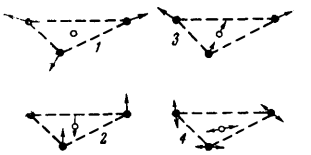


Fig. 3. Diagram of the vibrational motion of the oxygen and nitrogen atoms in the $NO_3^-$ ion. 1) Symmetric stretching vibrations with frequency $\nu_1$; 2) out-of-plane vibrations with frequency $\nu_2$; 3) antisymmetric stretching vibrations with frequency $\nu_3$; 4) bending vibrations with frequency $\nu_4$.

TABLE 3. Combination frequencies of the $NO_3^-$ ion.

| Frequency \ Salt | $LiNO_3$ | | | $NaNO_3$ | | $KNO_3$ | |
|---|---|---|---|---|---|---|---|
| | solution | crystal | melt | crystal | melt | crystal | melt |
| $\nu_4$ | 718 | 728 | 724 | 728 | 722 | 714 | 715 |
| $\nu_3$ | 1392 | 1391 | 1366, 1476 | 1387 | 1386 | 1361 | 1382 |
| $\nu_1$ | 1047 | 1086 | 1061 | 1069 | 1053 | 1050 | 1048 |

the free volume of the salt, which is calculated as the difference

$$V_f = V - \omega N, \qquad (7)$$

where $N$ is Avogadro's number, $\omega$ the sum of the volumes of the anion and cation, and $V$ the molar volume of the salt. The displacement of $\nu_1$ during the fusion of the salt is explained by its expansion.

Other work on Raman and infrared spectra also showed that the structure of complex anions in a melt is analogous to their structure in crystals and aqueous solutions. The existence of complex ions in halide melts has been demonstrated[74,81].

## 4. SCATTERING OF X-RAYS AND NEUTRONS IN MOLTEN SALTS

During passage through a thin layer of liquid the X-rays scattered by any atom interfere with the rays scattered by its nearest neighbours, and since the number of these neighbours and the distance between them alter due to thermal motion the diffraction picture which can be observed is the result of some mean distribution of atoms and is independent of which atom was chosen at the start of the reading.

Usually the distribution of the atoms in the liquid is characterised by the function $\rho(r)$, defined as the mean number of atoms in unit volume at a distance $r$ from the central atom. The number of atoms in the spherical layer from $r$ to $r + dr$ equals $\rho(r)4\pi r^2 dr$.

Since in a liquid there is not a strict ordering in the position of the atoms, function $\rho(r)$ gives a continuous curve with maxima corresponding to the most probable distances. As the distance from the central atom increases, all distances become equally probable and the maxima disappear from the $\rho(r)$ curve.

Zernicke and Prins[82] and Debye[83] found a relation between the experimental scattering curve in a monatomic liquid and the radial distribution function $4\pi r^2\rho(r)$ or $\rho(r)$. This theory, which enabled an averaged picture of the distribution of particles in the liquid to be obtained from the experimental results on scattering of X-rays, was then developed by Warren *et al.*[84] for polyatomic liquids. The method of X-ray scattering was used successfully in the case of molecular liquids, particularly $CCl_4$ (Fig. 4). The radial distribution function for carbon tetrachloride has two narrow isolated peaks at 1.74 and 2.92 Å, corresponding to the distances between the atoms C–Cl and Cl–Cl in the $CCl_4$ molecule, and a series of subsequent maxima (3.5, 5.0, and 6.4 Å), corresponding to the most probable distance between the atoms of carbon and chlorine in the neighbour molecules. The form of the first two maxima shows that the $CCl_4$ molecule is not dissociated in the liquid. Ritter and coworkers[86-88] obtained similar results in investigating molten salts such as $AlCl_3$ and $SnI_4$, which are

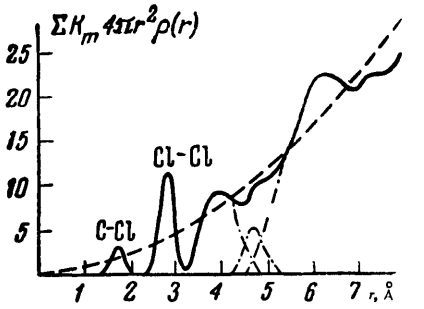



Fig. 4. Radial distribution function for $CCl_4$ at 25°.[85]

not electrolytes†. Experiments with molten $CdI_2$ showed that the coordination number 6 characteristic for the crystal‡, is retained here, but two of the iodine atoms are situated somewhat closer to the cadmium atom than are the others. This shows that $CdI_2$ molecules are formed in the melt as well as $Cd^{2+}$ and $I^-$ ions. Similarly, the distribution curve for $InCl_3$ shows that the ions $In^{3+}$ and $Cl^-$ and the dimer $In_2Cl_6$ can be formed in the melt.

In recent years there have been investigations of the scattering of X-rays in typically ionic liquids — halides, nitrates, and carbonates of the alkali metals, etc.[90-107] Fig. 5 shows a typical radial distribution curve for these melts. Despite some quantitative discrepancy between the results of different workers, they all obtained quantitatively similar results. There have been studies[89-91,96-104] devoted to the structure of alkali and alkaline earth metal halides, both with X-ray diffraction and also by neutron diffraction[102]. Alkali metal nitrates[94,95,105], molten NaOH and KOH,[93] and alkali metal carbonates and sulphates[107] have been studied. Furukawa[106] attempted to generalise the results of these investigations.

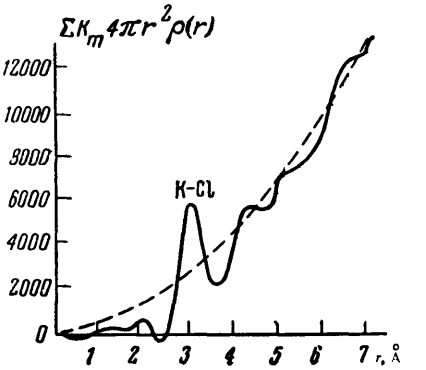



Fig. 5. Radial distribution function for molten KCl.[92]

† On fusion these salts not only give no ions but even also form dimeric molecules, for example, $Al_2Cl_6$.

‡ The coordination number is calculated from the area under the given peak of the radial distribution curve.

TABLE 4. Characteristics of the first coordination sphere — the $M^+-X^-$ interaction — in melts and crystals of alkali metal halides [101,102].

| Salt | Melts | | Crystals | | |
|---|---|---|---|---|---|
| | $r'_{max}$, Å | $N_1$ | $r'_{crit}$, Å (t°) | $r'_{crit}$, Å (20°) | $N_1$ |
| LiCl | 2.47 | 4.0 | 2.66 | 2.57 | 6 |
| LiI | 2.85 | 5.6 | 3.12 | 3.00 | 6 |
| NaCl | 2.88 | 4.7 | 2.95 | — | 6 |
| NaI | 3.15 | 4.0 | 3.35 | 3.23 | 6 |
| KCl | 3.10 | 3.7 | 3.26 | 3.14 | 6 |
| CsCl | 3.53 | 4.6 | 3.57 | 3.57 | 6(8) |
| CsI | 3.85 | 4.5 | 3.94 | 3.95 | 6(8) |

The maxima on the radial distribution curve were in all cases close to the corresponding inter-ion distances in the crystals ($r_{cryst}$), but the coordination numbers in the first ($M^+-X^-$) and second ($M^+-M^+$, $X^-X^-$) coordination spheres ($N_1$, $N_2$) are considerably less than in the crystal lattices (Table 4).

It is interesting that the values of $r'_{max}$ for melts are usually somewhat less than in crystals close to the melting point — the ions in melts are more closely packed on account of the break-down of the symmetry of the field. The considerable breadth of the first peak shows that the true distance between the ions $M^+-X^-$ can be also much greater and less than $r'_{max}$. The closest possible distance between ions in melts is close to the $M^+-X^-$ distance in gaseous molecules.

The absence of accurately determined values of the inter-ion distances in melts implies that the ions associate in separate groups, between which are distributed unoccupied voids and vacancies. In the small groups the ions are more closely packed, as in gaseous molecules; the coarse groups represent as it were fragments of the crystal lattice. These groups are in dynamic equilibrium, continuously forming and decomposing.

The second peak on the radial distribution curves is still more diffuse than the first. The sharpest second peak, that is, the greatest indication of uniformity in $M^+-M^+$ and $X^-X^-$ distances and the degree of ordering of the melt structure are observed for salts with a small cation (lithium and sodium halides). In potassium and caesium salts the second peak is very diffuse, which is evidence of a less regular structure.

There are interesting prospects in studying the structure of molten salts, not only by the methods considered above, but also by $\gamma$-radiation absorption [108] and nuclear magnetic resonance [79,109]. However, there has not yet been proper development in these directions.

## 5. DENSITY AND MOLAR VOLUME

Investigation of the nature of molten salts and their practical application necessitate a knowledge of their physical properties, including density.

Melt densities are measured either pyknometrically or by hydrostatic weighing [5,2]. The results obtained before 1939 — and particularly the work of Jaeger [110,111], Klemm [112,113], and others [114-119] cannot now be considered sufficiently reliable. The most reliable data on densities of the alkali metal halides have been published by Yaffe and van Artsdalen [120]; they fit (see Table 5) Mendeleev's linear equation:

TABLE 5. Densities of molten alkali metal halides in g $cm^{-3}$ — parameters of Eqn. (8).

| Salt | a | $10^3 b$ | Salt | a | $10^3 b$ | Salt | a | $10^3 b$ |
|---|---|---|---|---|---|---|---|---|
| LiCl | 1.7660 | 0.4328 | NaI | 3.3683 | 0.9191 | RbBr | 3.4464 | 1.0718 |
| LiBr | 2.8878 | 0.6520 | KCl | 1.9767 | 0.5831 | RbI | 3.6377 | 1.1435 |
| LiI | 3.5397 | 0.9176 | KBr | 2.7333 | 0.8252 | CsCl | 3.4782 | 1.0650 |
| NaCl | 1.9911 | 0.5430 | KI | 3.0985 | 0.9557 | CsBr | 3.9109 | 1.2234 |
| NaBr | 2.9518 | 0.8169 | RbCl | 2.8799 | 0.8832 | CsI | 3.9179 | 1.1834 |

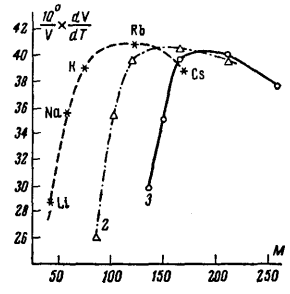



Fig. 6. Dependence of the volume coefficient of expansion of molten salts at the melting point on the molecular weight [120]: 1) chlorides; 2) bromides; 3) iodides.

$$\rho = a - bt. \qquad (8)$$

Careful measurements have been made [121,122,130,131] of the density of alkali metal nitrates and carbonates. There is less systematic information about the density of salts of the alkaline earth metals and the metals of the auxiliary subgroups, particularly $MgCl_2$, [123,124] $CaCl_2$, [125] and $BaCl_2$, [126] mercury halides [81,128], alkaline earth fluorides [127], and various other salts [132-135]. In all cases Eqn. (8) is obeyed.

The volume coefficients of thermal expansion of molten salts:

$$\alpha = \frac{1}{V}\times\frac{dV}{dt} = -\frac{1}{\rho}\times\frac{d\rho}{dt} = \frac{b}{\rho}, \qquad (9)$$

and their molar volumes:

$$V = M/\rho. \qquad (10)$$

are entirely determined by their internal structure. In particular, it is characteristic of the alkali metal halides that the coefficients of thermal expansion of the lithium and sodium salts are relatively small, whereas those of the potassium, rubidium, and caesium salts are relatively large and almost independent of the nature of the salt (Fig. 6). This difference is probably connected with the above-mentioned expanded structure for salts with a large cation.

Comparison of the molar volumes of molten salts [5,16,21] shows that those of typically ionic melts are relatively small, whereas those of molecular liquids ($CCl_4$, $SiCl_4$, etc.) are large. It is also noted that salts formed by metals of auxiliary subgroups have smaller molar volumes than are usually associated with complex formation on melting.

## 6. COMPRESSIBILITY

The compressibility of molten salts has been determined in practice from measurements of the velocity of ultrasonic waves ($u_L$), which is related with the adiabatic compressibility by the relation:

$$\beta_s = -1/V(\partial v/\partial p)_s = \rho^{-1}u_L^{-2}. \quad (11)$$

To calculate the isothermal compressibility information about the isobaric ($C_p$) and isochoric ($C_V$) heat capacities of the melt:

$$\beta_T = -\frac{1}{V}\left(\frac{dV}{dp}\right)_T = \beta_s \times \frac{C_p}{C_V}, \quad (12)$$

is required.

There have been several measurements of ultrasonic velocity in molten salts[136,142] and it has been shown that melt compressibilities depend on temperature and increase with it (Table 6). For salts of a given type the compressibility also increases with the molecular weight.

The information about compressibility and ultrasonic velocity in salt melts obtained by Bockris and Richards[136] and other authors[139-141] differ considerably. In particular,

TABLE 6. Isothermal compressibility of alkali metal halides, $10^{12}$ cm$^2$ dyn$^{-1}$.[136]

| Salt | 700° | 800° | 900° | 1000° | Salt | 700° | 800° | 900° | 1000° |
|---|---|---|---|---|---|---|---|---|---|
| LiCl | 21.1 | 24.7 | 28.6 | 33.0 | KCl | — | 38.4 | 45.7 | 54.7 |
| LiBr | 25.8 | 29.4 | 33.6 | 38.4 | KBr | — | 43.8 | 52.1 | 62.1 |
| NaCl | — | 28.7 | 33.8 | 40.0 | KI | 49.9 | 59.9 | 72.0 | 87.3 |
| NaBr | — | 33.6 | 38.6 | 44.9 | CsCl | 42.9 | 51.2 | 62.7 | 76.3 |
| NaI | 40.0 | 47.3 | 65.6 | 65.6 | CsBr | 55.8 | 67.1 | 82.7 | 103.1 |

Bockris and Richards[136] state that the ultrasonic velocity is a linear function of $T^{\frac{1}{2}}$, whereas others[139,140] give $T$. The reason for this discrepancy is unexplained.

## 7. SURFACE TENSION

The surface tension of molten salts at their phase boundary with a vacuum or inert gas has been measured by the methods of lifting a ring, maximum bubble pressure, etc.[143]. The temperature dependence of surface tension is usually expressed by the linear equation[111]:

$$\sigma = a - bt, \quad (13)$$

although in some cases a quadratic interpolation formula has to be used. The measurements of the surface tension of molten salts made between 1900 and 1930 (for example, Jaeger[111], Arndt and Löwenstein[114]) are inaccurate, since the methods used in these works are not completely reliable. However, the results of later investigations often differ considerably from one another. Of work in recent years, reference may be made to measurements of the surface tension of halides[145-157,161], carbonates[122], and nitrates[145,158-160]. Table 7 summarises the most reliable results and shows that the surface tension depends greatly on the nature of the salt. According to Semenchenko's

TABLE 7. Surface tension of molten salts — coefficients of Eqn. (13).

| Salt | $a$ | $b$ | Reference | Salt | $a$ | $b$ | Reference |
|---|---|---|---|---|---|---|---|
| NaCl | 168.4 | 0.068 | 147 | $CaBr_2$ | 153.1 | 0.0459 | 154 |
| NaBr | 140.9 | 0.056 | 153 | $CaI_2$ | 98.7 | 0.0174 | 154 |
| NaI | 147.4 | 0.090 | 145 | $SrBr_2$ | 178.0 | 0.0439 | 154 |
| KCl | 156.3 | 0.075 | 147 | $SrI_2$ | 134.8 | 0.0383 | 154 |
| KBr | 142.2 | 0.072 | 145 | $BaCl_2$ | 225.0 | 0.078 | 156 |
| KI | 138.7 | 0.087 | 145 | $PbCl_2$ | 192.1 | 0.110 | 145 |
| $MgCl_2$ | 74.0 | 0.01 | 147 | $CdCl_2$ | 95.6 | 0.021 | 153 |
| $CaCl_2$ | 178.0 | 0.038 | 149 | AgCl | 202.2 | 0.052 | 153 |

theory, the surface tension of melts should be determined by the electrostatic interaction of the particles, that is, in the final reckoning, on their generalised moment $\mu = z/r$.[162,163] This probably explains the decrease in the surface tension of the alkali metal halides with increasing radii of cation and anion[163,164]. Salts of the alkaline earth metals show the reverse relation, which is thought[163] to be usually explained by the formation of autocomplexes on melting. However, this explanation cannot be considered exhaustive.

The parachor, the equation for which is given by Bachinskii[165]:

$$\Pi = \frac{M}{\rho_{liq} - \rho_{solid}}\sigma^{1/4}, \quad (14)$$

for molten salts usually varies only slightly with temperature. The problem whether the parachors of salts are the sums of the parachors of the individual ions has not been studied.

## 8. HEAT CAPACITY

The molar heat capacities of molten salts at constant pressure are almost independent of temperature. Values of $C_p$ have been tabulated by Kubaschewski and Evans[166] and elsewhere; more recent values are available[167-169]. Table 8 gives values of $C_p$ and the change of heat capacity on melting:

$$\Delta C_p = (C_p^{liq})_f - (C_p^{solid})_f. \quad (15)$$

It is seen that the heat capacity of molten salts is (within an accuracy of 5–10%):

$$C_p \approx 8\nu \text{ cal deg}^{-1} \text{ mole}^{-1}, \quad (16)$$

where $\nu$ is the number of ions formed by one molecule of salt.

However, this rule is inapplicable to salts with polyatomic anions. At the same time it is valid for salts such as $MgCl_2$, $PbCl_2$, etc., and this does not agree with the assumptions about the formation of autocomplexes in these melts.

TABLE 8. Heat capacity $C_p^{liq}$ and change in heat capacity during fusion $\Delta C_p$ for salts (cal deg$^{-1}$ mole$^{-1}$).[166-169]

| Salt | $C_p$ | $\Delta C_p$ | Salt | $C_p$ | $\Delta C_p$ | Salt | $C_p$ | $\Delta C_p$ |
|---|---|---|---|---|---|---|---|---|
| LiCl | 15.5 | 1.5 | $MgCl_2$ | 22.1 | 2.0 | $PbCl_2$ | 24.9 | 2.6 |
| NaCl | 15.9 | 0.6 | $CaCl_2$ | 24.7 | 4.35 | $PbBr_2$ | 26.3 | 5.6 |
| KCl | 16 0 | 1.35 | $SrCl_2$ | 26.2 | 5.1 | $PbI_2$ | 32.3 | 11.7 |
| RbCl | 15.3 | 1.3 | $CdCl_2$ | 26.7 | 4.9 | $BiCl_3$ | 34.3 | 8.2 |

For salts of one type there is also some increase in heat capacity with molecular weight. There is only approximate information about the jumps in heat capacity on melting. It must also be taken into account that the rise starts much below the melting point of the salt[170].

## 9. HEATS OF VAPORISATION AND VAPOUR PRESSURE

Usually the heat of vaporisation and boiling point of salts are known only approximately. The heat of vaporisation is determined either calorimetrically or by measuring the temperature dependence of vapour pressure[171]. Heats of vaporisation of salt melts have been published[166,172-176].

Salts with a strongly ionic type of bond (alkali metal halides) are typified by a higher boiling point and heat of vaporisation, and those with a considerable covalent bond fraction (for example, $BeCl_2$, $ZnCl_2$) by a lower one.

The alkali metal halides have been most fully studied. The entropy of vaporisation of these salts ($\Delta S^\circ_{vap} = L^\circ_{vap}/T_{boil}$) is 25–30 cal deg$^{-1}$ mole$^{-1}$, which is evidence that they have similar degrees of ordering. Pauling[177] showed that the heats of vaporisation and melting and the melting and boiling points of the alkali metal halides should exhibit a regular dependence on the inter-ionic distance in the crystals, since all these properties are associated with the lattice energy and this is determined by the sum of the ionic radii. However, the properties of real salts depart considerably from the expected relation. Pauling considers that these anomalies are due to the mutual repulsion of large anions which play a considerable part in lattices with small cations (Li and Na salts).

Investigations of the vapour pressure of molten salts have been reviewed[166,173,178], but recently new results about the composition of the vapours of inorganic salts have been obtained which compel critical consideration of the earlier measurements. Thus it was shown[179-185] that in alkali metal halide vapours there is a large proportion of dimers $(MX)_2$ and trimers $(MX)_3$. Formation of polymers was also found in $ThF_4$,[176] $FeCl_2$,[186] CuCl,[187] AgCl,[188] and other salt vapours. The heats of dissociation of the polymeric molecules are comparable with the heats of vaporisation.

The polymerisation in the salt vapours leads to a change in their molecular weight, a knowledge of which is necessary if the vapour pressure is determined by the vaporisation method, the effusion method, etc. Therefore the old data obtained by such methods[189,190] are incorrect. The most reliable absolute methods of determining vapour pressure — the static and the boiling point[171,191] methods — were used in references 192–203 and 174, 176 respectively.

TABLE 9. Vapour pressures of molten salts in mmHg[166,179,198].

| Salt | $-A$ | $-B$ | $D$ | Salt | $-A$ | $-B$ | $D$ | Salt | $-A$ | $-B$ | $D$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| LiF | 14500 | 4.02 | 23.56 | KCl | 11023 | 3.526 | 20.80 | CsBr | 10270 | 3.52 | 20.65 |
| LiCl | 10760 | 4.02 | 22.30 | KBr | 10050 | 3.0 | 18.67 | CsI | 10230 | 3.52 | 20.70 |
| LiBr | 10170 | 3.52 | 20.55 | KI | 14560 | 3.52 | 20.41 | $BeCl_2$ | 6340 | — | 10.64 |
| LiI | 11110 | 3.52 | 21.70 | RbF | 11190 | 3.52 | 20.90 | $MgCl_2$ | 10840 | 5.03 | 25.53 |
| NaF | 13260 | 3.52 | 21.31 | RbCl | 10300 | 3.0 | 18.77 | $ZnCl_2$ | 8440 | 1.50 | 16.61 |
| NaCl | 11495 | 3.52 | 20.93 | RbBr | 10220 | 3.52 | 18.80 | $CdCl_2$ | 9183 | 5.04 | 25.91 |
| NaBr | 10500 | 3.0 | 18.81 | RbI | 10280 | 3.52 | 20.64 | $PbCl_2$ | 10168 | 6.65 | 31.73 |
| NaI | 10740 | 3.52 | 20.96 | CsF | 9850 | 3.52 | 20.52 | $FeCl_2$ | 9476 | 5.23 | 23.65 |
| KF | 11150 | 3.52 | 20.60 | CsCl | 10770 | 3.52 | 18.14 | $BiCl_3$ | 5980 | 7.04 | 31.38 |

Applying the Clausius–Clapeyron equation under conditions far from the critical, and assuming that the vapour will behave as an ideal gas, but that the temperature dependence of the heat of vaporisation is expressed by the relation $dL_{vap}/dT = \Delta C_p$, it is easy to obtain

$$\log p = \frac{A}{T} + B \log T + D, \qquad (17)$$

where $A = -L_{vap}/4.575$, $B = \Delta C_p/R$, $\Delta C_p$ is the difference between the heat capacities of liquid and vapour, $L^\circ_{vap}$ is the heat of vaporisation at the boiling point, and $D$ a constant. In some instances the term $B \log T$ can be neglected§.

Eqn. (17) is usually employed to express the experimental results, the coefficients $A$, $B$, and $D$ being determined empirically. Table 9 gives their values for several salts.

In certain cases[179] attempts have been made to calculate theoretically the coefficient $B = \Delta C_p/R$ from the experimental values of $C_p^{liq}$ and the calculated $C_p^{vap}$. In this, the values of $B$ should evidently be close within a particular series of salts. As Table 9 shows this requirement is fulfilled in many instances.

## 10. HEATS OF FUSION OF IONIC CRYSTALS

The fusion of crystals and the thermodynamic parameters of this process ($T_f$, $L_f$) are determined by the lattice energy, and thus in the end by the radii, polarisability, ionic charges, and the structure of the electron clouds of the ions. Heats of fusion are determined by calorimetric and cryoscopic methods and by measurement of the temperature coefficients of the e.m.f. of chemical cells[166,205,206]. The melting points and heats of fusion of salts are given in various reviews[166,172,207,208]. Recently these quantities have been determined[167,169,192,209-215], but the results obtained are often quite contradictory.

Table 10 gives the parameters for the fusion of alkali metal halides. An analysis of it and of the other available data suggests the following conclusions[5]:

TABLE 10. Heats (kcal mole$^{-1}$) and entropies (e.u.) of fusion of alkali metal halides[209].

| Salt | $L_f$ | $\Delta S_f$ | Salt | $L_f$ | $\Delta S_f$ | Salt | $L_f$ | $\Delta S_f$ |
|---|---|---|---|---|---|---|---|---|
| LiF | 6.47 | 5.77 | NaBr | 6.24 | 6.12 | RbF | 6.15 | 5.76 |
| LiCl | 4.76 | 5.39 | NaI | 5.64 | 6.04 | RbCl | 5.67 | 5.70 |
| LiBr | 4.22 | 5.13 | KF | 6.75 | 5.97 | RbBr | 5.57 | 5.77 |
| LiI | 3.50 | 4.72 | KCl | 6.34 | 6.08 | RbI | 5.27 | 5.73 |
| NaF | 7.78 | 6.14 | KBr | 6.10 | 6.06 | CsF | 5.19 | 5.23 |
| NaCl | 6.69 | 6.23 | KI | 5.74 | 5.02 | CsCl | 4.84 | 5.27 |
| | | | | | | CsBr | 5.64 | 6.20 |
| | | | | | | CsI | 5.64 | 6.27 |

§ Eqn. (17) can be derived from kinetic considerations[204]. Since the number of vacancies in a crystal[22] is $N = \alpha n_0 \exp(-L^\circ_{vap}/RT)$, where $n_0$ is the number of pairs of ions in 1 cm$^3$ and $\alpha$ a constant, we obtain for the density of the vapour

$$\rho = NM/N_A = \alpha \rho_{crit} \exp(-L^\circ_{vap}/RT),$$

where $\rho_{crit} = n_0 M/N_A$. And since $p = \rho_n RT/M$ and $\rho/M = 1/V$, then $\ln p = \ln \alpha RT - \ln V - L^\circ_{vap}/RT$, where $p$ is expressed in bars and $R$ in J mole$^{-1}$ deg$^{-1}$.[204]

1. Crystals with doubly-charged ions melt at a higher temperature than those formed by similar singly-charged ions.

2. In a series of salts with the same cation, the melting point falls as the anion radius increases.

3. The melting points of crystals containing cations with 18-electron and incomplete clouds are lower than those of crystals with ions of similar radii but having inert gas shells.

4. As the bond covalency increases the melting point of the salt decreases. In particular, crystals with layer lattices ($CdI_2$, $MgCl_2$, $ZnCl_2$) have low melting points. The fall in melting point on going from the fluorides to the iodides of the alkaline earth metals is also explained by the increase in the degree of covalency of the bond.

5. Salts with molecular lattices have very low melting points and are not electrolytes, for example $SiCl_4$($t_f$ = 68°), $TiCl_4$ (-30°), $PbCl_4$ (-15°), etc. However, the same elements in a lower oxidation state give ionic salts with high melting points: $TiCl_2$ (400°), $PbCl_2$ (501°), etc.

6. The melting point of salts is greatly dependent on the crystal lattice structure. Pauling[117] noted that the low melting points of lithium salts are explained by the small radius of the $Li^+$ ion, as a result of which anion–anion contact occurs in the lattice and the mutual repulsion of the anions reduces the lattice energy. A linear relationship between the melting point and the ratio of the radii of the ions has been reported[216] for alkali metal halides.

The entropies of fusion for the alkali metal halides $\Delta S_f = L_f/T_f$ are close to 6 e.u. mole$^{-1}$, which corresponds to 3 e.u. g-ion$^{-1}$. Remembering that the entropy of fusion of the monatomic noble gases is also close to 3 e.u. × × g-atom$^{-1}$, this can be considered as confirmation of the purely ionic structure of the melts. The marked departure from this value for some salts is usually considered as an argument in support of the hypothesis concerning the formation of autocomplexes in the fusion of the salts.

## 11. VISCOSITY

The viscosity of molten salts has been determined by use of both static (falling sphere[217,218]) methods, the capillary flow method[217,219], and also dynamic methods (for example, measurement of the damping of harmonic oscillations of a body of rotation suspended in the melt by an elastic filament[217-220]). Dynamic methods usually introduce errors on account of the impossibility of allowing for all the factors which affect the measurement[217]. Static methods are generally more reliable but serious difficulties are encountered when working with melts. Hence completely reliable and systematic data on the viscosity of molten salts are still lacking.

The temperature dependence of viscosity is usually expressed by the equation[22,221-223]:

$$\eta = A_\eta \exp(E_\eta/RT). \qquad (18)$$

In the theory of absolute reaction rates[221,224] the preexponential factor is given by:

$$A_\eta = 1.09 \times 10^{-3} \rho^{2/3} T^{3/2} / M^{1/2} \Delta E_{vap}, \qquad (19)$$

where $\Delta E_{vap} = L_{vap} - RT$ is the energy of vaporisation, and $M$ the molecular weight. Panchenkov[225,226], starting from the assumption that the transfer of momentum between the particles of the liquid takes place during separation of the particles from one another, deduced the equation:

$$\eta = A\rho^{4/3} T^{1/2} \exp(2\Delta E_{vap}/\gamma RT)[1 - \exp(-2\Delta E_{vap}/\gamma RT)], \qquad (20)$$

where $\gamma$ is the coordination number and $A$ a constant.

Panchenkov's equation was applied successfully to the viscosity of melts of NaCl and $NaNO_3$, the constants $\gamma$ and $A$ being determined empirically[225].

Equation (18) is usually employed in practice[19,227], the coefficients being found empirically. Table 11 gives values of the viscosity at $1.1T_f$ °K and the parameters $A\eta$ and $E\eta$, calculated for various salts from published results.

TABLE 11. Viscosity of molten salts.

| Salt | $10^4 A_\eta$, P | $E_\eta$, kcal × × mole$^{-1}$ | $10^2 \eta_{1.1T_f}$, P | Reference | Salt | $10^4 A_\eta$, P | $E_\eta$, kcal × × mole$^{-1}$ | $10^2 \eta_{1.1T_f}$, P | Reference |
|---|---|---|---|---|---|---|---|---|---|
| LiCl | 1.64 | 8.35 | 1.27 | 274 | AgI | 15.8 | 5.13 | 2.90 | 230 |
| NaCl | 2.11 | 9.10 | 1.02 | 228 | $MgCl_2$ | 35.5 | 5.25 | 4.08 | 233 |
| KCl | 4.29 | 7.40 | 1.10 | 228 | $CaCl_2$ | 86.3 | 3.70 | 4.34 | 150 |
| LiBr | 7.07 | 5.30 | 1.38 | 227 | $CdCl_2$ | 22.9 | 3.98 | 2.04 | 231 |
| NaBr | 2.85 | 8.00 | 1.06 | 229 | $CdBr_2$ | 21.9 | 4.30 | 2.30 | 232 |
| KBr | 2.92 | 7.96 | 1.14 | 229 | $PbCl_2$ | 5.37 | 6.77 | 3.05 | 231 |
| RbBr | 12.07 | 4.73 | 1.15 | 227 | $PbBr_2$ | 7.95 | 6.25 | 3.47 | 232 |
| AgCl | 7.64 | 5.30 | 2.13 | 230 | $AgNO_3$ | 18.2 | 3.08 | 2.06 | 234 |
| AgBr | 11.7 | 4.85 | 2.71 | 220 | | — | — | — | — |

Equation (18) is usually employed in practice[19,227], the coefficients being found empirically. Table 11 gives values of the viscosity at $1.1T_f$ °K and the parameters $A\eta$ and $E\eta$, calculated for various salts from published results.

The relation between viscosity and the nature of the salt has been insufficiently studied. Several investigators[223,235] note a relation between the activation energy for viscous flow $E\eta$ and the melting point. In particular, for alkali metal halides the ratio $E\eta/L_f$ is close to 1.2. Melts of the halides of bivalent metals have a much greater viscosity, which is probably due to the appreciable fractions of covalent and van-der-Waals interactions. Bachinskii[236] considers that viscosity is not a direct function of temperature but is connected with the molar volume of the liquid:

$$\eta = \frac{C}{V - \omega}, \qquad (21)$$

where $C$ and $\omega$ are constants, $V - \omega$ having the physical interpretation of the volume available for the motion of the particles in the liquid, that is, the free volume. The applicability of Eqn. (21) to molten salts has been demonstrated[19,237], the difference $V - \omega$ usually being 2–6 cm$^3$ × × mole$^{-1}$, and $\omega$ always considerably exceeding the volume of the solid at the melting point. The constant $C$ depends on the radii of the ions[19]. Ideas about the relation between viscosity and the free volume of a molten salt have also been developed elsewhere[139,140].

## 12. DIFFUSION

Information about coefficients of self-diffusion in molten salts have only been obtained in recent years thanks to the use of radioactive isotopes. Table 12 gives the values of the empirical coefficients of the exponential equation:

$$\Delta = \Delta_0 \exp\left(-\frac{E_\Delta}{RT}\right), \qquad (22)$$

calculated from the experimental results of various authors. Many investigators[238-240,242,248] have tried to apply to salts the Stokes–Einstein equation:

$$\Delta = \frac{kT}{6\pi\eta r_i}, \qquad (23)$$

TABLE 12. Coefficients of self-diffusion of ions in molten salts.

| Salt | $10^5\Delta_0^+$, $cm^2\ s^{-1}$ | $E_\Delta^+$, kcal $mole^{-1}$ | $10^5\Delta_0^-$, $cm^2\ s^{-1}$ | $E_\Delta^-$, kcal $mole^{-1}$ | Reference |
|---|---|---|---|---|---|
| NaCl | 3.36 | 7.65 | 3.02 | 8.37 | 238, 239 |
| RbCl | 2.51 | 8.00 | 1.67 | 7.42 | 238 |
| CsCl | 1.73 | 7.30 | 2.46 | 7.82 | 238 |
| NaI | 0.63 | 4.00 | 0.43 | 4.41 | 238 |
| TlCl | 0.76 | 4.60 | — | — | 244 |
| $ZnBr_2$ | 79.0 | 16.0 | — | — | 243 |
| $PbCl_2$ | 0.773 | 6.75 | 0.895 | 7.10 | 241, 242 |
| $LiNO_3$ | 2.47 | 5.50 | 1.95 | 6.32 | 246 |
| $NaNO_3$ | 1.29 | 4.96 | 0.90 | 5.07 | 245, 246 |
| $KNO_3$ | 1.32 | 5.52 | 1.42 | 5.75 | 246 |
| $CsNO_3$ | 1.13 | 5.60 | 1.78 | 6.27 | 246 |
| $AgNO_3$ | 0.49 | 3.72 | 0.31 | 3.84 | 246 |
| $Na_2CO_3$ | 0.192 | (900°) | 0.279 | (900°) | 247 |

where $r_i$ is the ionic radius. However, comparison of Tables 12 and 11 shows that Eqn. (23) is scarcely applicable, owing to the absence of the required equality between the activation energies for the diffusion of cations and anions and a regular connection between $\Delta_0$ and the radii of the ions¶.

The Nernst–Einstein equation:

$$\Lambda = \frac{F^2}{RT}(\Delta^+ + \Delta^-), \qquad (24)$$

where $\Lambda$ is the molar conductivity, is also probably inapplicable to melts. This question has been studied[238-240,248] and the inapplicability of Eqn. (24) was attributed to the interaction of ions in the diffusion of ion pairs.

Recently Panchenkov[249] derived an equation connecting the diffusion coefficients with the molar volume, heat of vaporisation, and coordination number of the liquid. The possibility of using this equation for molten salts has not been verified.

Several investigators[22,250-252] link the coefficients for the diffusion of ions with the free volume of the liquid. In particular, Cohen and Turnbull[250] derive the equation:

$$\Delta = gau\exp(-\gamma V/V_f), \qquad (25)$$

where $g$ and $\gamma$ are constants, $a$ is the diameter of the molecule, $u$ the gas kinetic velocity, $V$ the molar volume, and $V_f$ the free volume. This equation has been verified for melts[238,251], but the results of various authors contradict one another. Bockris[238] considers that the Fürth–Frenkel' vacancy theory is more applicable to salts (see below).

## 13. ELECTRICAL CONDUCTIVITY

There have been many papers devoted to the electrical conductivity of molten salts; a review of the early investigations was given in monograph by Lorenz[253]. The later works, including those of Jaeger and Kapma[254], Sandonini[117], Goodwin and Mailey[255], and Arndt[256,257], were discussed by Biltz and Klemm[258] and then by Drossbach[259] and Antipin *et al.*[21] The results of these workers can now be considered only as approximate.

The method of measuring the electrical conductivity of salt melts has been described[120,125,260-268]. The most important point here is the necessity of using a very sensitive a.c. bridge which permits the compensation of both ohmic and capacitative components of the cell impedance over a wide range of frequencies. The electrical conductivity of the alkali metal halides was determined[120,149,150,254,258,261,269-278], but the results often do not agree with one another. The most reliable values have been given[120]. The electrical conductivity of the alkaline earth halides has been measured[123,126,149,150,279-283] and the halides of the auxiliary subgroup metals[81,125,130,279,284-288] have been studied. Bockris *et al.* give the most reliable data[279]. The electrical conductivity of nitrates[130,131,134,268,285,289-292], carbonates[122], pyrophosphates[133], etc. have also been studied.

The temperature dependence of the electrical conductivity of molten salts is usually expressed by Kohlraush's formula[293]:

$$\kappa = a + bt + ct^2, \qquad (26)$$

which usually fits the experimental data well, often without the quadratic term (that is, with $c = 0$). However, this formula has no physical basis.

Frenkel'[22] showed that the equation:

$$\Lambda = \kappa M/\rho = A_\Lambda \exp(-E_\Lambda/RT), \qquad (27)$$

should hold for molar conductance. This idea was developed by Eyring, who used the theory of absolute reaction rates to derive the relationship[120]:

$$\Lambda = 5.18\times10^{18}(D+d)d_i^2\exp(\Delta S^*/R)\exp(-\Delta H^*/RT), \qquad (28)$$

where $D$ is the dielectric constant of the melt, $d_i$ half the inter-ion distance, and $\Delta S^*$ and $\Delta H^*$ the entropy and heat of activation of the migration. For the alkali metal halides $\Delta S^*$ is 6.0–8.5 cal $mole^{-1}\ deg^{-1}$. Formula (26) corresponds to the conductance of a single ion. In the general case, according to Frenkel'[22]:

$$\Lambda = a_1\exp(-E_1/RT) + a_2\exp(-E_2/RT), \qquad (29)$$

and this transforms into (26) when $E_1 \simeq E_2$, $E_1 \gg E_2$, or $E_1 \ll E_2$. Analogously to (26) we can write:

$$\kappa = A_\kappa\exp(-E_\kappa/RT), \qquad (30)$$

in which[294]:

$$E_\Delta = E_\kappa + RT^2\alpha. \qquad (31)$$

The measurements of Yaffe and van Artsdalen[120] showed that at least for the alkali metal halides $\Delta H^* = f(T)$ and Eqns. (26) and (30) are not obeyed. For example, the true relations are:

for LiBr,

$$\Lambda = \exp(5.5709 - 694.83/T + 0.43261\times10^{-3}T),$$

and for CsBr,

$$\Lambda = \exp(9.4173 - 3980.3/T + 1.1528\times10^{-3}T),$$

etc., but these have no theoretical basis. At the same time many authors consider that Eqns. (26) and (30) are obeyed by most molten salts, at least in the range of temperatures studied[122,131,284].

The relation between $\Lambda$ or $\kappa$ and viscosity is interesting. Walden's well-known rule[295]:

$$\Lambda\eta = \text{const}, \qquad (32)$$

evidently does not apply to molten salts. This was shown, for example, by Erdey-Gruz[296], who attributed the inapplicability of Eqn. (32) to the possibility of a Grotthus mechanism of migration. Such an explanation cannot withstand criticism, since the electrical conductivity of a molten salt

¶ It is possible, however, that this discrepancy is due to experimental errors (for example, see Bockris and coworkers[238-240]).

calculated by the Nernst–Einstein equation (24) is always greater than the actual value. For the same reason the hypothesis of Abraham and Brenet[297] about the existence of considerable electronic conductivity in pure molten salts cannot be accepted.

Barzakovskii[21] considers that since the Stokes–Einstein equation (23) forms the basis of the Walden formula, the inapplicability of formula (32) is explained by the inapplicability of (23) for melts. Actually the matter is complicated because the mechanisms of viscous flow and migration in molten salts are not identical. As Frenkel' notes, in the first case the large ions play the chief part, and in the second the smaller ions.

Several investigators have discussed the applicability to melts of the formula[275,298-301]:

$$\Lambda^n\eta = \text{const}, \qquad (33)$$

but as Delimarskii and Markov showed[7], Eqn. (33) is the simple consequence of the exponential temperature dependence of $\Lambda$ and $\eta$ and completely fails to reveal a connection between these quantities.

Comparison of the data shown in Tables 14 and 13 shows a significant relation between the conductivity of melts and the nature of the salt. Biltz and Klemm[258] associate the value of $\Lambda$ at an appropriate temperature (for example, at a temperature equal to 1.1 $T_f$, °K) with the position of the cation of the salt in Mendeleev's table. The electrical conductivity of the melt increases with the ionic nature of the bond. On the other hand, salts with a high fraction of covalent bonding (such as the mercury halides) are poor conductors. Biltz[302] noted that the temperature coefficient of conductivity also increases with the covalency of the bond.

TABLE 13. Coefficients of the electrical conductivity equation, Eqn. (26).[120]

| Salt | $a$ | $10^2b$ | $10^{4.6}c$ | Salt | $a$ | $10^2b$ | $10^{4.6}c$ |
|---|---|---|---|---|---|---|---|
| LiCl | +0.5285 | 1.1250 | 4.554 | KI | −1.7100 | 0.6408 | 1.965 |
| LiBr | +1.0095 | 0.7834 | 2.057 | RbCl | −1.8097 | 0.6176 | 2.1985 |
| LiI | −0.5780 | 1.348 | 9.695 | RbBr | −3.0505 | 0.9104 | 4.510 |
| NaCl | −0.1697 | 0.6259 | 1.953 | RbI | −1.0798 | 0.4055 | 1.6305 |
| NaBr | −0.4392 | 0.5632 | 1.572 | CsCl | −1.8023 | 0.5628 | 1.765 |
| NaI | −0.8202 | 0.5940 | 1.976 | CsBr | −1.4137 | 0.4255 | 1.228 |
| KCl | −1.7491 | 0.738 | 3.000 | CsI | −1.3313 | 0.3958 | 1.305 |
| KBr | −3.2261 | 1.0124 | 4.828 | — | — | — | — |

TABLE 14. Electrical conductivity of molten halides from published results[130,260,279,281].

| Salt | $\chi_{t,t}T_f$ | $a$ | $10^2b$ | Salt | $\chi_{t,t}T_f$ | $a$ | $10^2b$ | $10^6c$ |
|---|---|---|---|---|---|---|---|---|
| $BeCl_2$ | 0.0095 | −0.0385 | 0.01 | $BaI_2$ | 0.896 * | −0.932 | 0.229 | — |
| $MgCl_2$ | 1.196 | −0.424 | 0.200 | $ZnCl_2$ | 0.035 | 0.550 | −0.292 | 4.0 |
| $MgBr_2$ | 0.869 | −0.690 | 0.925 | $ZnBr_2$ | 0.050 | 0.550 | −0.293 | 4.0 |
| $MgI_2$ | 0.671* | −0.735 | 0.1765 | $ZnI_2$ | 0.105 * | 0.302 | −0.202 | 3.26 |
| $CaCl_2$ | 2.480 | −1.450 | 0.445 | $CdCl_2$ | 2.075 | 0.510 | 0.240 | — |
| $CaBr_2$ | 1.467 | −0.896 | 0.309 | $CdBr_2$ | 1.220 | −0.080 | 0.200 | — |
| CaI | 1.392* | −0.350 | 0.193 | $CdI_2$ | 0.325 | −0.660 | 0.215 | — |
| $SrCl_2$ | 2.410 | −1.360 | 0.384 | $HgCl_2$ | $5.12\cdot10^{-5}$ | $-7.32\cdot10^{-5}$ | $3.75\cdot10^{-7}$ | — |
| $SrBr_2$ | 1.091 | −1.150 | 0.309 | $HgBr_2$ | $2.27\cdot10^{-4}$ | $-3.31\cdot10^{-4}$ | $1.95\cdot10^{-6}$ | — |
| $SrI_2$ | 0.864 | −0.725 | 0.227 | $HgI_2$ | $2.41\cdot10^{-3}$ | $5.82\cdot10^{-3}$ | $1.1\cdot10^{-4}$ | — |
| $BaCl_2$ | 2.452 | −1.378 | 0.355 | $PbCl_2$ | 1.819 | −0.889 | 0.470 | — |
| $BaBr_2$ | 1.488 | −1.120 | 0.270 | AgCl | 4.074 | 2.154 | 0.366 | — |

* $\chi$ is given for $MgI_2$ at 800°, $CaI_2$ at 900°, $SrI_2$ at 700°, $BaI_2$ at 800°, and $ZnI_2$ at 490°.

The low electrical conductivity of molten salts is often considered as an index of the formation in the melt of low-mobility autocomplexes and neutral molecules. However, this type of hypothesis requires confirmation by analysis of all the properties of the molten salt.

## 14. TRANSPORT NUMBERS

Various methods based on the use of radioactive isotopes are employed in determining the transport numbers of the ions in molten salts, but the analysis of the results thus obtained presents difficulties if one is speaking of the transport numbers in the pure salt. The transport numbers in an inert solvent are determined as the ratios:

$$\left.\begin{aligned} t_+ &= \frac{\Lambda^+}{\Lambda_+ + \Lambda_-} = \frac{u_+}{u_+ + u_-} \\ t_- &= \frac{\Lambda_-}{\Lambda_+ + \Lambda_-} = \frac{u_-}{u_+ + u_-} \end{aligned}\right\}, \qquad (34)$$

where $\Lambda_i$ are the ionic conductivities, $u_i$ the mobilities, that is, the rates of movement of the ions under unit potential gradient. In aqueous solutions the rate of motion of the ions is considered relative to the immovable mass of solvent. Understandably, it is more difficult to determine the rate in a melt. In this connection several authors[303-305] have generally denied the possibility of determining transport numbers in molten salts on account of the absence of a "coordinate system", whose part in solvents and crystals is played by the solvent or the lattice. Sundheim[304], starting from the principle of conservation of momentum and applying it to the electrolysis process, derived a formula relating the transport numbers to the masses of the ions:

$$t_- = \frac{M_+}{M_+ + M_-}, \quad t_+ = \frac{M_-}{M_+ + M_-}. \qquad (35)$$

This theory was supported by various investigators[306-308] but disputed in other papers[11,309]. Esin *et al.*[310] showed the fallibility in Sundheim's theory, pointing out that in molten salts the change in momentum is not zero[311] because of internal friction. Esin showed further that in the melt the transport of charges is effected not by the whole mass of the ions, but only by the small fraction of them which have sufficient energy (the activation energy of migration). These ions at any particular moment move relative to the melt, which acts as the same "coordinate system" as the crystal lattice in solid salts. Laity[312] developed a formal theory of migration and diffusion in molten salts based on a consideration of the inter-ion coefficients of friction.

Mulcahy and Heymann[313] proposed an empirical equation for the molar conductance of alkali metal halides close to the melting point†:

$$\Lambda = 105(1/r_+ + 1/r_-), \qquad (36)$$

where $r_i$ is the ionic radius. From this equation the relationship found by Duke[314,315]‡ can be easily obtained:

$$t_- = \frac{r_+}{r_+ + r_-}; \quad t_+ = \frac{r_-}{r_+ + r_-}, \qquad (37)$$

which often agrees well with experiment.

† Markov and Delimarskii[316] showed that another relationship is more accurate:

$$\Lambda = \text{const}\,(1/r_+^2 + 1/r_-^2).$$

‡ Duke obtained his equations by comparing the force of internal friction and the electric field $zeE = kr_i u_i$, whence $r_+/r_- = u_-/u_+$.

TABLE 15. Transport numbers in molten salts.

| Salt | $\frac{r_+}{r_+ + r_-}$ | $t_-$ | Reference | Salt | $\frac{r_+}{r_+ + r_-}$ | $t_-$ | Reference | Salt | $\frac{r_+}{r_+ + r_-}$ | $t_-$ | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| LiCl | 0.25 | 0.25 | 323 | TlCl | 0.47 | 0.50 | 314, 315 | $LiNO_3$ | 0.18 | 0.16 | 314 |
| NaCl | 0.34 | 0.38 | 323 | $ZnCl_2$ | 0.28 | 0.40 | 328 | $NaNO_3$ | 0.29 | 0.29 | 314 |
| KCl | 0.42 | 0.38 | 323 | $CdCl_2$ | 0.35 | 0.34 | 321 | $KNO_3$ | 0.37 | 0.40 | 314 |
| RbCl | 0.45 | 0.42 | 323 | $PbCl_2$ | 0.42 | 0.78 | 318 | $CsNO_3$ | 0.55 | 0.60 | 327 |
| CsCl | 0.48 | 0.36 | 323 | | | 0.75 | 320 | $TlNO_3$ | 0.55 | 0.69 | 326 |
| AgCl | 0.42 | 0.46 | 325 | | | 0.39 | 321 | $AgNO_3$ | 0.35 | 0.28 | 314 |
| | | 0.17 | 329 | $PbBr_2$ | 0.40 | 0.83 | 319 | | | 0.25 | 330 |
| | — | — | — | | 0.40 | 0.92 | 319 | | | | |

There have been several investigations of transport numbers in salt melts[317-336]. The methods of measurement have been discussed[337]. Almost all the investigators used a cell with a diaphragm separating the electrode spaces, and the decrease in volume of the melt in one of the compartments during electrolysis was compensated for by the constant addition of salt to it. The absence of a flow of salt under the action of gravity is usually verified by the position of a bubble in a capillary joining the two parts of the vessel, or by some other means.

The most reliable results of the measurements of transport numbers are given in Table 15.

Most authors consider that transport numbers are almost independent of temperature but Duke *et al.*[329] have found a considerable increase in $t_-$ for AgCl on raising the temperature from 650° to 925°. An analysis of the results given in Table 15 shows that in many instances Eqn. (37) agrees well with experiment. There are considerable deviations only for lead and zinc halides and for silver and thallium nitrates.

Characteristically, most solid states exhibit unipolar conductivity. Thus, the transport numbers of the cation in NaCl and KCl decrease from 1.00 to 0.93 and 0.88 respectively as the temperature is raised from 400° to 600°, whereas in the melt $t_+$ for both salts is 0.38. Lead chloride exhibits anionic conductivity in the solid state ($t_- = 1.0$) but in the melt $t_- \simeq 0.70$. Hence, fusion changes the mechanism of electrical conductivity, and the widely-held opinion that the conductivity of molten salts is also unipolar is incorrect.

## 15. THERMAL CONDUCTIVITY

Bloom[13], Gambill[338], and Turnbull[339] have investigated the thermal conductivity of molten salts. The thermal conductivity of potassium and sodium nitrates is $11.25 \times 10^{-4}$ and $13.50 \times 10^{-4}$ cal $cm^{-1}$ $s^{-1}$ $deg^{-1}$ respectively. According to Turnbull, the thermal conductivity of molten salts is made up of vibrational $\mu_{vib}$ and diffusion $\mu_{dif}$ constituents:

$$\mu_{vib} = 2.85 \times 10^{-3} (T_f \nu / M)^{1/2} (V_{solid}/\nu)^{2/3}, \quad (38)$$

$$\mu_{dif} = 2\Delta C_V / V, \quad (39)$$

where $C_V$ is the heat capacity and $\nu$ the number of ions in a salt molecule.

To a first approximation thermal conductivity can be calculated by Vargaftik's formula[340]:

$$\mu = 4.28 \times 10^{-3} C_p \rho^{4/3} / M^{1/3}, \quad (40)$$

where $M$ is the molecular weight of the salt.

## 16. VOLUME CHANGE DURING FUSION OF IONIC CRYSTALS

The fusion of ionic crystals is characterised by the following features:

1. The volume of the salt increases sharply during melting.

2. The anisotropy of the properties of the crystals disappears during fusion, this being the direct consequence of the disappearance of ordering in the position of the particles. As X-ray analysis shows, in the liquid state ordering is retained only in the nearest surrounding particles (short-range order). There is no order at greater distances (long-range order).

3. During fusion there is a marked change in electrical conductivity, heat capacity, diffusion coefficients, and other properties of the salt[18,234,341], which is evidence of the break-down of structure. It is characteristic that these changes start below the melting point (premelting effect) and are greatly dependent on the nature of the salt.

All these features permit a liquid to be considered as a disordered crystal and the melting process as one of partial breakdown of the crystal lattice. In crystals of the inert gases, alkali metal halides, and similar materials, there is probably a single possible means of breakdown of the lattice — the transfer of ions from the lattice positions into the interstices and to the surface of the crystal. For more complicated crystals with polyatomic complex anions or ions with easily distorted shells the destruction of order can proceed by a change in the orientation of the complex ions, the formation of new types of molecular packing, and also the formation of autocomplexes owing to the degeneration of the ionic bond and the increase in polarisation interactions[342-347].

The most important characteristic of the fusion process is the volume change. The increase in molar volume during fusion can be termed the surplus volume of the melt, and this has been measured in several studies[347-355]. Table 16 gives Schinke and Sauerwald's results[348], recalculated with allowance for other data[120], and calculated values of $\Delta V$, derived using the latest data on the coefficients of linear expansion of crystals[356] at room temperature (in parentheses).

Table 16 shows that the surplus volume depends markedly on the nature of the salt. For alkali metal halides, as for crystals of inert gases, it is 20–25%; for Ca, Sr, and Ba

TABLE 16. Excess volume of molten salts ($cm^3$ $mole^{-1}$).

| Salt | $\Delta V$ | $\frac{\Delta V}{V_{solid}}$, % | Salt | $\Delta V$ | $\frac{\Delta V}{V_{solid}}$, % | Salt | $\Delta V$ | $\frac{\Delta V}{V_{solid}}$, % | Salt | $\Delta V$ | $\frac{\Delta V}{V_{solid}}$, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| LiF | 3.27 | 29.4 | NaBr | 8.09 | 22.5 | KI | 9.34 | 16.0 | CsI[a] | 18.0 | 28.3 |
| LiCl | 5.84 | 26.1 | | (8.90) | (25.3) | | (10.20) | (17.7) | $AgCl^b$ | 2.41 | 8.9 |
| | (6.16) | (27.9) | NaI | 8.42 | 18.3 | RbCl | 6.81 | 14.5 | $AgBr^b$ | 2.54 | 8.2 |
| LiBr | 6.89 | 25.1 | | (9.98) | (22.5) | | (6.79) | (14.5) | $CaCl_2$ | 0.49 | 0.9 |
| | (7.24) | (26.7) | KF | 4.45 | 17.2 | RbBr | 7.11 | 13.3 | $SrCl_2$ | 2.35 | 4.2 |
| LiI | (7.60) | (22.1) | KCl | 7.30 | 17.6 | | (7.81) | (14.7) | $BaCl_2$ | 2.27 | 3.5 |
| NaF | 4.64 | 27.4 | | (8.10) | (19.9) | RbI | (8.55) | (13.2) | $LiNO_3^c$ | | 28.2 |
| NaCl | 7.36 | 24.4 | KBr | 7.77 | 16.2 | CsCl | 6.16 | 11.4 | $NaNO_3^c$ | | 11.0 |
| | (8.05) | 27.3 | | (8.82) | (18.8) | CsBr[a] | 14.3 | 26.8 | $KNO_3^c$ | — | 1.0 |

[a] See Johnson *et al.*[352]; [b] see Strelkov[353]; [c] see Davis *et al.*[234] and Landon and Ubbelohde[347].

halides it is only a few per cent, just as for nitrates, and this is due to the degeneration of the ionic bond and reorientation.

The "surplus" volume is in general not the "free volume of the liquid", if by this term we understand that part of the volume available for the translational and vibrational motion of the ions, since part of the surplus volume is screened by the force fields of the neighbour particles[357]. The value of the "free volume" of the liquid can be determined as follows[358]. It is known that the statistical partition fnnction of a system with particles oscillating in closed micro-cells which they cannot vacate has the form:

$$\Phi_m = \left[\frac{(2\pi mkT)^{3/2}}{h^3} \times \frac{V_f}{N}\right]^N [\Phi_{int} \exp(-E/RT)]^N, \quad (41)$$

where $V_f$ is the total free volume, $N$ Avogadro's number, $m$ the mass of the particle, $h$ Planck's constant, $\Phi_{int}$ the internal partition function, and $E$ the potential energy, determinable as the energy for the transformation of the system into ideal gas at 0°K.

Virtually, this partition function corresponds to a crystal expanded to the volume of the liquid. The difference between the crystal and the liquid is that in the latter the particles are not localised in their cells and therefore:

$$\Phi_{liq} = \frac{1}{N!}\left[\frac{(2\pi mkT)^{3/2}}{h^3} \times V_f\right]^N [\Phi_{int} \exp(-E/RT)]^N. \quad (42)$$

When this equation is combined with the known relation:

$$p = RT(\partial \ln \Phi/\partial V), \quad (43)$$

an equation of state of the liquid, similar to the van der Waals equation, is obtained

$$V_f[p + (\partial E/\partial V)_T] = RT, \quad (44)$$

where the derivative $\partial E/\partial V$ has the significance of the internal pressure of the system. To calculate the free volume, another well-known relationship can be used:

$$(\partial E/\partial V)_T = T\frac{\alpha}{\beta} - p, \quad (45)$$

which in combination with (44) gives:

$$V_f = R\beta/\alpha. \quad (46)$$

Another method of calculating the free volume involves the determination of the entropy of vaporisation of the liquid, which equals[359,360]

$$\Delta S_{vap} = R \ln(V_{gas}/V_f), \quad (47)$$

and

$$L_{vap} = -RT \ln(V_b/V_{gas}), \quad (48)$$

but since for a gas $V_{gas} = RT/P$, then:

$$V_f = \frac{RT}{p}\exp\left(-\frac{L_{vap}}{RT}\right) = \frac{RT}{P_b}\exp\left(-\frac{L^\circ_{vap}}{RT_b}\right). \quad (49)$$

TABLE 17. Free volumes of alkali metal halides at 800°, $cm^3\ mole^{-1}$.

| Salt | $V_f$ (Ref. 46) |
|---|---|
| LiCl | 6.84 |
| NaCl | 6.84 |
| KCl | 8.26 |
| CsCl | 10.50 |

However, the results of calculations by Eqns. (46) and (49) usually differ by an order of magnitude.

We note that the physical significance of the concept of free volume has not been finally determined and is still the subject of discussion, so that some authors understand other quantities as free volume[360-362].

## 17. THEORY OF THE FUSION OF IONIC CRYSTALS

The important theories of fusion can be classified into a few groups. The vibrational theories of fusion link the crystal → liquid change with the vibrational motion of the particles[363-376]. The basis of the vibrational theories is the idea of the mechanical instability of the crystal lattice, which appears with increase in the amplitude of the vibrations of the ions. Lindemann[363], by considering the collision of the vibrating particles as a criterion of fusion, obtained a formula for the melting point:

$$T_f = \text{const}\, V/\beta. \quad (50)$$

In later works Born[367,368], Fürth[370-373], Patrushev[376], and Thompson[369] also developed different variants of the vibrational theory. As Mott showed[374,375] Born's concept of the melting point as the temperature for the disappearance of the elastic properties of a crystal due to the vibration of the atoms is erroneous. However, there is also a grain of truth in the vibrational theories. In particular, this applies to Patrushev's theory which connects the increase in volume during fusion with the heats of fusion and sublimation:

$$L_f/L_s = \text{const} \times \Delta V/V_{solid}. \quad (51)$$

The theory of disordering is seen as the basis of the melting process in the disappearance of the order peculiar to the crystal. Frenkel'[22] and Bresler[377] have considered this question most fully. To characterise the order in the system they introduce the concepts of degree of short- and long-range order. In a crystal MX the long-range order is expressed by the cations and anions occupying completely determined ("cationic and anionic") positions, and short-range order by each ion $M^+$ being surrounded by six $X^-$ ions and vice versa. The breakdown of long-range order signifies that a fraction $N''_+$ of the cationic places, out of the total number $N_+ = N'_+ + N''_+$, is occupied by anions. The Bragg–Williams criterion[378]

$$\gamma = \frac{N'_+ - N''_+}{N'_+ + N''_+} = \frac{2N'_+ - N_+}{N_+} \quad (52)$$

serves as a measure of the long-range order. For the ideal crystal $N'_+ = N_+$, $N''_+ = 0$, $\gamma = 1$. With complete disorder, $N'_+ = N''_+$, $\gamma = 0$. When out of the total number $p$ of nearest neighbours the mean number of neighbours of the same kind is $n$, and that of the other kind is $m$, then the degree of short-range order can be characterised by Bethe's criterion[379]:

$$\xi = \frac{m-n}{p} = \frac{m-n}{m+n} = \frac{2m-p}{p}. \quad (53)$$

For the ideal crystal $n = 0$, $m = p$, and $\xi = 1$; with complete disorder, $m = n = p/2$, and $\xi = 0$.

Frenkel' gives[22] the following assumptions: (a) melting corresponds to complete disappearance of long-range order; (b) the probability of transfer of an ion to a "foreign" site is determined by the Boltzmann relation, that is,

$$N''_+ = N'_+ \exp(-\varepsilon/kT), \quad (54)$$

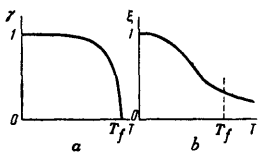



Fig. 7. Change in the degrees of long-range ($\gamma$) and close-range ($\xi$) order with rise in temperature[22].

in which $\epsilon = \gamma\epsilon_0$; (c) the probability of differently charged ions occupying neighbouring positions is determined by the relation:

$$n = m\exp(-\Delta\epsilon/kT), \quad (55)$$

where $\Delta\epsilon$ is the mean difference in energies of interaction of the pairs $M^+-M^+$, $X^--X^-$. In this case we can obtain:

$$\gamma = \tanh(\epsilon_0\gamma/2kT), \quad (56)$$

$$\xi = \tanh(\Delta\epsilon/2kT). \quad (57)$$

Graphs of these functions (Fig. 7) show that long-range order disappears by a sharp jump at a definite temperature $T_f$, at which an appreciable fraction of short-range order is retained.

Despite the qualitative agreement with experiment, this theory is not completely accurate since the change in volume during melting is not taken into account, that is, in the final reckoning the part played by "holes" in the destruction of order§ is not considered. An attempt to allow for this feature was made by Bresler[377], who determined the degree of short-range order as the probability of the coordination number $p$ and of disorder as reduction in the coordination number to $(p - 1)$, which gives:

$$\xi = [1 + p\exp(-\epsilon/kT)]^{-1}, \quad (58)$$

where $\epsilon$ is the energy of the system.

A more detailed statistical theory of fusion has been developed[383-389]. Kurosawa[390] and Karpachev and Karasik[391] attempted to create a quantitative theory of fusion of ionic crystals. The former considered the liquid as a solution of holes in an ionic medium and the application of the Debye–Hückel theory to the interaction of holes enabled several properties of molten salts to be calculated (melting point, etc.). The entropy of fusion of ionic crystals has been calculated[391] as the result of the expansion of the crystal and the appearance in it of unoccupied sites (vacancies). The relation finally obtained was:

$$\Delta S_f = -\frac{\alpha}{\beta}\Delta V + 4.6R[\log(1 + \Delta V/V_{solid}) + (\Delta V/V_{solid})\log(1 + V_{solid}/\Delta V)]. \quad (59)$$

## 18. THEORY OF MOLTEN SALTS

The theory of ionic liquids has been developed in the last few years as part of the general theory of the liquid state. Its first considerable success was connected with the development of the hole theory (Frenkel'[22], Fürth[392,393] and others[394,395]) which is based on the concept of a liquid as a quasi-crystal with a large number of vacant sites – the holes. The holes are attributed with the ability to migrate and a spherical form, and the liquid itself is regarded as a continuous medium. The energy of formation of a hole of radius $r$ is[393]:

$$e_g = 4\pi r^2\sigma, \quad (60)$$

and the mean volume of a hole is:

$$v_g = 0.68(kT/\sigma)^{3/2}. \quad (61)$$

Frenkel'[22] and Kurosawa used the idea of hole theory to explain the diffusion and viscosity of molten salts. Bockris and coworkers[136,238] used the same viewpoint in handling their experimental results on diffusion and ultrasonic velocity in melts.

One of the first theories of the liquid state[396] considered a liquid as a dynamic combination of microregions with an ordered structure (sibotaxic group), situated in mobile equilibrium internally and with the molecules forming irregular transition regions. A development of this theory is the theory of significant structures[397-400], according to which in a liquid there coexist regions with a crystal lattice structure, regions containing "gaslike" molecules, and also dislocations, vacancies, holes, and other defect structures. The degree of bonding of the molecules in the liquid is characterised by the ratio $V_{solid}/V_{liq}$, and the statistical sum of states is determined as the product of the partition functions of the "gaslike" and "solidlike" particles. By applying the theory of significant structures to molten alkali metal halides, Eyring and others[399,400] found for the partition function:

$$\Phi = \left\{\frac{\exp(E/2RT)(V_{liq}/V_{solid})^{1/3}}{[1-\exp(-\theta/T)]^3}\left[1 + N_g\exp\left(-\frac{aE}{2N_gRT}\left(\frac{V_{liq}}{V_{solid}}\right)^{1/3}\right)\right]\right\}^{2NV_{solid}/V_{liq}} \times$$

$$\times\left\{\frac{(2\pi mkT)^{3/2}}{Nh^3}eV_{liq}\frac{8\pi^2IkT}{h^2}[1-\exp(-h\nu/kT)]^{-1}\right\}^{(1-V_{solid}/V_{liq})N}, \quad (62)$$

where $E$ is the potential energy of the salt at $T_f$, $\theta$ is the Einstein characteristic temperature, $m$, $I$, and $\nu$ are the mass, moment of inertia, and fundamental vibration frequency of the halide molecule, $a$ is an empirical parameter, $N$ Avogadro's number, and $N_g \simeq 10(V_{liq} - V_{solid})/V_{solid}$ the concentration of holes. A comparison of the fusion parameters, calculated by Eqn. (62), with the experimental values shows good agreement (Table 18). However, unfortunately Eqn. (62) contains the empirical coefficient $a$.

Eyring[383] and Lennard-Jones and Devonshire[384] developed a theory representing a liquid as an expansion of a crystal in which each molecule can move freely in a certain volume, equal to $\omega/N$, where $\omega$ is the total free volume of the cell. Assuming it to be equal to the free volume of the liquid and using Eqns. (40), (41), and

$$S = k\{\ln\Phi + T(\partial\ln\Phi/\partial T)_V\}, \quad (63)$$

TABLE 18. Comparison of theory of significant structures with experiment[399].

| Salt | $T_f$, °K | | $\Delta S_f$, cal deg$^{-1}$ mole$^{-1}$ | | $V_{liq}$, cm$^3$ mole$^{-1}$ | |
|---|---|---|---|---|---|---|
| | calc. | expt. | calc. | expt. | calc. | expt. |
| NaCl | 1070 | 1073 | 7.75 | 6.21 | 38.1 | 37.6 |
| KCl | 1023 | 1043 | 5.40 | 6.06 | 49.1 | 48.9 |
| NaBr | 1023 | 1020 | 6.14 | 6.12 | 43.8 | 49.6 |
| KBr | 1008 | 1007 | 4.83 | 6.06 | 56.1 | 55.8 |

§ Samoilov[380-382] considered the decrease in coordination number during fusion.

we can obtain the change in entropy due to the removal of the prohibition for movement of a molecule from one cell to another:

$$\Delta S^* = k \ln (N^N/N!) \simeq kN = R. \quad (64)$$

This quantity was termed the communal entropy of the liquid and identified with the entropy of fusion. The latter, of course, is incorrect, since Eqn. (40) relates to a conventional crystal and the complete freedom of mixing of the particles is reached only in vaporisation of the liquid[385].

The quantity $\omega$ in the Eyring-Lennard-Jones and Devonshire theories is determined as follows[401]. In a three-dimensional cubic lattice let only a central molecule move and six of its neighbours be immovably fixed; the volume bounded by these neighbours for all $N$ molecules is

$$\omega = 8N[v^{1/3} - \sigma]^3, \quad (65)$$

where $\sigma$ is the diameter of the molecule, and $v^{\frac{1}{3}} = (V/N)^{\frac{1}{3}}$ is the distance between the centres of neighbouring molecules. The quantity $\omega$, calculated for molten salts[136], is 0.5–1.0 cm$^3$ mole$^{-1}$ for alkali metal halides, which is much smaller than the actual free volume (compare Table 18).

The ideas of Lennard-Jones and Devonshire were applied to salt melts and developed by McQuarrie[402] who obtained, in particular, an equation for vapour pressure:

$$\log p = \frac{0.434\,(D_0 - \alpha\epsilon^2/a)}{kT} + 0.217 \log T + \log \left\{ \frac{\left(\frac{M}{M_+M_-}\right)^{\frac{3}{2}} (8\pi k)^{\frac{1}{2}} hI \times 7.6 \times 10^4}{V_f^2 \epsilon^2} \right\}, \quad (66)$$

where $M$ is the mass of diatomic molecules, $M_+$ and $M_-$ are the masses of the cation and anion, $I$ is the moment of inertia, $\epsilon$ the charge of the ions, $D_0$ the energy for the decomposition of the molecule into ions, and $\alpha$ the Madelung constant. The values of $V_f$ obtained from Eqn. (66) were of the order of 0.05 cm$^3$ mole$^{-1}$ for the alkali metal halides. However, McQuarrie's calculations of the entropy of fusion of NaCl and KCl (2.84 and 2.40 cal deg$^{-1}$ g-ion$^{-1}$) were close to the experimental values.

The progress in the statistical theory of the liquid state associated with the use of the methods of Kirkwood, Bogolyubov, and Green[403-408], based on the calculation of molecular distribution functions permits these methods to be applied to molten salts. Calculation of the correlation functions with allowance for both coulombic forces and short-acting repulsive forces:

$$U(r) = \epsilon^2/r + U_0(r), \quad (67)$$

still meets with insuperable mathematical difficulties. Bogolyubov[405] proposed, as a first approximation, the use of smoothing coulombic potentials

$$U(r) = \epsilon^2 [1 - \exp(-\alpha r)]/r. \quad (68)$$

This idea was employed in several works[409-411], which related, however, to aqueous solutions of electrolytes. Works on the theory of ionic liquids[412-419] were all based on a model in which the ions were represented by rigid charged spheres. The question as to how far this model is suitable for describing the properties of molten salts is still not solved. Undoubtedly some successes have been achieved in this direction. In particular, mention can be made of works[417,418] in which a formula was derived for the surface tension of melts:

$$\sigma = \frac{kT}{4\pi a^2} \left[ \frac{12y}{1-y} + \frac{18y^2}{(1-y)^2} \right], \quad (69)$$

TABLE 19. Verification of the Reiss–Mayer equation, Eqn. (69).

| Salt | $t$, °C | $\sigma$, dyn cm$^{-1}$ | |
|---|---|---|---|
| | | expt. | calc. |
| NaCl | 1000 | 98 | 111 |
| KCl | 900 | 90 | 96 |
| RbCl | 828 | 89 | 81 |
| CsCl | 830 | 78 | 79 |
| $BaCl_2$ | 1000 | 157 | 152 |

where $y = \pi a^3 \rho/\sigma$, $a$ is the mean diameter of the ions, and $\rho$ the density. This formula agrees well with experiment (Table 19). Satisfactory results were also obtained by Rice[419] in calculating the diffusion coefficients, viscosity, and thermal conductivity of melts.

All the theories considered relate only to molten alkali metal halides. With other molten salts the matter is more complicated. As already noted, in many instances the formation of autocomplexes of the type $BeCl^+$, $BeCl_3^-$, etc.[316] on melting is assumed. However, it is possible that in addition to autocomplexes the melt retains fragments of the crystal lattice in several instances, for example, $ZnBr_2$.[240] Finally, in melts of the mercury halide type the equilibrium

$$HgX_2 \rightleftarrows HgX^+ + HgX_3$$

is probably established, with a strong displacement towards the side of formation of neutral molecules[421]. Naturally the construction of a theory for such complicated ionic-molecular systems is encountering great difficulties.


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# ALCOHOL DERIVATIVES OF THE ALKALI AND ALKALINE EARTH METALS, MAGNESIUM, AND THALLIUM(I)

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## I. CLASSIFICATION OF THE ALCOHOL DERIVATIVES OF THE ELEMENTS

Alcohol derivatives of the type $E(OR)_n$ are now known for almost all the elements of the Periodic System. Even as long ago as 1899, Tishchenko noted that "the form of alcoholates is as general and besides much more stable (in respect of thermal stability) than the hydroxide form"[1]. However, the alcohol derivatives of many rare metals have been prepared and studied intensively only recently — the difficult-to-prepare compounds of the multivalent elements of Groups IV, V, and VI, and also the alkoxides of the platinum group metals and actinides.

The properties of the alcohol derivatives — unlike hydroxides — are not determined solely by the nature of the element, but depend also on the nature of the alcohol radical in the $E(OR)_n$ molecule. Therefore the acidity of the alcohol (that is, the lability of the hydrogen atom of the hydroxyl group) and the electronegativity of the element obviously must be taken as the basis of the classification of the alcohol derivatives of the various elements of the Periodic System. From this standpoint the following groups of compounds of type $E(OR)_n$ can be distinguished:

1. Compounds formed by elements with sharply expressed metallic properties and the radicals from alcohols having a strongly acid character ($K_{diss} \geqslant 10^{-10}$). This group includes the derivatives of the alkali and alkaline earth metals and thallium(I) with phenols, naphthols, anthrols, etc. Subsequently we will term them phenoxides. These compounds are saltlike, and as "salts of strong bases and acids of medium strength" are capable of existing in aqueous solution. They are insoluble in organic solvents (even in absolute ethanol), have usually a definite melting point, exhibit a high thermal stability, and evidently do not exist in the gaseous state.

2. The other boundary case consists of the derivatives of non-metallic elements and alcohols whose acid function is weakly expressed — the esters of inorganic acids. Low melting and boiling points, high vapour pressure, solubility in organic solvents, and instability with even traces of water are characteristic here. The molecules of esters are of very low polarity, usually strongly associated, and tend to form complexes. As characteristic examples of esters we may mention the alkyl borates, whose properties have been reviewed in detail[2,3]. However, it should be noted that the above-mentioned general features of the compounds

of this group are also distinctive of the alcohol derivatives of the metals of Groups III–VIII of the Periodic System.

3. The characteristic representatives of the compounds of the third group — the alkoxides (into whose composition there enter an active metal and the alkoxy radical of an alcohol with an acid dissociation constant $\ll 10^{-10}$) — are the derivatives of the metals of the principal subgroups of Groups I and II and thallium(I) with the aliphatic alcohols. From the character of the M–OR bond they occupy an intermediate position between the polar phenoxides and the non-polar esters. This is evidently fundamental and determines their unique properties. The alkoxides, like the esters of inorganic acids, are extremely sensitive to the action of moisture, are sometimes (as in the case of Li) associated, and tend to form complexes. By analogy with phenoxides, alkoxides are capable of electrolytic dissociation (in alcoholic solutions they exhibit appreciable electrical conductivity and sometimes react in an ionic form), and are insoluble in organic solvents (with the exception of alcohols). However, unlike the compounds of the first two classes, the alkoxides do not melt or sublime, but undergo thermal decomposition at 200–300°.

These three classes of alcohol derivatives of elements are only boundary cases, since their characteristic representatives are the compounds of elements which exhibit clearly expressed metallic or non-metallic character. At the same time the vast majority of metals of the main subgroups (starting with beryllium and Group III) and the elements of all the auxiliary subgroups form alcohol derivatives combining simultaneously the properties of alkoxides and esters of inorganic acids.

The present review is devoted to the alcohol derivatives of the alkali and alkaline earth metals, magnesium, and thallium(I), which are characteristic representatives of two of the classes mentioned above: the alkoxides and phenoxides. Most of the compounds considered have been known for over a century, but the most important investigations devoted to their synthesis and also to their chemical and most physicochemical properties were only completed in the last 20–30 years. This is due on the one hand to the improvements in experimental techniques, which permit work with substances that decompose in the presence of traces of moisture, oxygen, or carbon dioxide, and on the other to the important part which alkoxides and phenoxides play in the technology of contemporary organic and inorganic syntheses. This review will not deal with the rather large group of inner complex (chelate) compounds of the elements mentioned, which are only formal analogues of alkoxides and phenoxides†. There have been other reviews devoted[4-9] mainly to the use of sodium alkoxides in organic syntheses. The reactions of mixed magnesium halide alkoxides was considered in detail in a monograph by Ioffe and Nesmeyanov[10], published in 1963. In Bradley's reviews[11,12] attention was mainly directed towards the alkoxide compounds of multivalent metals‡.

† This refers to the metal derivatives of polyfunctional organic molecules (hydroxyketones and diketones, ketoenols, alkyl salicylates, nitro- and amino-phenols, hydroxy-pyridines, -quinolines, etc.) and also to most "acid" phenoxides — the incompletely substituted derivatives of polyhydroxy-compounds.

‡ After this review had been prepared for publication, there appeared a volume of Houben ("Houben–Weyl: Methoden der organischen Chemie. 4. Aufl. Band VI. Spezielle chemische Methoden. Teil 2. Sauerstoffverbindungen I. 2", Thieme, Stuttgart, 1963) containing a review of the literature on alcohol derivatives of metals.

## II. ALKOXIDES OF THE ALKALI AND ALKALINE EARTH METALS, MAGNESIUM, AND THALLIUM(I)

### A. METHODS OF PREPARATION

#### Method I. Reaction of Metals with Alcohols

The action of potassium and sodium on ethanol was first observed by Liebig in 1837; in 1840 Kuhlmann (who proposed the term "alcoholate"), on the basis of this reaction, considered compounds of type MOR to be alkali metal salts in which an alcohol plays the part of an acid[1].

The alkali and alkaline earth metals react very readily with at least the first members of the series of aliphatic alcohols but nevertheless the reaction goes to completion only with a large excess of the absolute alcohol or on continuous heating[13]. As a result alkoxide solvates of the type $M(OR)_n.xROH$ ($x$ = 2 or 3) are formed, which lose the alcohol of crystallisation only on heating (sometimes to 150–200° in a stream of inert gas). To obtain the unsolvated alkali metal alkoxides at low temperatures (such preparations exhibit the greatest reactivity), Brühl[14] suggested carrying out the reaction using the stoichiometric quantity of the alcohol with finely dispersed Na or K in a medium of hydrocarbon or diethyl ether[15,16]. Fisher and MacElvain[17] perfected this method: the metal (in a massive state) was put in the filter in a Soxhlet apparatus and a mixture of high-boiling inert solvent (xylene or dioxan) with the calculated quantity of the alcohol was put in the flask. Utilising the insolubility of unsolvated alkoxides in hydrocarbons or ethers, the alcohol was quantitatively converted into the alkoxide. In a similar way Mamedov[18] synthesised disodium ethylenedioxide, which is not readily available (aniline was the reaction medium). In all cases the syntheses (as in general work with alkali and alkaline earth metal alkoxides) were carried out under nitrogen or hydrogen.

This reaction (in the synthesis of derivatives of higher aliphatic alcohols or magnesium alkoxides) has often been catalysed by mercury(II) chloride (or directly with the metal amalgam)[20-26], and also with iodine (first employed by N.D. Zelinskii in 1903), bromine[19,27,28], or with mercury(II) chloride and iodine together[27,29-31]. Nevertheless, reaction between magnesium amalgam and tertiary alcohols has not been achieved, even on heating to 100°.

In Germany in 1932 a commercial scheme was worked out for the production of aliphatic, aromatic, and hydroaromatic alkoxides of sodium — important intermediates in organic synthesis. It was based on an electrolytic process for the decomposition of an aqueous NaCl solution usually employed for the production of chlorine and alkali (the chlorine is liberated at a graphite anode, and the sodium is discharged at a moving mercury cathode and is removed from the cell as an amalgam). The next stage of the process was the decomposition of the sodium amalgam with an absolute alcohol; it was effected in reactors and then in columns filled with pieces of graphite, and the countercurrent principle was employed to ensure that the reaction went to completion. Subsequently this scheme was perfected: the decomposition of the amalgam by the alcohol was accelerated considerably by using a contact electrode not susceptible to amalgamation (of graphite or stainless steel)§. The economics of the process were improved

§ A recent patent claims[32] carrying out the reaction between the amalgam and alcohol in the presence of graphite containing 2–3% iron.

because of the greater utilisation of the sodium: the residues of amalgam contained in the spent mercury were decomposed with water and then the mercury and solution of alkali were recycled to the electrolyser. The heat set free in the formation of NaOH was used to raise the temperature of the reaction between Na/Hg and the alcohol. This method was used in the USA in 1944 by the Mathieson Alkali Works for the production of sodium methoxide on an industrial scale. The purity of the unsolvated $NaOCH_3$ (obtained after vacuum distillation of methanol) was $\leqslant 95\%$, the main impurities being 2% NaOH + $Na_2CO_3$ and < 3% $CH_3OH$.[5,8,9,33].

The rate of reaction of a particular metal with various alcohols can serve as a measure of the lability of the hydrogen atom in the ROH molecule. Using the reaction of magnesium[34] and aluminium[1] amalgams it was found that the acid function of alcohols are in the order primary > secondary > tertiary, and in each of these the values of $K_{diss}$ decrease along the homologous series. Fig. 1 gives values of the enthalpies of formation of the alkali metal alkoxides of a series of alcohols, after Forcrand[35-37] plotted against the logarithm of the reciprocal of the acid dissociation constant of the alcohols[38]. The thermal effect for the replacement of the first hydrogen atom in molecules of polyhydric alcohols considerably exceeds $\Delta H$ for the replacement of subsequent H atoms (thus the value shown in Fig. 1 for $\Delta H$ of the reaction of Na with glycerol relates to the monosodium salt and is 1.5 times that of the corresponding value for the disodium salt)[40].

## Method II. Reaction of Ammines of Metals with Alcohols in Liquid $NH_3$ as Solvent

The solubility of the alkali and alkaline earth metals in liquid ammonia, permits their homogeneous reaction with alcohols (unlike the previous reaction). On account of the liberation of hydrogen and precipitation of the alkoxides

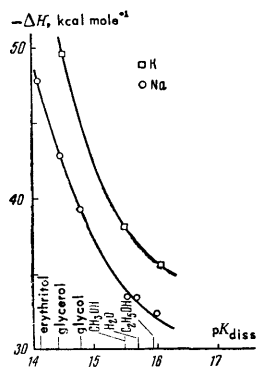



Fig. 1. Relation between the acidity function of alcohols and the heats of formation of the alkali metal alkoxides by the reaction:

$$M_{solid} + ROH_{liquid} = MOR_{solid} + \tfrac{1}{2}H_{2\,gas}.$$

The value of $\Delta H$ of formation of the sodium salt of erythritol was calculated from Forcrand's data on the heat of reaction of solid erythritol with allowance for the heat of fusion of $C_4H_{10}O_4$ (10.2 kcal mole$^{-1}$).[39]

(which are usually insoluble in ammonia[41]), the equilibrium of the ionic reaction:

$$M(NH_3)_6 + nROH \xrightleftharpoons{NH_3} M(OR)_n + n/2\,H_2 \ (n=1 \text{ or } 2),$$

is almost instantaneously shifted to the right for primary alcohols; with secondary and tertiary alcohols the rate is somewhat less[42]¶.

This method was proposed in 1905 by Chablay for the synthesis of sodium alkoxides[42], but he subsequently extended it to the other alkali metals[43] and the alkaline earth metals[44,45]. The field of application of this reaction now extends to the higher, unsaturated, and polyhydric alcohols[43,45-47] — including the mono- and poly-saccharides, cellulose[48-50], poly(vinyl alcohol)[51], etc.

## Method III. Decomposition of Hydrides, Organometallic Compounds, Carbides, Nitrides, Amides, or Sulphides by Alcohols

This reaction is based on the alcoholysis of compounds which are sensitive to the action of "active hydrogen", and leads to the formation of alkoxides and gaseous products according to the scheme: MX + HOR → MOR + HX↑, where X = H, R, C≡C, ≡N, $NH_2$, or SH.

Judging by the patent literature, the reaction of various alcohols with NaH,[52,53] $Na_2S$,[54] calcium carbide[55-56], and magnesium carbide[57] is now a cheap industrial method for the production of alkoxides. White et al.[47,58] proposed to carry out the alcoholysis of alkali amides by alcohols of the aromatic series (whose acidity function is very low) in solution in liquid $NH_3$, where the equilibrium is shifted to the right, owing to the precipitation of the alkoxides.

The reaction described has found wide application in the field of organometallic compounds (mainly Grignard complexes). As Grignard showed, the alcoholysis of alkylmagnesium halides leads to the formation of alkoxymagnesium halides and the liberation of gaseous hydrocarbons. This reaction forms the basis of the method of quantitative determination of "active hydrogen" developed by Tserevitinov[59]. However, in recent years in the determination of active hydrogen simple and double hydrides have begun to displace the less readily available $CH_3MgI$.[60] Among the reactions of the hydro-derivatives is the recently described methanolysis of ethoxymagnesium hydride, leading to the formation of an unsymmetrical alkoxide, $CH_3OMgOC_2H_5$.[61]

## Method IV. Double Decompositions of Salts with Alkoxides

To effect the synthesis of alkoxides by the scheme: $EX + nM^{I}OR \rightarrow E(OR)_n + nMX$, it is necessary for one of the products to be removed from the sphere of reaction (usually by insolubility in the corresponding non-aqueous solvent). This method is widely used in the synthesis of the alkoxy-derivatives of multivalent elements, but has only limited application for the metals of the main subgroups of Groups I and II. Thus in 1923 Jones and Thomas[62] brought about the reaction $LiCl + NaOC_2H_5 = LiOC_2H_5 + NaCl$ by making use of the lower solubility of NaCl (compared with LiCl) in absolute alcohol.

¶ A side-reaction — the decomposition of the ammines with formation of metal amides, $MNH_2$ — can be disregarded because of its slowness under these conditions.

Menzies[63], and then Abbott[64] alkoxylated the dialkylthallium(III) halides with ethylsodium and ethylthallium(I) (in absolute alcohol):

$$R_2TlX + M^IOC_2H_5 = R_2TlOC_2H_5 + MX\downarrow.$$

The patent literature contains descriptions of the synthesis of KOR, by the reaction of KOH or $K_2CO_3$ with sodium or potassium alkoxides. The success of the reaction is decided by the choice of solvent, in which only one of the products should be soluble[56,65]. The double decomposition of a sodium alkyl carbonate with $Ba(OCH_3)_2$ (formed in a boiling methanol suspension of BaO) is interesting, and leads to the formation of $NaOCH_3$ and the precipitation of $BaCO_3$.[66]

Chablay made wide use of the double decomposition of sodium alkoxides with alkaline earth metal or thallium(I) nitrates in solution in liquid ammonia, utilising the fact that the alkoxides are usually precipitated but $NaNO_3$ is soluble in liquid ammonia. Alkoxy-derivatives of Ca, Sr, Ba, and $Tl^I$ with many mono-, di-, and poly-hydric alcohols were obtained in this way[44,45].

Jander and coworkers[67] succeeded in bringing about the double decomposition: $K_2SO_3\downarrow + (C_2H_5)_2SO = KOC_2H_5\downarrow + 2SO_2$ in liquid sulphur dioxide solution, because under these conditions the potassium ethoxide formed was less soluble than the original sulphite. The reaction:

$$NaH + B(OCH_3)_3 \longrightarrow Na[BH(OCH_3)_3] \xrightarrow{250^\circ} NaBH_4 + NaOCH_3 + B(OCH_3)_3\uparrow$$
$$Na[BH(OCH_3)_3] \xrightarrow{+NaH} NaBH_4 + NaOCH_3,$$

is used in the preparation of sodium and lithium tetrahydroborates[60,68] and is interesting in that the alkoxylating agent in this instance is trimethyl orthoborate (and not NaOR, as usually). The sodium and lithium methoxides which remain in large amounts after extraction of $NaBH_4$ with amines apparently find no use at present.

## Method V. Reaction of Oxides or Hydroxides with Alcohols

The oxides and hydroxides of the alkali and alkaline earth elements are much cheaper raw materials than the corresponding metals, therefore their use for the production of alkoxides on an industrial scale is especially promising. However, reactions (1) and (2) are reversible

$$M^IOH + ROH \rightleftarrows M^IOR + H_2O, \quad (1)$$

$$M^{II}O + 2ROH \rightleftarrows M^{II}(OR)_2 + H_2O, \quad (2)$$

and special conditions are required to separate the alkoxides from the reaction mixture in a particular case. As long ago as 1840 Kuhlmann[1] obtained $KOC_2H_5$ by the action of ethanol on "Gay-Lussac pyrophor" (a mixture of $K_2O$, $K_2S_n$, and carbon). Obviously the equilibrium is close to the alkoxide side on account of the reaction of water with the dipotassium polysulphide. Subsequently similar syntheses of alkoxides were repeatedly described in the patent literature. To remove the water from the reaction zone, calcium carbide[70] and oxide[71,72], and benzene (giving an azeotrope with water at atmospheric[73] or elevated pressure[74]) were used. The last of these methods was employed in Germany in the 1930's in the industrial production of sodium ethoxide and methoxide[8]. In 1946 a patent was taken out on the production of compounds of Ba and Sr with the higher aliphatic alcohols by the alcoholysis of hydroxides in a mineral oil medium[75].

Another way of shifting the equilibrium to the right is to precipitate the alkoxides. In particular, there has been a proposal[76] to carry out the reaction of alkalis with ethanol in the presence of anhydrous acetone, which probably "salts out" the sodium and potassium ethoxides.

The method described is used much more frequently under laboratory conditions for the synthesis of alkoxides of polyhydric alcohols (the water is then removed because of the high reaction temperature and its greater volatility in comparison with the reacting alcohols). The synthesis of sodium 2-hydroxyethoxide and disodium ethylenedioxide (by the reaction of NaOH with ethylene glycol in a vacuum at $\leq 110^\circ$) was patented[77] in 1926. Cross and Jacobs[78] obtained monopotassium and monosodium glycerolates analogously, and in 1891 Forcrand had obtained mono- and di-sodium derivatives of 1,2,3,4-tetrahydroxybutane[79]. Ushakov and his coworkers[51] synthesised in this way sodium poly(vinyl oxide) (the alkoxidic nature of which was demonstrated by infrared spectroscopy and also by a counter-synthesis by method II). The low solubility of the alkalis in the higher alcohols for long restricted the use of alcoholysis for synthesising the alkoxides[8]. However, in 1957–58 patents were taken out on the production of alkoxides in the reaction of solid NaOH or KOH[80] or their aqueous solutions[81] with higher alcohols (aliphatic, hydroaromatic, and aromatic). In the last case the reaction is brought about in countercurrent flow in a distillation column at high temperatures[81].

Here it is pertinent to mention the decomposition of alkali carbonates by glycol, as a result of which the corresponding 2-hydroxyethoxides are formed[54]. This reaction takes place at the boiling point of ethylene glycol (198°); in it the considerably weaker acid (ethylene glycol) displaces $H_2CO_3$ (whose dissociation constant at 25° exceeds that of ethylene glycol by a factor of over $10^9$).

According to the literature, this method plays the main part in the synthesis of thallium alkoxides. Owing to its low standard electrode potential, metallic thallium hardly reacts with alcohols (or with water). The reaction can be brought about only in a continuous stream of dry oxygen‡. Hence the essence of the method consists in the reaction of $Tl_2O$ (formed by oxidation of the metal and with properties similar to those of the alkali oxides) with the alcohol:

$$Tl + O_2 \rightarrow [Tl_2O] \xrightarrow{+ROH} TlOR + TlOH,$$
$$TlOH + ROH \rightleftarrows TlOR + H_2O.$$

After repeated treatment of TlOH with small portions of alcohol the solid is completely converted into a heavy oily liquid to which Menzies[63] and other authors after him[64,83–85] ascribe the formula $TlOC_2H_5$ (quoting at best only results

† The thermal decomposition of the alkoxyboron complexes — formed in the alcoholysis of $M[BH_4]_n$ or on dissolution of the metal in an alcohol in the presence of the corresponding $B(OR)_3$ (compare p. 172): $M[B(OR)_4] \rightarrow M(OR)_n + B(OR)_3\uparrow$) — can in turn serve as a convenient method of synthesis of unsolvated alkaline earth and alkali metal alkoxides[32,69].

‡ According to Forcrand's results[82] the hypothetical reaction of Tl with alcohols and water should be endothermic, for the difference of their $\Delta H$ and the $\Delta H$ of the analogous reactions of sodium is constant at 58.52 kcal mole$^{-1}$. Nevertheless the reaction of $Tl_2O$ and TlOH with ethanol has a weak exothermic effect ($\Delta H$ is respectively -2.742 and -1.132 kcal per mole alkoxide).

of determinations of the metal). Yet as long ago as 1919, Freudenberg[86] showed that the concentration of carbon in this oily product is approximately one-half that calculated for $TlOC_2H_5$. In Brauer's handbook[87] this method is even proposed as a method for preparing thallium hydroxide, not alkoxide. Hence despite the many results which relate supposedly to $TlOC_2H_5$, we are speaking in the present case not about an individual compound but about a mixture (or possibly a complex compound) of thallium hydroxide and ethoxide. It must be noted that the structure of the molecular associates of thallium alkoxides quoted in several reviews[11,12,88] and monographs[89,90] were proposed by Sidgwick and Sutton[83] on the basis of cryoscopic and ebullioscopic investigations of the oily product (in this, the molecular weight of the monomer was calculated for the formula $TlOC_2H_5$). In view of the absence of a complete chemical analysis of other thallium(I) alkoxides obtained by this method, the problem of the composition of these compounds must at present be considered open.

In conclusion, mention must be made of the special importance of this type of reaction in making alcohols absolute — since the position of equilibrium (2) (p. 164) determines the maximum possible degree of dehydration of the alcohol concerned. Thus the equilibrium in the reaction $NaOC_2H_5 + H_2O \rightleftharpoons NaOH + C_2H_5OH$ lying considerably to the left[91-93] does not permit sodium to be used for making alcohols absolute§. A series of authors up to the present day have recommended that alcohol should be made absolute with alkaline earth oxides[96]. Moreover, in 1938 Berner[97], and subsequently Scholder and Kreutz[98], showed conclusively that the equilibrium

$$MO + 2\,CH_3OH \rightleftarrows M(OCH_3)_2 + 2H_2O \rightleftarrows M(OCH_3)(OH) + CH_3OH + H_2O,$$

where M = Ca, Sr, Ba, which exists in the solution, leads to the appearance of water in the absolute alcohol put in contact with the alkaline earths. This conclusion is confirmed by an investigation of the isotopic exchange in the $CaO-C_2H_5OH-D_2O$ system[99]. Nevertheless under these conditions both alkoxides were isolated in an individual state. The normal methoxides of Ca, Sr, and Ba are formed when the reaction is carried out with a large excess of alcohol — they are precipitated on heating the solutions. The hydroxide methoxides are obtained as sparingly soluble crystalline powders on treating the oxides with a little alcohol (see also p. 174).

Most methods for making alcohols absolute employ metallic Mg or Ca (sometimes Ba)[96], but the expediency of using them has only been demonstrated preparatively[100] by the determination of the water concentration after distillation over the corresponding alkoxide. Thermodynamic data, which determine the equilibria in these important reactions, have not been published.

## Method VI. Double Decompositions of Alkoxides with Alcohols Leading to the Synthesis of New Alkoxides

This method is of rather limited application among the elements of the main subgroups of Groups I and II. The equilibrium of the double decomposition $M(OR)_n + nR^IOH \rightleftharpoons M(OR^I)_n + nROH$ usually lies to the right on account of the removal of the more volatile alcohol. Therefore this method is used mainly for the synthesis of the alkoxides of polyhydric alcohols, and alkali metal methoxides or ethoxides are used as starting materials. This is the only method for the preparation of the trisodium salt of glycerol (reaction of the monosodium glycerol salt with sodium ethoxide): the reaction of glycerol with metallic Na or with alkoxides of monohydric alcohols does not yield such highly substituted products[180].

As Forcrand showed, the first stage of an exchange reaction of this type is the formation of addition compounds, which decompose with liberation of alcohol only on prolonged heating:

$$C_3H_5(OH)_3 + KOC_2H_5 \longrightarrow C_3H_5(OH)_2(OK)\cdot C_2H_5OH \xrightarrow[-C_2H_5OH]{120^\circ} C_3H_5(OH)_2(OK)^{\P},$$

$$C_3H_5(OH)_2(ONa) + NaOC_2H_5 \longrightarrow C_3H_5(OH)_2(ONa)\cdot NaOC_2H_5 \P \xrightarrow[-C_2H_5OH]{180^\circ-190^\circ}$$

$$\xrightarrow[-C_2H_5OH]{180^\circ-190^\circ} C_3H_5(OH)(ONa)_2. \text{ (Ref. 101)}$$

According to Geiger and Nobs[102], the equilibrium of the reaction between the alkali metal derivatives of cellulose and an excess of methanol is almost completely in favour of formation of $NaOCH_3$.

## Method VII. Certain Reactions of Organometallic Compounds Leading to the Formation of Alkoxides

In this section we consider the reactions which form the basis of several important methods of synthesis in organic chemistry. Alkoxides are intermediate products of reactions, almost never liberated in the free state. This explains the absence from the literature of any physicochemical characteristics whatsoever for most alkali metal alkoxides or the unsymmetrical alkoxymagnesium halides, despite the large number of reactions leading to their formation which have been described.

(a) Oxidation of alkyl derivatives of metals by oxygen. The example of the alkyllithium compounds showed[103] that in the first stage of the reaction peroxides are formed, which give alkoxides on further reaction with LiR:

$$LiR + O_2 \longrightarrow R-O-OLi \xrightarrow{+LiR} 2\,[LiOR].$$

The compound is enclosed within square brackets to denote that its formation is inferred only from the hydrolysis products.

In the case of the Grignard complexes this reaction is only one of the possible oxidation paths[10]. On prolonged storage of ethereal solutions of ethylmagnesium iodide in dry air Meisenheimer succeeded in isolating crystals of $C_2H_5OMgI.(C_2H_5O)_2O$, and sometimes also more oxidised (and probably, partly hydrolysed) products of composition $3[C_2H_5OMgI.(C_2H_5)_2O].MgO$.[104] †

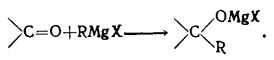
(b) Reduction of carbonyl-containing compounds. This class includes, firstly, many reduction

§ According to Caldin and Long[94] and to Murto[95] the equilibrium constant of the reaction: $C_2H_5OH + OH^- \rightleftharpoons C_2H_5O^- + H_2O$ is 0.68 at 25°, that is, in a 0.1 M solution of NaOH in 99% ethanol 96% of the sodium is present as $NaOC_2H_5$.

¶ Obviously it is more correct to consider such compounds as alcohol addition compounds of disubstituted glycerol salts, $C_3H_5(OH)(ONa)_2.C_2H_5OH$.

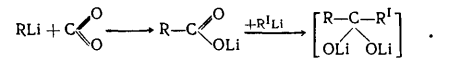
† This reference is incorrect. References to Meisenheimer's work in this area are to be found in "Grignard Reactions of Nonmetallic Substances" by M. S. Kharasch and O. Reinmuth, Constable, London, 1954, pp. 1264–1276 (Ed. of Translation).

reactions of Grignard complexes which are accompanied by the formation of alkoxymagnesium halides — derivatives of secondary and tertiary alcohols:

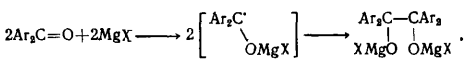


That the products of this reaction were alkoxides was finally decided only in 1941 by Nesmeyanov and Sazonova. Until then many authors had considered them to be addition compounds of RMgX and oxo-compounds [10].

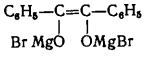
After the discovery of the Grignard synthesis, the possibility of using alkylsodium and alkyllithium compounds [105,106] as reductants for carbonyl compounds was demonstrated. The reaction of organolithium compounds with carbon dioxide, described by Gulman, must be mentioned. As a result of addition of LiR at both double bonds, derivatives of the hydrate forms of ketones are produced [106]:



In 1927 Gomberg and Bachmann [107] employed unusual reductants, magnesium monoiodide and monobromide, obtained by the reaction: $2Mg + X_2 \xrightarrow{ether} 2MgX$. Their reaction with ketones, which is accompanied by an intense coloration (due to the formation of free radicals — metalketyls), led to the pairing of the radicals and the synthesis of pinacolates:



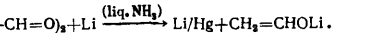
An alkoxide of a special type, an enolate of structure



was obtained in the reduction of the $\alpha$-diketone, benzil, as a colourless solvate with two molecules of ether. The solutions of this compound are always coloured (probably on account of the equilibrium between the ketyl and the dimer) [108].

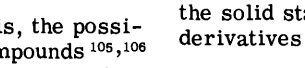
The formation of metalketyls occurs also in the action of metallic sodium or potassium on aromatic and aliphatic ketones [109,110]. The reaction of dialkyl and diaryl carbonates with sodium takes place quantitatively and serves for the production of extremely pure carbon monoxide. In this case, alkoxides are only side-products of the synthesis [111].

There is great interest in the reduction of bis-2-oxoethylmercury with alkali metals (lithium and sodium) in a solution of liquid ammonia. In this way Nesmeyanov et al. [112] synthesised lithium and sodium enolates which were derivatives of vinyl alcohols; for example,



The products form colourless hygroscopic crystals; the existence of a double bond and the absence of a carbonyl group in the molecules were shown convincingly by their infrared spectra [113].

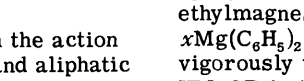
The reaction of carbon monoxide with the alkali and alkaline earth metals also belongs formally to this class of reactions. The pyrophoric "carbonyls" formed as a result have attracted the attention of chemists since the time of Liebig. Until very recently it was thought that they were salts of hexahydroxybenzene — for example $(COK)_6$ is $C_6(OK)_6$ [114] — or derivatives of glyoxal — of the type O=C–Cs
| . [115] However, in 1963–64 Weiss and Büchner [116,117]
O=C–Cs
found, in an X-ray investigation of the potassium, rubidium, and caesium "carbonyls", that the distance between the carbon atoms in them corresponds to a triple bond and the metal is bound to the carbon through oxygen, as in ordinary alkoxides. Hence it can obviously be considered as proved that in the reaction between the alkali metals and CO (in the solid state or in solution in liquid $NH_3$), disubstituted derivatives of the hypothetical acetylenediol are formed:



(c) Cleavage of the C–O bond in ethers with the aid of metal alkyls (Shorygin reaction). In 1910 Shorygin [105], in attempting to carry out in ethereal solution the exchange reaction of sodium with a dialkylmercury, obtained sodium ethoxide instead of the organosodium compound expected. The instability of ethers in relation to an alkyl derivative of alkali metals was thus observed for the first time.

Wittig [118] succeeded in carrying out the Shorygin reaction with tetrahydrofuran (the ether bond in which is usually unreactive). In the reaction with $(C_6H_5)CNa$, tetrahydrofuran was introduced as a complex with diphenylberyllium (in the molecule of which the C–O bond was weakened by coordination). It was shown subsequently that this reaction takes place much more vigorously with organolithium compounds [119].

An interesting compound — a lithium organotinethoxide [the alkoxide of 2-hydroxyethyltriphenyltin (Ed. of Translation)] — is formed by the action of an organotin complex on epoxyethane [120]:



Among the organomagnesium compounds, particularly the Grignard complexes, the Shorygin reaction was known until recently only for the least stable cyclic ethers — epoxyethane and oxetan [10,121]. Bauer [122] observed that ethylmagnesium hydride — obtained by the reaction: $x\mathrm{Mg}(C_6H_5)_2 + SiH_4 = HMgC_2H_5 + SiH_{4-x}(C_2H_5)_x$ — reacts vigorously with diethyl ether. The reaction product HMgOR is insoluble in ether and exhibits quite considerable thermal stability. Huston [123] made a detailed investigation of the mechanism of the reaction of epoxides with symmetrical and unsymmetrical alkylmagnesium compounds. The formation of a series of magnesium alkoxides and halide alkoxides was established. Compounds of analogous type were also obtained in reactions of epoxyethane and its homologues with $MgBr_2.2(C_2H_5)_2O$. [124] However, the compounds synthesised were characterised in the best instance solely by chemical analyses.

## Method VIII. Electrochemical Methods of Synthesising Alkoxides

Numerous instances of the formation of alkoxides in electrochemical processes are noted, particularly in the anodic oxidation of metals during the electrolysis of alcoholic solutions. Szilard [125] isolated pure magnesium ethoxide (and also $Pb^{II}$ and $Cu^{II}$ methoxides) during the electrolysis of alcoholic solutions of sodium alkoxides with various anodes (at low current densities).

The reaction of metals with alcohols (with the aim of obtaining alkoxides) can be considerably accelerated by the setting up of an internal e.m.f. (by the introduction of a second — platinum — electrode)[126] or by connection to a source of current (reacting metal–anode)[127].

The electrolysis of $MgCl_2$ solutions[128] (and various other chlorides)[129] leading to the formation of magnesium alkoxides at the cathode is obviously not of interest from the synthetic aspect.

## B. PHYSICAL PROPERTIES OF ALKOXIDES AND CERTAIN STRUCTURAL PROBLEMS

The alkali metal and alkaline earth metal alkoxides are white, infusible substances, very sensitive to oxygen, moisture, and carbon dioxide (however, $CsOC_2H_5$, $CsOC_3H_7$, and $KOC_3H_7$ are completely liquid by the time decomposition starts[13]). Oxidation, hydrolysis, and carbonation are accompanied by such an appreciable liberation of heat that in air the spontaneous ignition of unsolvated alkali metal alkoxides is possible[5,130]. The potassium and caesium alkoxides are the least stable in this respect (alcohol derivatives of rubidium are still unknown): even in an atmosphere dried by phosphorus pentoxide they rapidly darken and liquefy. To prevent oxidation of solid alkoxides and also of their alcoholic solutions, the patent literature proposes the use of antioxidants: imines, iminium chlorides, and amides[132]. Thallium(I) alkoxides — derivatives of primary normal alcohols (with the exception of methoxide) — are heavy liquids, readily soluble in alcohols and hydrocarbons (Tables 1, 4, and 5).

Most authors refer to the amorphous nature of the alcohol derivatives of the alkali and alkaline earth metals, but adequately sharp reflections are present on the X-ray powder diagrams of all the alkoxides yet studied, including $LiOCH_3$,[133,134] $NaOCH_3$, $NaOCH_3.2CH_3OH$,[133] $KOCH_3$,[133,135] $KOCH_3.nCH_3OH$ ($n$ = 1 or 3)[133], $NaOC_2H_5$,[136] $Sr(OCH_3)_2$.[97]

In 1960–63 the first structural investigations of alkoxides were completed: lithium[133,134], potassium[135], and thallium(I)[88] methoxides. According to Wheatley's results[133], $LiOCH_3$ has a layer structure, analogous to LiOH, of the type ABCBA/AB, . . . . , where A = $CH_3$, B = O, C = Li. Each Li atom in this lattice is surrounded by a distorted tetrahedron of oxygen atoms; the coordination polyhedron of the oxygen is a pyramid with four Li atoms for the base and a $CH_3$ group for the vertex. Hence the basis of the bridge structure of lithium methoxide consists of polymeric chains of $[LiO_4]$ tetrahedra.

TABLE 1. Alkali metal alkoxides. The Roman numerals here and subsequently denote the method of preparation (see the text on pp. 162–167).

| ROH | Li | Na | K | Cs |
|---|---|---|---|---|
| $CH_3OH$ | LiOR, decomp. > 360[137] tetr., $a$ = 3.63 $c$ = 7, 62A, $Z$ = 2, sp.gp. $P4/nmm$, str. type LiOH [133, 134]; I[138, 139]; II[43] | NaOR · 3ROH NaOR · 2 ROH, decomp. 190° NaOR, decomp. 300°, [140] o-rh., $a$ = 4.32, $b$ = 7.42 $c$ = 8, 73A, $Z$ = 4[133] $d$ = 1.28, $c_{p\ 298}$ = 16.6, $s^\circ$ = 26.43 $H_T^0 - H_0^0$ = 3374, $\Phi^*$ = — 15.12[141]; I[14–16, 142, 143]; II[42, 43]; III[52, 54]; V[73, 8, 81] | KOR · 3 ROH, mon. $a$ = 14.96, $b$ = 7.68, $c$ = 13.24A, $\beta$ = 93.8°, $Z$ = 8, sp.gp. $P2_1/n_i$ KOR · ROH, mon. $a$ = 14.75, $b$ = 15.04, $c$ = 9.33 Å $Z$ = 6, decomp. 190°[133] KOR, decomp. 350°, tetr. $a$ = 3.94, $b$ = 8.76A, $Z$ = 2, sp.gp. $P4/nmm$[135] I[14, 37]; II[43]; IV[65] | CsOR · ROH decomp. 20°, CsOR, decomp. 330°, I[13] |
| $C_2H_5OH$ | LiOR · 2 ROH (?)[144] LiOR, I[138, 139, 144]; II[43]; III[144]; IV[62] | NaOR · 3 ROH NaOR · 2 ROH, decomp. 200° NaOR, decomp. 320°[140] (240°[145]), I[14–16]; II[41, 43]; III[52]; V[8, 71–74, 76] | KOR · ROH KOR, decomp. 250° I[13, 14, 37]; II[43]; III[47]; V[76, 80, 146] | CsOR · ROH decomp. 50° CsOR, m.p. 200° (decomp.) I[13] |
| n-$C_3H_7OH$ | LiOR, I[139]; III[119] | NaOR · 2 ROH, decomp. 220° NaOR, decomp. 320°, I[17, 142, 147] | KOR, m.p. 250° decomp., I[13, 148] | CsOR · ROH decomp. 100° CsOR, m.p. 250°, I[13] |
| iso-$C_3H_7OH$ | LiOR, subl. > 100° per $5 \times 10^{-2}$ mmHg, $\alpha$ = 3—5 I[139, 149] | NaOR · 3 ROH NaOR, I[17, 150–152] | KOR, I[152]; V[80] | |
| n-$C_4H_9OH$ | LiOR, I[139, 153]; II[43] | NaOR · 2 ROH NaOR, I[17, 154]; II[41, 43]; V[73, 81]; VI[8] | KOR, II[43]; V[73] | |
| iso-$C_4H_9OH$ | LiOR, subl., $\alpha$ = 3 — 5, I[139, 149]; II[43]; III[155] | NaOR · 2 ROH NaOR, I[17, 154]; II[43] | KOR, I[148]; II[43] | |
| s-$C_4H_9OH$ | LiOR, I[149] | NaOR · 3 ROH, decomp. 200° NaOR, I[17, 147, 148, 154]; V[80] | KOR, I[156]; V[80] | |

TABLE 1 (contd.)

| ROH | Li | Na | K | Cs |
|---|---|---|---|---|
| t-$C_4H_9OH$ | LiOR, subl. $\mu = 0.74$ D $\alpha = 6-9$, I[139, 149, 157] | NaOR · 2 ROH I[154, 156]; III[52] | KOR, decomp. 250°[158] subl.[159]; I[139, 156, 160, 161] | |
| iso $C_5H_{11}OH$ | LiOR, $\alpha$=3—5; I[139]; II[43] | NaOR, decomp. 270° I[14, 162]; II[43]; V[162] | KOR, decomp. 250° I[14, 146]; II[43] | |
| s-$C_5H_{11}OH$ | LiOR, I[149] | NaOR, VI[8] | KOR, V[80] | |
| $(CH_3)_2(C_2H_5)COH$ | LiOR, I[149] | | | |
| n-$C_6H_{13}OH$ | | NaOR, VI[8] | | |
| n-$C_8H_{17}OH$ | LiOR, I[156] | NaOR, I[9, 156]; V[81] | KOR, I[156] | |
| $C_6H_5CH_2OH$ | | NaOR, I[4, 163] | KOR, I[47]; V[80] | |
| $(C_6H_5)_2CHOH$ | | NaOR, I[164] | KOR, III; VII[58] | |
| $(C_6H_5)_3COH$ | | NaOR, $\alpha = 1$, $\mu = 1.62$D (25°), I[165] | | |
| $CH_2{=}CHCH_2OH$ | | NaOR, II[43] | | |
| $[CH_2{=}CHOH]$ | LiOR, VII[112] | NaOR, VII[112] | KOR, CsOR — glass, formed in pyrolysis of ethoxides (?)[13] | |
| $C_6H_5COH$ ‖ $C_6H_5COH$ | | | $(KO)_2R$, VII[110] | |
| $CH_2OH$ \| $CH_2OH$ | LiOROH, dispropor. 170° $(LiO)_2R$, II[43] | NaOROH · $R(OH)_2$ I[166, 167]; II[43, 47, 49]; V[77]; VI[43, 168] $(NaO)_2R$, I[18]; II[43]; V[77, 169]; VI[170] | KOROH $(KO)_2R$, II[43] | |
| $[HOC{\equiv}COH]$ | $(LiO)_2R$ VII*b* [171, 172] | $(NaO)_2R$ VII*b* [172, 173] | $(KO)_2R$[172, 174] \| $(RbO)_2R$[171, 172] \| $(CsO)_2R$[115, 172, 175] (VII)*b* tetr., sp.gp., $I4/mmm$, $Z = 2$ $a = 3.93$ A \| $= 4.13$ A \| $= 4.37$ A $c = 12.75$ A \| $= 13.05$ A \| $= 13.52$ A $d = 2.27$[116] \| $= 3.38$[117] \| $= 4.14$[117] | |
| $HOCH_2(CH_3)CHOH$ | | | $(KO)_2R$[170] | |
| $CH_3CHOH$ \| $CH_3CHOH$ | | | $(KO)_2R$[170] | |
| $O(CH_2CH_2OH)_2$ | | (NaO) ROH · $R(OH)_2$, VI[176] | | |
| $HOCH(CH_2OH)_2$ | | (NaO) $R(OH)_2$ AlkOH, decomp. 120° (NaO) $R(OH)_2$, decomp. 245° I[177]; II[49]; V[54, 78]; VI[35, 168, 177] $(NaO)_2$ROH, m.p. 220°(decomp.) I[40]; VI[101, 179] $(NaO)_3R$, VI[180] | KOR $(OH)_2$ · AlkOH, decomp. 120° V[78]; VI[35, 178] $(KO)_2$ROH, VI[101] | |
| $(C_6H_{10}O_5)_x$ | | NaOR $(OH)_2$, II[48, 49]; VI[50] derivatives of starch, inulin, lichenin, glycogen $(NaO)_3R$, II[50], derivatives of celluloses | KOR $(OH)_2$, II[48, 49] | |
| $CH_2OH$ \| $(CHOH)_2$ \| $CH_2OH$ | $(LiO)_2R(OH)_2$ II[43] | NaOR $(OH)_3$ · X (X=$H_2O$, $CH_3OH$) II[43]; V[36, 79, 181]; VI[182] $(NaO)_2R(OH)_2 \cdot x H_2O$, decomp. 140° $(NaO)_2R(OH)_2$, V[79] | KOR $(OH)_3 \cdot H_2O$ KOR $(OH)_3$ II[43]; V; VI[79] | |
| Methylglucosides | | NaOR $(OH)_5$; II[48] | KOR $(OH)_5$, II[48] | |
| Mannitol | $(LiO)_2R(OH)_4$, II[43] | NaOR $(OH)_5$, II[43, 48]; VI[182] | KOR $(OH)_5$, II[43, 48] | |
| Hexoses | | NaOR $(OH)_4$ — derivatives of fructoses and glucoses, II[49] | | |

Potassium methoxide also crystallises in a layer structure (the space group of both methoxides is $P4nmm$), in which the linear $KOCH_3$ molecules are situated perpendicular to the plane of the layers. The coordination number of potassium is five and the oxygen atom is at the centre of a distorted octahedron, five of the vertices of which are occupied by $K^+$ and the sixth by a methyl group [135].

Lithium alkoxides retain their polymeric nature in solutions and even in the vapour. The degree of association of LiOR, soluble in organic solvents, varies from 3 to 9. [149,157] For insoluble LiOR with radicals of normal structure the association should be even greater [139]. Because the position of the Li–O stretching vibration frequency in the infrared spectra of $LiOBu^t$ vapour (at 200°) is almost the same as that for the solid alkoxide‡, Simonov and coworkers [183] suggested that there was association in the gas phase.

‡ The association of the LiOR molecule leads to a great reduction in the frequency of the Li–O stretching vibrations by ~ 1000 $cm^{-1}$ compared with the value calculated for the isolated molecule [139].

TABLE 2. Solubility of NaOR in the corresponding alcohols at 20°. [160]

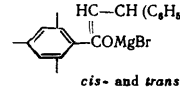
| R | Solubility, moles NaOR litre$^{-1}$ | R | Solubility, moles NaOR litre$^{-1}$ |
|---|---|---|---|
| $n$-$C_3H_7$ | >1 | iso-$C_4H_9$ | 0.63 |
| iso-$C_3H_7$ | 0.22 | s-$C_4H_9$ | 0.66 |
| $n$-$C_4H_9$ | >1 | t-$C_4H_9$ | 0.34(27°) |

TABLE 3. Equivalent electrical conductivity at infinite dilution of alcoholic solutions of alkoxides at 25°. [187]

| Solvent | LiOR | NaOR | KOR | $Ca(OR)_2$ | $Al(OR)_3$ |
|---|---|---|---|---|---|
| $CH_3OH$ | 94.0 | 98.4 | 106.8 [188] | ~85 | — |
| $C_2H_5OH$ | 39.6 | 43.0 [189] | 46.6 [188] | — | (83°) $9.8\cdot10^{-6}$ * |
| $H_2O$ | — | NaOH—210 | KOH~210 | — | — |

* Calculated from published data [190].

TABLE 4. Magnesium and alkaline earth metal alkoxides.

| ROH | Mg | Ca | Sr | Ba, Ra |
|---|---|---|---|---|
| $CH_3OH$ | $Mg(OR)_2\cdot 4ROH$ (—20°)<br>$Mg(OR)_2\cdot 3ROH$, decomp. 40°<br>$Mg(OR)_2$, decomp. 350°<br>I[21—26]; III[57, 191, 192] | $Ca(OR)_2$, decomp. > 150°<br>I[193, 194]; II[44, 45];<br>III[55, 56, 192, 195];<br>IV[45]; V[97] | $Sr(OR)_2$<br>II[44]; IV[45];<br>V[97] | $Ba(OR)_2$<br>decomp. 250°<br>I[28]; II[44, 45];<br>IV[45]; V[28, 140] |
| $C_2H_5OH$ | $Mg(OR)_2\cdot x ROH$<br>$Mg(OR)_2$, I[21, 25—31];<br>III[57]; VIII[125]<br>$C_2H_5OMgOCH_3$, III[61]<br>$C_2H_5OMgX$, X=H, $BH_4$, $AlH_4$<br>VIIc[61, 122]; X=$C_2H_5$, VIIa[201] | $Ca(OR)_2\cdot 2ROH$, decomp. 50°<br>I[193, 194, 197, 31]; II[45];<br>III[193, 196—199];<br>IV[45]<br>$Ca(OR)_2$ | $Sr(OR)_2$<br>II[44, 45];<br>IV[45] | $Ba(OR)_2$<br>II[44, 45];<br>IV[45]<br>$Ra(OR)_2$[200] |
| $n$-$C_3H_7OH$ | $Mg(OR)_2$, I[19, 24] | $Ca(OR)_2$, I[193] | | |
| iso-$C_3H_7OH$ | $Mg(OR)_2$, I[20, 152]; III[57] | | | |
| iso-$C_4H_9OH$ | $Mg(OR)_2$, I[19] | $Ca(OR)_2$, II[44, 45]; IV[45] | | $Ba(OR^n)_2$, II[202] |
| iso-$C_5H_{11}OH$ | $Mg(OR)_2$, I[19, 26] | $Ca(OR)_2$, II[44, 45]; IV[45]; V[70] | | |
| $C_6H_5CH_2OH$ | $Mg(OR)_2$, VI[203] | $Ca(OR)_2$, I[193]; VI[203] | | $Ba(OR)_2$, V[75] |
| $CH_2OH$<br>\|<br>$CH_2OH$ | $MgO_2R$, III[57] | $CaO_2R$, II[45,202]; IV[45];<br>$Ca[OROH]_2$, IV[45] | $SrO_2R$<br>II[46, 202];<br>IV[46] | $BaO_2R$, II,<br>IV[46] |
| $HOCH(CH_2OH)_2$ | $MgO_2ROH$, III[57] | $CaO_2ROH$, V[204] | | |
| $HOCH_2CHOH$<br>\|<br>$HOCH_2CHOH$ | | $CaO_2R(OH)_2$, II[45] | | |
| [HOC≡COH] (?) VII*b* | | $CaO_2R$[171] | $SrO_2R$[205] | $BaO_2R$[206] |
| $MgX(OC_2H_5)$, X=Cl, Br, I[10, 29, 104, 207] | $RMgOC_3H_7$-iso, $RMgOC_4H_9$—t, III; IV[131] | $[(C_6H_5)(BrMgO)C=]_2\cdot(C_2H_5)_2O$<br>VII[107] |  <br>*cis*- and *trans*- VII[208] | |

The explanation of such a marked intermolecular interaction for LiOR (in relation to other alkali and alkaline earth alkoxides for which the question remains open) is as follows: (1) the possibility of the formation of "tricentric bonds" from the Li *p* orbital of one molecule and electrons of the Li–O σ bond of another; (2) donor–acceptor interaction between the free *p* orbital of an Li atom and the oxygen lone pair of a neighbouring molecule [139].

A recent investigation of the nuclear magnetic resonance spectra showed that the nature of the bonding of LiOR trimers in n- and t-butoxides is essentially different up to values of $\alpha$ of 6 and 9 respectively§. Whereas in the first case the interaction is of a donor–acceptor character, in the second the formation of multicentre orbitals has the main role [157]. The authors assume that [157] elementary associates, $(LiOR)_3$, form almost planar six-membered rings of alternating lithium and oxygen atoms.

As Table 5 shows, thallium(I) alkoxides are also associated, with formation of tetramers. However, as already indicated on pp. 164–165, the absence of reliable data on the individuality of the products investigated reduces considerably the value of the molecular weight determinations here [83,184]. The existence of tetramers in the $TlOCH_3$ crystal lattice was recently established by X-ray diffraction. Following Sidgwick [83], the authors assume that such a molecular associate is a distorted cube at the vertices of which are four Tl atoms and four oxygen atoms [88]. Unfortunately in this work also only the analyses for the metal are given.

The most important characteristic, which influences all the physicochemical properties of the metal alkoxides being considered, is the considerable polarisation of the M–O bond. However, direct measurement of the dipole moments of the most polar alkoxides is impossible, owing to their insolubility in dipole-free liquids and their involatility. In addition, the published information about the negligible dipole moments of $NaOC(C_6H_5)_3$ ($\mu$ = 1.62 D) [165] and $LiOBu^t$ ($\mu$ = 0.74 D) [139] — compounds which are readily soluble in non-polar solvents — cannot be considered as evidence of the covalent character of the M–O bonds in alkoxides in general (as is done, for example, by Nazarova [165]), in view of the fact that the constants of acid dissociation of $(C_6H_5)_3COH$ and $t\text{-}C_4H_9OH$ are three orders of magnitude less than the corresponding values for the first members of the aliphatic series of alcohols.

Of all the compounds of the class considered, volatility (in a high vacuum) is distinctive for only lithium secondary and tertiary alkoxides [149], potassium tertiary t-butoxide [159], and thallium(I) pentyl oxide [184] — the least polar of the aliphatic alkoxides.

Unsolvated alkoxides, as a rule, are insoluble in most organic solvents (with the exception of alcohols, in which dissolution is effected by the formation of solvates), in liquid ammonia, sulphur dioxide, etc. With increase in size and complexity of the radicals the solubility of MOR in non-polar solvents usually increases. As already mentioned, the LiOR products of normal primary alcohols are insoluble even in the "parent" alcohols, whereas alkoxides with iso-radicals are soluble in any organic solvent (including alkane, hydroaromatic, and aromatic hydrocarbons) except alcohols [149]. Sodium normal alkoxides are readily soluble in alcohols, but as the branching of the radicals is increased the solubility of NaOR in the corresponding alcohols falls considerably (Table 2).

§ $\alpha$ is the degree of association (Ed. of Translation).

TABLE 5. Thallium(I) alkoxides and phenoxides*.

| Formula | Method of preparation | Appearance | M.p., °C | *d* | Degree of association, α (Ref. 83) |
|---|---|---|---|---|---|
| $CH_3OTl$ | IV[45]; V[83, 209, 210] | o-rh. crystals $a$=13.80, $b$=6.98, $c$=13.66, $Z$=16, sp.gp. $Pca2_1$ [88] | 120°–decomp. | 4.75 | 3.86 |
| $C_2H_5OTl$ (?) | IV[45, 63] V[63, 82, 85, 209-211] | oily liquid | −3 80° decomp. | $d_4^{20}$ 3.522 $n_D^{20}$ 1.678 | 4.45 |
| n-$C_3H_7OTl$ | V[211] | crystals | — | — | — |
| n-$C_4H_9OTl$ | V[211] | oily liquid | — | — | — |
| iso-$C_4H_9OTl$ | V, VI[211] | crystals | — | — | — |
| iso-$C_5H_{11}OTl$ (?) | IV[45]; VI[209] | heavy liquid | −80 | 2.465 | — |
| t-$C_5H_{11}OTl$ | VI[184] | liquid | decomp. 50° distils at 20° in a vacuum | — | 4.0 |
| $C_6H_{11}OTl$ | V[82]; VI[83, 209] | powder | — | — | 3.16 |
| $C_6H_5CH_2OTl$ | VI[83] | colourless tablets | 74 | — | 3.94 |
| $HOCH_2CH_2OTl$, VI[210] | $(CH_2OTl)_2$, IV[45] | $(CH_2OTl)_2 \cdot TlOH \cdot H_2O$, V[212] | $CH_2(CH_2OTl)_2$, VI[212] | | |
| Glycerolates $R(OH)_2(OTl)$, VI[210]; $R(OTl)_3$, V[212] | | $C(CH_2OTl)_4 \cdot xTlOH$ VI[212] | methylglucoside $R(OH)(OTl)_3$, V[212] | | |
| $R(OTl)_6$-sorbitol [213] | Stereoisomeric hexides $R(OTl)_x(OH)_{6-x}$, $x$=5—6; mannitol, dulcitol, IV[45]; VI[213] | | $R(OT)_6$-mannitol, V[214] | | |
| (>CHOTl)$_6$-inositol V[212] | $C_{12}H_{16}O_7(OTl)_4$ sucrose, V[212] | α-methylarabinoside $R(OTl)_3$, decomp. 160° V[213] | $CH_2OTl$ IV; V[217] (CHOTl)$_4$ COOTl | | |
| $C_6H_5OTl$ | V[215,216]; VI[83,210] | colourless needles | 235 | | 3.83 |
| 2-$CH_3C_6H_4OTl$ | V[217] | crystals | 164° with decomp. | | — |
| 3-$CH_3C_6H_4OTl$ | V[83,215,217] | » | 199 | | — |
| 4-$CH_3C_6H_4OTl$ | V[217] | » | 203 | | — |
| α-$C_{10}H_7OTl$ | V[215] | tablets | 180 | | — |
| β-$C_{10}H_7OTl$ | V[216] | crystals | — | | — |
| 5-$CH_3$—2 (iso-$C_3H_7$) $C_6H_3OTl$ | V[217] | crystals | 164 decomp. | | — |
| 2-$CH_3$—5 (iso-$C_3H_7$) $C_6H_3OTl$ | V[217] | » | 158 decomp. | | — |
| 2-$CH_3OC_6H_4OTl$ | V[215,217]; VI[83] | rhomb-like tablets | 161 | | — |
| 3-$CH_3OC_6H_4OTl$ | V[215,217]; VI[83] | prisms | 147 | | — |
| 4-$CH_3OC_6H_4OTl$ | V[217] | » | 196 | | — |
| 4-CHO-2 ($CH_3O$) $C_6H_3OTl$ | V[215]; VI[83] | yellow crystals | 142 | | 1.99 |
| 2-$CH_3O$-4 ($CH_2CH{=}CH_2$) $C_6H_3OTl$ | V[217] | ditto | 148 decomp. | | — |
| 2-$CHOC_6H_4OTl$ | V[217,219]; VI[83] | » | 197 | | — |
| $C_6H_4(OTl)_2$-1,3 | V[216] | » | decomp. without melting | | — |
| 5-$CH_3C_6H_3(OTl)$-1,3 | V[216] | » | | | — |
| $(CH_3)_2Tl^{III}OCH_3$ | IV[63] | solid darkening in air | 181 | | — |
| $(CH_3)_2Tl^{III}OC_2H_5$ | IV[63] | colourless mobile liquid | b.p. 110°/15 mmHg | | — |
| $(C_2H_5)_2Tl^{III}OC_2H_5$ | IV[64] | crystals | 45; b.p. 101°/0.1 mmHg | | — |

* See pp. 164–165.

The solubility of alkali metal alkoxides in liquid $NH_3$ increases with the size of R; [41] with potassium ethoxide it is somewhat greater than with sodium ethoxide [47] (almost insoluble), but Chablay [45] noted a further decrease in solubility on going from the alkali to the alkaline earth alkoxides.

The higher sodium alkoxides — primary isopentyl oxide, triphenylmethoxide — are, unlike the derivatives of alcohols of normal chain structure, readily soluble in benzene, dioxan, etc. (see Table 1). According to McEwen [185], the solubility of $NaOCH_3$ in benzene at room temperature is $3–9 \times 10^{-4}$ M.

The alkaline earth and magnesium alkoxides are much more inert towards organic solvents — even in alcohols their solubility is very restricted and falls on heating (probably owing to a decrease in the solvation of $M^{2+}$ ions with

the alcohols). The solubility of $Mg(OCH_3)_2$ in methanol is given by Bjerrum[186] as 0.9 M at 18°, but Quinet[25] gives 0.118 moles per 100 g at 20°, or ~0.99 M, taking the density of $Mg(OCH_3)_2$ as 1.34.

The polar nature of the M–O bond in alkoxides is responsible for their capability of electrolytic dissociation and consequently their appreciable conductivity in polar solvents. Table 3 gives the equivalent conductance of alkoxides in alcoholic solutions (at infinite dilution). The corresponding quantities for aqueous alkalis and aluminium ethoxide (molten) are also given for comparison.

Thus the electrical conductivity of the alkali metal alkoxides in alcohols is only a few times less than the solubility of such strong electrolytes as NaOH and KOH; it is of the same order as $\lambda_\infty$ of an aqueous solution of sodium acetate and exceeds the electrical conductivity of $Al(OC_2H_5)_3$ by ~6 orders of magnitude, $Al(OC_2H_5)_3$ being a compound whose properties lie at the boundary between typical alkoxides and the esters of inorganic acids.

Grenier and Westrem[141] determined the main thermodynamic functions of sodium methoxide (Table 1); such data are not available for other alkoxides. The variation of heat capacity with temperature, measured between 5° and 340°K, had an anomaly at 34°K, for which the surplus entropy was ~0.43 e.u.

## C. CHEMICAL PROPERTIES OF ALKOXIDES AND THEIR MAIN APPLICATIONS IN ORGANIC AND INORGANIC PREPARATIONS

### 1. Addition Reactions

(a) Complex formation. Meerwein's "alkoxysalts" crystalline alcohol addition compounds. Magnesium halide alkoxides. The tendency of the alkali metal and alkaline earth metal alkoxides to various complex-forming reactions is due to the acceptor and donor abilities of their molecules. A clear demonstration of this "dual" function is the polymerisation of molecules of alkoxides (see p. 169).

The most studied class of oxonium compounds of the alkoxides are their complexes with alcohols. Although the formation of such compounds is due mainly to valence bonds, intermolecular interaction also plays a significant part here, as was shown above. The results of Forcrand's thermochemical investigations (Table 6) suggest that for a single alkoxide the heats of formation of its oxonium complexes from the components decrease along the homologous series of alcohols.

TABLE 6. $\Delta H$ of formation of the crystalline alcohol addition compounds (after Forcrand's results)[166,178,197,220,221]

| Alkoxide | Addend | Composition of complex | $-\Delta H$, kcal (mole complex)$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Na | K | Ca |
| $MOCH_3$ | $CH_3OH$ | 1:1 | 8.84 | — | — |
| $MOC_2H_5$ | $C_2H_5OH$ | 1:2 | 8.06 | — | 8.5 |
| $MOC_2H_5$ | $C_2H_5OH$ | 1:3 | 8.64 | — | — |
| $MOCH_2-CH_2OH$ | $(-CH_2OH)_2$ | 1:1 | 7.02 | — | — |
| $CH_2-OM$ \| $CH-OH$ \| $CH_2-OH$ | $CH_3OH$ | 1:1 | 5.04 | 3.65 | — |
| | $C_2H_5OH$ | 1:1 | 4.58 | 2.69 | — |
| | n-$C_3H_7OH$ | 1:1 | 4.67 | 3.76 | — |
| | iso-$C_3H_9OH$ | 1:1 | 2.71 | — | — |
| | iso-$C_5H_{11}OH$ | 1:1 | 2.80 | 1.78 | — |

A still more definite conclusion can be drawn from Chelintsev's results[207] on the heats of formation of the compounds of type $C_2H_5OMgI.3ROH$. On plotting the total thermal effects for addition against the dielectric constants of the alcohols (Fig. 2) we observed a relation very close to a straight line (there is a departure only for the first member of the series, $CH_3OH$). A comparison of the thermal effects for the addition of the first molecules of ligand made by Chelintsev is incorrect, since there is no information about the existence of products of an intermediate composition other than 1 : 3 (see, for example, Tolstopyatov[104]). Since in the series of alcohols there is almost no change in the chemical nature of the molecule or the donor properties of the oxygen atom, the observable effect can evidently be ascribed to interaction of entire molecules, not individual atoms (donor and acceptor). The principal role in this interaction is obviously played by the dispersion effect. (In view of the constancy in the dipole moments throughout the homologous series the orientation interaction cannot be great. The induction effect must also be negligible, since in the case under consideration $\mu$ and the polarisability of the donor and acceptor molecules differ little from one another.)

All this at first seems to be contradicted by the results of Frölich[142] and Thomas[13] on the thermal stability of the sodium and caesium alkoxide–alcohol compounds shown in Table 7.

In the examples quoted the desolvation temperatures rise along the homologous series of alcohols, but it must be borne in mind that the acceptor-molecules are different.

For the derivatives of a single alcohol, the enthalpy of formation (Table 6) and thermal stability (Table 1) of the compounds with alcohol of crystallisation decreases from

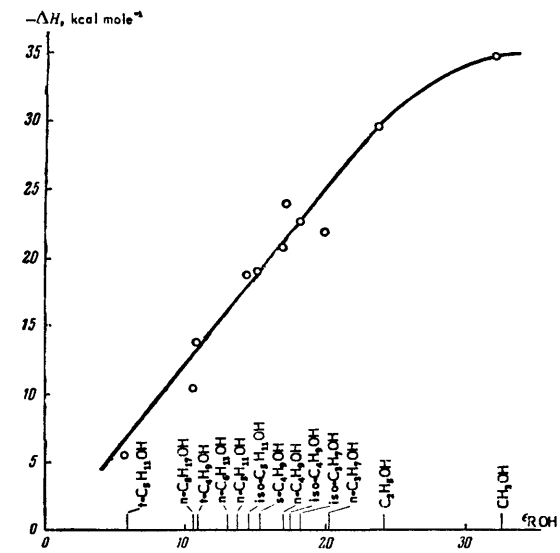



Fig. 2. Relation between the heats of formation of the alcohol addition compounds by the reaction:

$$C_2H_5OMgI + 3ROH = C_2H_5OMgI.3ROH$$

and the dielectric constant of the ligands.

TABLE 7. Temperatures of desolvation of the crystalline alcohol addition compounds.

| | R | | |
|---|---|---|---|
| | $CH_3$ | $C_2H_5$ | $n\text{-}C_3H_7$ |
| $NaOR \cdot 2ROH$[143] | 170° | 200° | 220° |
| $CsOR \cdot ROH$[13] (decomp. in a vacuum) | 20—30° | 50° | 100° |

sodium to potassium. However, Thomas[13] thinks that the tendency of CsOR to solvation by alcohols is somewhat greater than that of KOR.

The coordination compounds of alkoxides with alcohols obviously exist in solution as well as in the solid state. In 1963, Kęcki and Witanowski showed[222] that solutions of Li and Na methoxides in $CH_3OH$ do not give the splitting of the NMR signal of the OH group and linked this with the rapid transfer of protons along the chain of a solvate macromolecule; they also considered the solutions to be systems in which strong intermolecular interaction led to a deficiency of protons.

Besides alcohols, the alkoxides are capable of forming "onium" compounds with many other organic molecules. In particular, the literature mentions the existence in solution of 1:1 and 1:2 complexes of $NaOCH_3$ with $HCOOCH_3$ (from electrical conductivity)[223], and complexes of KOR with dimethoxyethane and ethylenediamine. In the last two cases complex formation with the solvent determines the catalytic activity of alkali metal alkoxides in reactions of anionic polymerisation[224].

A special place among the complex formation reactions of the alcohol derivatives of the alkali and alkaline earth metals is taken by their interaction with formal analogues — the esters of inorganic acids. Even in the last century thanks to the work of Kopo and later Cambi[225] it became known that stable saltlike compounds of the type $M[B(OR)_4]$ were formed during crystallisation of alcoholic solutions containing borate esters and Li, Na, K, or Ca alkoxides.

Meerwein and Bersin observed[226] that the alkoxy-derivatives of most of the elements of Groups III–VI undergo alcoholysis in alcoholic solutions with formation of "alkoxy--acids" of type $H[E(OR)_n]$. Their reaction with the "strong bases" $M^IOR$ is analogous to neutralisation:

$$H[E(OR)_n] + M^IOR \longrightarrow M[E(OR)_n] + ROH.$$

The complexes which are formed have acquired the name "Meerwein's alkoxy-salts". In many cases these authors[226] succeeded in titrating with alcoholic solutions of $M^IOR$. Subsequently synthesis of alkoxy-salts progressed and now compounds of the type $M[E(OR)_n]$ and also the mixed salts $M[EX_m(OR)_{n-m}]$ (where X is H, halogen, $NH_2$, OH, OR′, or R′) are known for almost every element in the Periodic System. Table 8 gives brief information about them.

These complex alkoxides crystallise readily and are much less reactive than their components. The most stable of them even shows some stability towards water and does not react with methyl iodide; in their alcoholic solutions the inversion of methone does not take place — in other words, the most characteristic reactions of the alkali metal alkoxides do not occur[226,230]. Meerwein notes that the instability constant of the complex anion depends on the nature of the alkoxy-group to an even greater extent than on the central atom. As might be expected, under strictly equal conditions it decreases as the "acidity" of the alcohol increases; therefore maximum stability is shown by the compounds of the polyhydric alcohols and phenols; these are usually inner complexes which do not even decompose in aqueous solutions.

Just as in some respects the alkoxides behave like the hydrides of the corresponding metals (tendency to solvation, polymerisation, extreme sensitivity to moisture, oxygen, $CO_2$, etc.), their "alkoxy-salts" show in several properties a similarity with double hydrides (by the alcoholysis of which they can readily be obtained). A consideration of the physicochemical properties of the complex alkoxides enables them to be classified roughly (by analogy with the double hydrides) into molecular and saltlike. It is interesting that the nature of the metal–complex anion bonds in the $M[EX_n]$ molecules which contain atoms of the same elements obviously do not change significantly on going from hydrides to alkoxides. The considerable difference in the polarity of the E–O and M–O bonds in the components leads to the formation of saltlike complex alkoxides, characteristic representatives of which are the alkali and alkaline earth metal methoxyborates. These compounds (like the corresponding hydroborates[68]) are insoluble in non-polar organic solvents but their alcoholic solutions exhibit considerable electrical conductivity; their thermal decomposition takes place at high temperatures and is accompanied by the detachment of $B(OR)_3$. Meanwhile $M[B(OC_2H_5)_4]_2$ (where M is an alkaline earth metal) are soluble in (as well as alcohols) tetrahydrofuran, benzene, cyclohexane, and ether, their solubility falling in this order of the solvents[69]. At the same time, $Mg[Al(OC_2H_5)_4]_2$ or the recently described $Li[AlH(OBu^t)_3]$ and $Ca[U(OC_2H_5)_6]_2$ are readily soluble in ethers and hydrocarbons and distil without decomposition — the b.p. of $Mg[Al(OC_2H_5)_4]_2$ is 235–237°/1 mmHg,[238] and the sublimation temperatures of $Li[AlH(OBu^t)_3]$ is 280°/1 mmHg,[237,242] and of $Ca[U(OC_2H_5)_6]_2$ 200°/0.01 mmHg.[255]

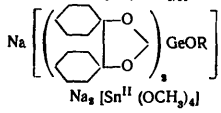
Hence their molecules, by analogy, for example, with $Al[BH_4]_3$, appear entirely covalent and it can be assumed that there is something in common between the molecular structures of "alkoxy-salts" and the corresponding double hydrides. In connection with this, there is the interesting question of the nature of the reaction of barium and titanium methoxides. According to the patent literature[259], on boiling an alcoholic solution of these alkoxides $Ba_2TiO_4$ is precipitated, and this can be explained only by the instability of the double methoxide which is probably formed in the first stage.

In the last 15–20 years interest in the complex alkoxides has grown considerably, in connection with their possible use as efficient catalysts. Thus, the "amphoteric" nature of $Mg[Al(OR)_4]_2$ determines the peculiar catalytic action of this alkoxy-salt[260]. The "strong base" $Mg(OR)_2$ present in the molecule brings about the aldol condensation, but the "acid" $Al(OR)_3$ leads to the Tishchenko reaction between the hydroxyaldehyde formed in the first stage and a molecule of the original aldehyde (to a glycol ester)[261]:

$$RCH_2CHO + CH_2CHO \longrightarrow \underset{\displaystyle R}{RCH_2CH}\!-\!\underset{\displaystyle OH}{CH}\!-\!\underset{\displaystyle R}{CHO} \xrightarrow{+RCH_2CHO} \xrightarrow{+RCH_2CHO} RCH_2COOCH_2\!-\!\underset{\displaystyle R}{CH}\!-\!\underset{\displaystyle OH}{CH}\!-\!CH_2R.$$

Hydroalkoxy-complexes — for example, $Li[AlH(OBu^t)_3]$ — are valuable reductants. They differ from $LiAlH_4$ by

TABLE 8. The complex alkoxides $M[E(OR)_n]$

| Formula | M | R | References |
|---|---|---|---|
| $K[Li(iso\text{-}OC_3H_7)_2]$ | — | — | 226 |
| $K_2[Be(OC_2H_5)_4]$ * | — | — | 226 |
| $Na_2[Mg(OR)_4]$ | — | $C_2H_5$, n-$C_3H_7$ | 81, 226 |
| $K_2[Ca(OCH_2C_6H_5)_4]$ | — | — | 226 |
| $MH[Zn(OR)_4]$ | Na, K | $CH_3$, $C_2H_5$ | 226 |
| $M^I[B(OR)_4]$ | Li, Na, K, Rb, Cs, $Tl^I$ | $CH_3$, $C_2H_5$, n-$C_3H_7$ n-, iso-, t-$C_4H_9$, $C_6H_5CH_2$— | 225, 227—229 |
| $M^{II}[B(OR)_4]_2$ | Mg, Ca, Sr, Ba, Zn | $CH_3$, $C_2H_5$ | 89, 225, 229, 230 |
| $Na[BH_{4-n}(OR)_n]$ | — | $CH_3$, $C_2H_5$, $C_3H_7$ (iso-, t-) | 231—233 |
| $M[BF_3(OCH_3)]_n$ | Na, K, Hg | — | 233, 234 |
| $M[B(OR)_3R']$ | Li, Na | $CH_3$, $C_2H_5$; (R'=$C_2H_5$, $C_4H_9$) | 230, 235 |
| $K[B(NH_2)(OCH_3)_3]$ | — | — | 236 |
| $M[Al(OR)_4]$ | Li, Na, K, Tl | $CH_3$, $C_2H_5$, n-, iso-$C_3H_7$, n-, t-$C_4H_9$ iso-$C_5H_{11}$, $C_6H_{11}$, $C_6H_5CH_2$ | 226, 227 |
| $M[Al(OR)_4]_2$ | Mg, Ca, $Cu^{II}$, Ni, Co | $C_2H_5$, n-$C_3H_7$, n-$C_4H_9$ | 226, 238 |
| $Mg_2[Al(OC_2H_5)_6]_2$ | — | — | 239 |
| $M[AlH_{4-n}(OR)_n]$ | Li, Na, $[(C_6H_5)_3Sn]$ $[(C_6H_{11})_3Sn]$ | $C_2H_5$, t-$C_4H_9$ | 237, 240—242 |
| $Na[Al(OR)(OC_2H_5)_3]$ | — | — | 226 |
| $K[Al(NH_2)(OC_2H_5)_3]$ | — | — | 236 |
| $M[Al(OR)_x R'_{4-x}]_n$ | Na, K, Ca, Sr, Ba | $C_2H_5$, $C_4H_9$ (n-, s-) (R'=$CH_3$, $C_2H_5$ etc.) | 225, 243, 244 |
| $M[AlH_2(OR)(C_2H_5)]_n$ | Na, Ca | $C_2H_5$, $C_4H_9$, $C_6H_5$ ... | 245 |
| $K[Si(OCH_3)_5]$ | — | — | 246 |
|  | — | $CH_3$, $C_2H_5$ | 247 |
| $Na_2[Sn^{II}(OCH_3)_4]$ | — | — | 246 |
| $Na[Sn_2(OC_2H_5)_5]$ (?) | — | — | 226, 249, 250 |
| $M_2[Sn(OC_2H_5)_6]$ (?) | (NaH), K, $Sn^{II}$ | — | 226, 250, 251 |
| $KH_3[Ti(OC_4H_9)_6]_2$ | — | — | 226 |
| $K_2[Ti(NH_2)_2(OCH_3)_4]$ | — | — | 226 |
| $M[Zr_2(OR)_9]$ | Li, Na, K, Tl, $(C_2H_5)_4N$— | $C_2H_5$, $C_3H_7$ (n-, iso-), $C_4H_9$ (n-, s-) | 252 |
| $Na[Sb^{III}(OR)_4]$ | — | $CH_3$, $C_2H_5$ | 226 |
| $Na[Sb^{V}(OC_2H_5)_6]$ | — | — | 226 |
| $Na[Sb^{V}Cl(OC_2H_5)_5]$ | — | — | 226 |
| $K_n[Cr_2(NH)(NH_2)_4(OC_6H_{11})]_n$ | — | — | 253 |
| $NaH[Se^{IV}(OC_2H_5)_6]$ | — | — | 226 |
| $M[Se^{IV}O_3(OCH_3)]$ | K, $NH_4$ | — | 254 |
| $NaH[Te^{IV}(OR)_6]$ | — | $CH_3$, $C_2H_5$ | 226 |
| $Ca[U^{IV}(OC_2H_5)_6]_2$ | — | — | 255 |
| $M[Fe^{III}(OC_2H_5)_4]$ | Li, Na, K, Tl | — | 226 |
| $Na_m[Fe^{III}(OCH_3)_n]$ | $m$=2—4, $n$=5—7 | — | 98 |
| $BaH[Fe(OCH_3)_4]_2$ | — | — | 98 |
| $Na[Fe(OR)(CO)_5]$ ** | — | $CH_3$, $C_2H_5$ | 256 |
| $K_2[Os^{VI}O_2(OCH_3)_4]$ | — | — | 257 |

* According to our observations[258], this compound could not be prepared, either under the conditions described by Meerwein[226] or on reaction of the two alkoxides.

** This is the probable formula, judging from the properties of the complex carbonyl described by Feigl and Krumholz[256].

their gentler and more selective reducing action for certain classes of organic compounds and also for metal halides [242,262].

A second, much wider field of use of alkoxyborates is connected with the synthesis of hydroborates, for example:

$$M[B(OCH_3)_4] \text{ or } Na[BH(OCH_3)_3] + B_2H_6 \longrightarrow M[BH_4] + B(OCH_3)_3$$

M = Li, Na, K, Mg, Ca, Sr, Ba, [60,68,69,263]

$$Na[BH(OCH_3)_3] \xrightarrow[\text{(diglyme)}]{} NaBH_4 + \downarrow Na[B(OCH_3)_4]^{263}.$$

A much less studied class of complex alkoxides comprises the products of addition to inorganic halides. At present such compounds (given the formula X–M–OR) are known only for magnesium among the group of elements covered by this review (see p. 165). By common crystallisation of alcoholic solutions of $MgCl_2$ and $Mg(OC_2H_5)_2$, Meerwein and Schmidt [29] separated a 1 : 1 addition product, which could be recrystallised with partial decomposition from boiling alcohol. On carrying out the reaction with magnesium methoxide under similar conditions, Quinet [264] obtained the crystalline complex $3Mg(OCH_3)_2.MgCl_2.11CH_3OH$, which easily loses its alcohol of crystallisation.

Tolstopyatov and coworkers [104], in a detailed investigation of the alcoholysis of the alkylmagnesium halides, proposed a convenient method for isolating crystalline ROMgI: precipitation as a complex with benzophenone or benzaldehyde. It was shown simultaneously that the higher alcohols (starting with n-propanol) do not form stable magnesium alkoxides. The equilibrium of the symmetrisation: $ROMgX \rightleftharpoons Mg(OR)_2 + MgX_2$, which the authors [104,265] think exists in ether solutions is easily shifted to the right by the precipitation of $MgI_2.3(C_6H_5)_2CO$ (which is insoluble in ether). The scanty data [266,267] suggest that the crystalline magnesium bromide alkoxides (obtained on the alcoholysis of RMgBr) are considerably less soluble in ether than the iodides, and are less reactive.

In further investigations of this theoretically interesting class of compounds it is proposed, apparently, first to solve the problem of the identity of the halide alkoxides obtained by different paths: (1) the addition, $MgX_2 + Mg(OR)_2$; (2) alcoholysis of a Grignard reagent — it has recently become known that the nearest analogues of ROMgX (the alkylmagnesium halides) are different from the molecular compounds of the type $MgX_2.MgR_2.x(C_2H_5)_2O$, synthesised in the reaction of ethereal solutions of $MgX_2$ and $MgR_2$. [268]

(b) Reactions with the anhydrides of inorganic acids. The reactions of alkoxides with $SO_2$, $CO_2$, $CS_2$, and other anhydrides of inorganic acids are accompanied by addition of the metal and alkoxy-group at a double bond of the anhydride to form salts of alkyl hydrogen sulphites [7,10,191,269], alkyl hydrogen carbonates, [8,191,270–272] and alkyl hydrogen monothiocarbonates [5], thus:

$$MOR + E\begin{matrix}X\\X\end{matrix} \longrightarrow X=E\begin{matrix}M\P\\OR\end{matrix},$$

where E = S or C; X = O or S; and M = Na, K, ½Mg, or ½Ba.

¶ Presumably the authors intended to write the scheme:

$$MOR + E\begin{matrix}X\\X\end{matrix} \rightarrow RO-E\begin{matrix}X^-\\X\end{matrix}\ M^+$$

for $SO_2$ and $CO_2$ at least; however, this would give an xanthate with $CS_2$ (Ed. of Translation).

The reaction of alkali metal alkoxides with carbon monoxide is more complex and the composition of the products is greatly dependent on the temperature and pressure [7]. The reaction of CO with alcohols in the presence of solid NaOR is now used for making formate esters [160,273], or (under different conditions) for the synthesis of salts of the higher carboxylic acids by lengthening of the hydrocarbon chain [5]. In inorganic preparations sodium alkoxides are sometimes used as mild reagents for binding CO molecules. Thus, in the reaction of pentacarbonyliron with NaOR in alcohol solution tris(tetracarbonyliron) $[Fe(CO)_4]_3$ was obtained [274]. The information about the products of the reaction between the alkali metal alkoxides and $S_2O_3$ is contradictory [275].

## 2. Substitution Reactions

(a) Interaction with acids — reaction analogous to neutralisation:

$$MOR + HX \underset{(ROH)}{\rightleftharpoons} MX + ROH. \quad (1)$$

The use of this reaction (usually brought about in alcohol solutions) for preparative purposes has a series of advantages in comparison with the neutralisation of the corresponding bases in aqueous solution. Firstly, the greater volatility of alcohols, and also the lower solubility of the salts formed ensure that equilibrium (1) is displaced to the right. Secondly, under the conditions described anhydrous salts are formed (in the case of fatty acids, soaps) [5].

Of the reactions of alkoxides with inorganic acids, those with hydrogen sulphide which lead to the formation of sulphides or hydrogen sulphides of Li, [62] Na, [276] K, [114] Tl, [85] Ca [194] have been studied most:

$$MOR + H_2S \rightleftharpoons MHS \xrightarrow[(ROH)]{t^\circ} M_2S\downarrow.$$

This reaction is the most convenient method for preparing alkali metal hydrogen sulphides (their salting out from alcohol solutions is effected with ether or benzene [114]).

It is interesting to note that solutions of $H_2S$ in aromatic hydrocarbons or $CHCl_3$ (unlike aqueous solutions) are titrated by alkoxides, despite the almost complete absence of electrical conductivity. This fact served at the time as one of the first proofs of the unsuitability of the Arrhenius "aqueous" theory of acids and bases [260].

Here it is pertinent to refer to the reaction of disubstituted potassium glycerolate with silicic acid — in the form of amorphous silica or the hydrolysis products of $Si(OR)_4$. According to Toropov [204] and Kreshkov [277] this reaction enables calcium silicates soluble in glycerol to be obtained in quantitative yield.

(b) Reaction with water. Products of partial hydrolysis of the alkoxides of Group II metals. Whereas the alkali metal alkoxides with even traces of water undergo hydrolysis in accordance with the equation: $MOR + H_2O \rightleftharpoons MOH + ROH$, the alkoxy-derivatives of bivalent metals (alkaline earth elements and Mg) form intermediate products, hydroxide alkoxides of the type M(OH)(OR) (see also p. 165). In most of the old work on the alkaline earth alkoxides compounds are described (obviously of individual composition) which crystallise from alcohol solutions in those cases where the alkoxides undergo partial hydrolysis or reaction with the corresponding

metal oxide or hydroxide. Even Dumas and Berthelot, and then Forcrand[278] considered them to be oxides with alcohol of crystallisation, MO.$n$ROH. Szarwasy[191] succeeded in isolating the normal basic magnesium methoxides by using the fall in solubility of $Mg(OCH_3)_2$ on raising the temperature (on boiling the alcohol solution, pure magnesium methoxide is precipitated). Szarwasy proposed the formula $Mg(OH)(OCH_3)$ for the partial hydrolysis product on the principle that this compound had considerable thermal stability, with no loss of alcohol on heating (as would have occurred for ROH of crystallisation). Berner[97], as already noted, isolated analogous compounds of Ca and Sr (which in alcoholic solution exist in equilibrium with the normal methoxide and oxide) and showed their individuality by X-ray analysis. Scholder and Kreutz[98] made a systematic investigation of the solid phases existing in equilibrium with solutions of BaO in methanol. Forcrand's results[279] on the overall composition of the compounds formed were confirmed, but from the information on the decomposition of the compounds in a high vacuum at 20° the authors proposed different structural formulae (Table 9). From the results of work[98] on the solubility of various hydrolysis products of $Ba(OCH_3)_2$ in methanol, we attempted to construct an approximate equilibrium diagram for the $Ba(OCH_3)_2 + H_2O \rightleftharpoons CH_3OH + Ba(OH)_2$ reciprocal system (by Jänecke's method). As Fig. 3 shows there are four solid phases in this system at 20°; one of the hydrolysis products is the barium hydroxide alkoxide and the other is a solvate of $Ba(OH)_2$ with the alcohol.

Table 9 lists the compounds of this type mentioned in the literature; we assume that hydroxide alkoxides analogous in composition and method of preparation to the barium compounds[98] possess the same structure.

(c) Reactions with alcohols. These have received detailed consideration above (p. 165). The exchange reactions of alkoxides with β-dicarbonyl or β-hydroxycarbonyl compounds (which obviously react in an enol form) are of definite preparative interest. The products — the β-diketone derivatives of the alkali and alkaline earth metals, Mg and $Tl^I$ — are inner complexes and are therefore not considered in this review. However, it must be noted that there is an important difference between the derivatives of these metals. Whereas all the derivatives of acetoacetic ester (except that of Li) are readily soluble in benzene, resist the action of water, have low melting points, and volatilise easily (that is, they are typical chelates), the analogous Li or sodium compounds of alkylmalonic esters are insoluble in hydrocarbons, decompose without melting, and do not sublime[281]. Hence despite their formal analogy with typical chelates, the latter resemble more closely the alkoxides, a fact which is probably linked with the more polar nature of their molecules and the lower stability of the rings formed.

TABLE 9. Magnesium and alkaline earth metal hydroxide alkoxides.

| ROH | Mg | Ca | Sr | Ba |
|---|---|---|---|---|
| $CH_3OH$ | Mg(OR)(OH)[191] | Ca(OR)(OH)[97] | Sr(OR)(OH)[97] | Ba(OR)(OH)·ROH<br>Ba(OR)(OH)·0.33ROH<br>$Ba(OH)_2 \cdot 2ROH \cdot H_2O$[98,197,279] |
| $C_2H_5OH$ | | Ca(OR)(OH)·0.33ROH[197,198,280]<br>Ca(OR)(OH)[272] | | Ba(OR)(OH)·0.33ROH[197,279] |

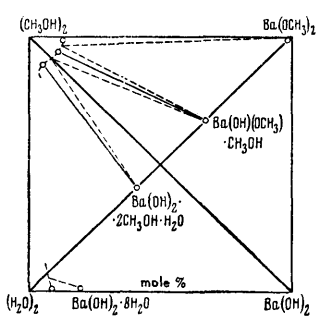



Fig. 3. Approximate solubility diagram for the $Ba(OCH_3)_2$–$CH_3OH$–$H_2O$ system (20°) after Scholder and Kreutz[98].

(d) Reactions with inorganic and organic halides. These play a large part in organic synthesis, where alkoxides are used as alkoxylating agents. The reaction of alkali metal alkoxides with inorganic halides in a medium of organic solvents — or, more correctly, with solvato-acids of the type $H[EX_n(OR)_m]$ is usually the most general method of synthesis of the alkoxy-derivatives of all the elements of the Periodic System: $nMOR + EX_n \rightarrow E(OR)_n + nMX$. This reaction is ionic and, as stated above[226], in many instances titration in alcoholic solution is possible (for example, $HgCl_2$ may be titrated by sodium ethoxide against phenolphthalein)[260]. Whereas the reaction of alkoxides with alkyl halides which are used for the synthesis of ethers (Williamson reaction): $MOR + R'X \rightarrow R'OR + MX$, takes place by an entirely different mechanism (nucleophilic substitution at the carbon atom). But the most ionic Na and K phenoxides generally do not react with alkyl halides, therefore silver phenoxides are used to introduce phenoxy-groups into molecules[282].

In addition to the Na, K, and Li alkoxides, usually used as alkoxylating agents in the Williamson and Schotten–Baumann reactions[283], several authors[24,284] recommend the use of magnesium alkoxides, which sometimes give higher yields of the main reaction product. An unusual application of the Schotten–Baumann reaction appeared recently in the work of Lebl; the reaction of potassium methoxide with acetyl chloride was proposed as a method for obtaining KCl of high purity[285].

(e) Reaction with hydrides. Wiberg and Hartwimmer[69] synthesised borohydrides of the alkaline earth elements directly from alkoxides in tetrahydrofuran:

$$3M(OR)_2 + 4B_2H_6 \xrightarrow[\text{T.H.F.}]{\text{(boiling}} 3M[BH_4]_2 + 2B(OR)_3.$$

Earlier the tetrahydroborates of metals of Groups I and II were made by Schlesinger's method, starting from the corresponding alkoxyborates[69]:

$$M[B(OR)_4] + B_2H_6 \longrightarrow M[BH_4] + 4B(OR)_3.$$

Rossmanith and Macalka[286] carried out an analogous reaction with mixed tetrahydroborates–chlorides of the rare-earth elements. In a solution in tetrahydrofuran, in addition to replacement of chlorine in the molecule of the complex hydride there is replacement of one $[BH_4]$ by a methoxy-group and then also partial alcoholysis of $[BH_4]$:

$$NaOCH_3 + LnCl[BH_4]_2 \xrightarrow{-NaBH_4,\ -NaCl} Ln(OCH_3)_2[BH]_4 \longrightarrow Ln(OCH_3)_2[BH_3(OCH_3)],$$

where Ln = Gd, Dy, Y, Sm, Er, etc.

### 3. Oxidation Reactions

The alkali and alkaline earth metal alkoxides are readily oxidised by oxygen in the cold in the solid state, in solution, or as suspensions in organic solvents. The oxidation products of the derivatives of primary alcohols are mainly salts of carboxylic acids, those of secondary alcohols are ketones and metal peroxides [5,287]. In the presence of diphenylmethanol oxygen oxidises sodium and potassium t-butoxides to hydroperoxides MOOH, peroxides, or superoxides, depending upon the reaction conditions (the ratio of the components and the nature of the solvent) [287]. In alcoholic solution in the presence of catalysts (platinum black, $Fe_2O_3$, or $Co_2O_3$) sodium alkoxides are smoothly oxidised to salts of the corresponding acids [5].

The action of chlorine or bromine on NaOR forms a mixture of various oxidation and halogenation products; with $Mg(OC_2H_5)_2$ the main product is acetaldehyde [21]. The reaction of sodium alkoxides with iodine [288] is accompanied by replacement of hydrogen and splitting of the hydrocarbon chain, for example:

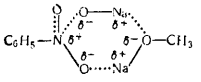
$$NaOC_2H_5+3I_2 \longrightarrow CH_2I_2+CHI_3+H_2O+NaI.$$

A detailed summary of work on the oxidation of alkoxides (mainly carried out at the end of the last century), is given in Dermer's review [7].

Aromatic nitro-compounds are reduced by alkali metal alkoxides quantitatively to azoxy-compounds [5,289]:

$$C_6H_5NO_2+CH_3ONa \longrightarrow C_6H_5-\overset{O}{\overset{|}{N}}=NC_6H_5+HCOONa+CH_2O+H_2O.$$

According to Ogata and Mibae [289], the reaction proceeds through a transition state of the type:



(and not through a quinoid structure, as was suggested earlier [290]).

Of all the compounds considered here, only the thallium(I) alkoxides act as oxidants. According to McHatton and Soulal [217], aromatic acyloins reduce TlOR to metallic thallium and are themselves quantitatively oxidised to $\alpha$-diketones:

$$Ar-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-Ar+2TlOR \longrightarrow Ar-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-Ar+2Tl+2ROH.$$

### 4. Thermal Decomposition of Alkoxides

Despite many investigations of the thermal decomposition of alkoxides, there is not yet a single opinion concerning the mechanism of this process. Tishchenko [1], on the basis of an analysis of the literature on the alkaline earth alkoxides [272] and his own studies of the thermal decomposition of $Al(OR)_3$, proposed the following general scheme for the pyrolysis of alkoxides:

$$M(OR)_n \rightarrow M_2O_n+C_nH_{2n}+ROH \quad (I)$$

$$M_2O_n+ROR \rightarrow (M_2O_n) \quad (II)$$

$$C_nH_{2n+2}+C_nH_{2n}CHO+H_2\ (III) \qquad M(OH)_n+C_nH_{2n}. \quad (IV)$$

The relative amounts of each of the reaction products depend on the decomposition temperature, the stability of the alkoxide group, and mainly on the catalytic properties of the oxide formed. In consequence, reaction (IV) proceeds quantitatively only in the decomposition of alkali and alkaline earth alkoxides (the oxides of which are capable of dehydrating ethers). Hence the primary products of the decomposition, according to Tishchenko, should be ethers or the original alcohols. Actually, when Tropsch and Philippovich [291] heated sodium methoxide to 240° in nitrogen they found dimethyl ether. The thermal decomposition of $Mg(OCH_3)_2$ [25] or of potassium tertiary fluorinated butoxides† [292] is accompanied by the formation of the corresponding alcohols.

The pyrolysis of alkali and alkaline earth metal alkoxides starts at 300–350°. On the basis of many results (given in Tables 1 and 4) it can be suggested that generally the thermal stability of the alkoxides decreases in the homologous series of the alcohols [145] and with increasing branching of the hydrocarbon radical [293]. It is difficult to draw any definite conclusions as to the influence of the metal. Zook et al. [293] gave the following series of decreasing thermal stability: Li > Na > K. An analogous series (including Cs) can also be given for ethoxides (Table 1).

Durand [140], and later Thomas [13] investigated in detail the mechanism of the thermal decomposition of MOR and $M(OR)_2$, and showed that the pyrolysis of the alkali metal methoxides follows a quite special path:

$$6MOCH_3=9H_2+2M_2CO_3+2C+M_2C_2 \quad ; \quad M_2C_2 \rightarrow 2M+2C$$

The second stage, the formation of the free metals, occurs only with K and Cs (sodium acetylide exhibits exceptional thermal stability). Kahlbaum et al. [211] observed the formation of metallic thallium in the decomposition of "thallium ethylate". In the first stage of the thermal dissociation of sodium, potassium, and caesium ethoxides and propoxides, dehydrogenation occurs, with formation of vitreous products of composition $C_nH_{2n-1}OM$, to which Thomas [13] ascribes a vinyl oxide structure: $RCH_2CH_2OM \rightarrow RCH=CHOM + H_2$. The subsequent course of the decomposition, connected with that of the vinyl oxides — and probably of poly(vinyl oxides) — is rather complex and depends on the nature of the radical and metal. For ethoxides, for example, the overall equation is:

$$3\,C_2H_5OM \longrightarrow 4H_2+4C+3MOH+C_2H_4. \ [13,145]$$

In the case of tertiary alkoxides, the gaseous reaction product is almost pure unsaturated hydrocarbon [130] — hence the decomposition proceeds quantitatively according to Eqn. (IV). It is worth noting the thermal decomposition of the "acid" alkoxides of dihydric alcohols [43,101], the first stage of which is symmetrisation by the scheme:

$$2\ \begin{matrix}CH_2OM\\|\\CH_2OH\end{matrix} \xrightarrow{t°<200°} (CH_2OM)_2+(CH_2OH)_2.$$

### 5. Catalytic Action of Alkoxides.

To conclude this review of the chemical properties of alkoxides brief reference must be made to their use as catalysts. This field of application is extremely important, since it is connected with the synthesis of many

† Such as $(CF_3)_2CMeOH$ and $CF_3CMe_2OH$ (Ed. of Translation).

dyestuffs and their intermediates, of pharmaceutical preparations (such as barbituric acid and its derivatives, vitamins B, etc.), perfumes and perfumery materials, and also a series of ketones, aldehydes, esters, and amines which find extensive use in industrial organic syntheses [5,7].

Among the reactions in which alkoxides are used as condensing agents, mention must first be made of the Guerbet reaction. In 1909 Guerbet observed that alcohols (starting with propanol) heated with sodium alkoxides in ampoules double, and sometimes treble, their molecular weight. Subsequently Thomas used potassium alkoxides in this reaction, and in the presence of CsOR was able to condense ethanol also [13]. According to Terent'ev's results [19], magnesium or calcium alkoxides can also act as catalysts for this reaction. Weissmann [13] proposed the following scheme for this reaction:

$$RCH_2CH_2\dot{O}H + H\dot{C}H(R')-CH_2OH \xrightarrow{(-H_2O)} RCH_2CH_2-CH(R')-CH_2OH.$$

In condensations of carbonyl-containing compounds — aldol and crotonaldehyde condensations with malonic or acetoacetic esters, etc. — the formal role of the alkali metal alkoxides is ascribed to dehydration action [4,5,294]. The use of various alkali metal alkoxides in the Claisen condensation is well known (for example, see Ioffe and Nesmeyanov [10], and Berkman and coworkers [294]); recently magnesium ethoxide has been used successfully by Laukkanen [295] for the cyclisation of esters of dibasic acids. It is appropriate here to mention the synthesis of barbituric acid by the condensation of malonic ester with urea using $Mg(OCH_3)_2$. [296]

In the Meerwein–Schmidt–Verley reaction alkoxides are used as reducing agents. To reduce aldehydes to primary alcohols, Meerwein and Schmidt [29] first used $Mg(OC_2H_5)_2$ and $ClMgOC_2H_5$. Simultaneously Verley [297] suggested using sodium alkoxides in this reaction, and Gomberg and Bachmann successfully employed magnesium iodide ethoxide and magnesium bromide ethoxide. The more fundamental nature of the catalysts mentioned is due to some specificity in their action compared with the $Al(OR)_3$ usually employed in this reaction [230,297].

Alkali metal alkoxides are used in the Wolff–Kishner reduction in the second stage only, the catalytic decomposition of hydrazones [294,298].

Information has also been published on the isomerising action of alkali metal alkoxides in relation to the different classes of unsaturated compounds. There is firstly isomerisation of acetylenic hydrocarbons into allenes [294], secondly migration of a triple bond [294], and finally migration of a double bond [156,299].

In the last five years there have been reports of the use of the alkoxides of metals of Groups I–III in processes for the polymerisation of epoxides [152,153,202,300], and of certain types of unsaturated compounds [161,301–304].

As well as the reactions mentioned, alkali metal alkoxides are also used as additions to catalysts. Thus the so-called "Alfin catalysts", which are mixtures of sodium isopropoxide and sodium alkenides, have been used for the polymerisation of dienes [305]. The hydrogenation of furfural diethyl acetal on nickel is much faster in the presence of sodium ethoxide [306].

Of other application of alkoxides we can note the use of NaOR as oil additions to facilitate their drying [5], and of Sr and Ba alkoxides as additives for lubricating oils [75]. Calcium methoxide is a stabiliser for vinyl resins [307], the calcium and magnesium higher alkoxides as additions to anti-knock agents to eliminate the precipitation of lead from them [308]. Vitreous films exhibiting valuable dielectric properties are formed by the heat treatment of barium or strontium alkoxides deposited on a surface by impregnation with alcoholic solutions of $M(OR)_2$. The formation of such films on the surface of fluorine-containing polymers increases their adhesive properties [309]. Thallium "ethylate" had been suggested as a heavy liquid ($d$ = 3.55) for determining the specific gravity of solids [211]. The derivatives of thallium and polyhydric alcohols (like other $Tl^I$ compounds) are used for the stripping of hair from hide [310].

## III. PHENOXIDES OF THE ALKALI AND ALKALINE EARTH METALS, MAGNESIUM, AND THALLIUM(I)

### A. METHODS OF PREPARATION

For the preparation of phenoxides it is possible in principle to use the same methods as for the preparation of alkoxides. Therefore for convenience in Table 10 the same symbols for the preparative methods (Roman numerals) are

TABLE 10. Alkali metal phenoxides.

| ArOH | Li, Na | | K, Cs |
|---|---|---|---|
| $C_6H_5OH$ | $LiOAr \cdot 2H_2O$ decomp. 450° [153], V[313,314] $LiOAr$, V[315] | $NaOAr \cdot 6ArOH$ (?) | $KOAr \cdot 3ArOH$, m.p. 114° |
| | | $NaOAr \cdot 2ArOH \cdot nH_2O$ ($n$ = 0; 3.5; 7; 8; m.p. respectively: > 100; 34.7; 19 decomp., 21°. | $KOAr \cdot 2H_2O$ |
| | | | $KOAr$, m.p. 104°; [317]; V[314,318,319,323,321]; VI[321]; IX[323] |
| | $Cr(o\text{-}C_6H_4OLi)_3 \cdot 2C_4H_8O$[316] | $NaOAr \cdot 3H_2O$; m.p. 52° | |
| | | $NaOAr \cdot NaOH \cdot 2.5H_2O$; m.p. > 100° | $CsOAr$, V[315] |
| | | $NaOAr \cdot 0.5C_4H_8O_2$ | |
| | | $NaOAr$, m.p. 60°, decomp. 450°; [17,317]; II[147]; V[318–320]; VI[321]; IX[322] | |
| $2\text{-}CH_3C_6H_4OH$ | $NaOAr \cdot 3ArOH$ | | $KOAr \cdot 3ArOH$ |
| | $NaOAr \cdot n\ ArOH \cdot 6H_2O$ ($n$=1 or 2) | | $KOAr$, V[318,319] |
| | $NaOAr \cdot H_2O$ | | |
| | $NaOAr \cdot 3NaOH \cdot 6H_2O$ | | |
| | $NaOAr$, m.p. < 0°, V[319,323]; VI[326] | | |

TABLE 10 (contd.)

| ArOH | Li, Na | K, Cs |
|---|---|---|
| 3-$CH_3C_6H_4OH$ | NaOAr, m.p. 94°, decomp. 450°; I[312]; II[47]; V[312,319]; VI[326] | KOAr·3ArOH, m.p. 88°<br>KOAr, m.p. 36°; V[312,319] |
| 4-$CH_3C_6H_4OH$ | NaOAr, m.p. 125°, decomp. 450°; I[312]; V[312,319]; VI[326] | KOAr·3ArOH, m.p. 148°<br>KOAr, m.p. 92°,<br>decomp. 420°; V[312,318,319,322] |
| 3,4-$(CH_3)_2C_6H_3OH$ | NaOAr, VI[326] | |
| 2,4-$(CH_3)_2C_6H_3OH$ | NaOAr, m.p. 43°; V[319]; VI[326] | KOAr, liquid; V[319] |
| 2,5-$(CH_3)_2C_6H_3OH$ | NaOAr, m.p. 83°; V[319]; VI[326] | KOAr, m.p. 35°; V[319] |
| 5-$CH_3$—2-(iso-$C_3H_7$)$C_6H_3OH$ | NaOAr, VI [27] | |
| 2-$CH_3$—5-(iso-$C_3H_7$)$C_6H_3OH$ | NaOAr, VI [27] | |
| α-$C_{10}H_7OH$ | NaOAr, m.p. 45°; II[47]; V[319,322]; VI[326] | KOAr·4ArOH·$5H_2O$<br>KOAr, liquid; V[319,323] |
| β-$C_{10}H_7OH$ | LiOAr, I[316]<br>NaOAr, m.p. 120°; I[320] V[319,323]; VI[326] | KOAr·2ArOH·$5H_2O$<br>KOAr, m.p. 40°<br>I[316]; V[319,323] |
| 2-$CH_3OC_6H_4OH$ | 2NaOAr·5ArOH·$2H_2O$, m.p. 139°<br>NaOAr·5ArOH, m.p. 172°<br>NaOAr, m.p.. 120°; V[319,323]; VI[327] | KOAr·3ArOH<br>KOAr·ArOH·$1.5H_2O$, m.p. 188°<br>KOAr, m.p. 168°;<br>V[319,323,330] |
| 2-$CH_3O$—4-($CH_2CH{=}CH_2$)$C_6H_3OH$ | NaOAr, m.p. 115°; V[319] | KOAr, m.p. 128°; V[319] |
| 2-$ClC_6H_4OH$ | NaOAr, I[331] | |
| 3-$ClC_6H_4OH$ | NaOAr, I[331] | |
| 2-Cl—6—$CH_3OC_6H_3OH$ | | KOAr·ArOH, m.p. 146°<br>KOAr, m.p. 160°; V[323] |
| 4-$ClC_6H_4OH$ | NaOAr; I[331] | KOAr·2ArOH; V[332] |
| 3-$CH_3$—4—$ClC_6H_3OH$ | 2NaOAr·ArOH;<br>NaOAr, V[332] | KOAr·2ArOH;<br>KOAr·ArOH, V[332] |
| 4-$BrC_6H_4OH$ | | KOAr·2ArOH, V[332] |
| 2,4-$Cl_2C_6H_3OH$ | | KOAr, decomp. 70—80°; V[332] |
| 2,4,6-$Cl_3C_6H_2OH$ | NaOAr·$H_2O$<br>NaOAr, decomp. 220°; V[283] | |
| 2,4,6-$Br_3C_6H_2OH$ | | KOAr·2ArOH<br>KOAr, V[332,333] |
| 2,4,6-$I_3C_6H_2OH$ | | KOAr·$2C_2H_5OH$<br>KOAr, decomp. 90°;<br>α ~ 5 (in $CHBr_3$); V[283] |
| 2,3,4,6-$Cl_4C_6HOH$ | NaOAr, m.p.. 370°; V[334] | |
| 4-$CH_3O$—2,3,5,6-$Br_4C_6OH$ | NaOAr, V[332] | KOAr·$H_2O$, V[332] |
| $Cl_5C_6OH$ | LiOAr·$H_2O$ V[335]<br>NaOAr·$H_2O$; V[334,335]<br>NaOAr, m.p. 373° | KOAr·$H_2O$ V[335]<br>CsOAr·ArOH V[330] |
| $Br_5C_6OH$ | NaOAr; V[336] | |
| $C_6H_4(OH)_2$-1,2 | 2NaOAr (OH)·Ar $(OH)_2$·$6H_2O$<br>NaOAr (OH)·Ar $(OH)_2$<br>$(NaO)_2$Ar; V[323,337]; VI[326] | KOAr (OH)·Ar $(OH)_2$·$2H_2O$<br>KOAr (OH)·Ar $(OH)_2$·$0.5H_2O$<br>V[323,337,330] |
| $C_6H_4(OH)_2$-1,3 | NaOAr (OH)<br>$(NaO)_2$ Ar, V[326]; VI[326]; IX[324] | KOAr (OH)·$2H_2O$, IX[323]<br>KOAr (OH)<br>$(KO)_2$Ar·$4H_2O$, V[314]; VI[329] |
| $C_6H_4$ $(OH)_2$-1,4 | NaOAr (OH)·4ArOH<br>NaOAr (OH)<br>$(NaO)_2$Ar, V[323]; VI[326] | KOAr (OH)·7Ar $(OH)_2$,<br>V[323] |
| $C_6H_3$ $(OH)_3$-1,2,3 | NaOAr $(OH)_2$<br>$(NaO)_2$ Ar (OH)<br>$(NaO)_2$ Ar, VI[340] | |
| | 2-$NaOC_6H_3$—$C_6H_3OH$-2', V[330]<br>4,4'—$Cl_2$ $(C_6H_3)_2CH_2$ (OH) (ONa)-2,2', V[330] | |

used as in Tables 1, 4, and 5. The data in Table 10 show that phenoxides are most frequently obtained by the reaction of metal hydroxides with phenols in alcohol, benzene, or aqueous solutions or in the melt (method V). The use of this method in a particular case (unlike alkoxides) is almost without limitation owing to the considerable resistance of phenoxides to the action of water, already referred to.

A special method which can be used only for preparing phenoxides (method IX) consists in fusing aromatic sulphonic acids with alkalis. It is well known that in industry this important method is usually used indirectly for the preparation of phenols. Analogous conversions (usually with formation of disubstituted resorcinolates) also occur under specified conditions with isomeric chlorophenols or benzenedisulphonic acids.

## B. PROPERTIES OF PHENOXIDES

The phenoxides (with the exception of $LiOC_6H_5$), because of their saltlike nature, are insoluble in organic solvents and even in absolute ethanol (they dissolve only on addition of water). However, they are readily soluble in water and the solutions exhibit a strongly alkaline reaction. The dissociation constant of $C_6H_5OH$ ($10^{-10}$) is six orders of magnitude greater than that of water, therefore the equilibrium for the hydrolysis of alkali metal phenoxides is completely shifted to the right only on prolonged heating. However, potassium phenoxide, according to Selivanov's results [311] hydrolyses rather more readily: for example, $Ca(OH)_2$ is formed by the action of benzene or ether on its hydrate, $Ca(OC_6H_5)_2.2H_2O$. Obviously, in this case the hydrolytic equilibrium is displaced to the right by extraction of phenol into the organic phase. In general, naphtholates ($K_{diss}$ of naphthols is $10^{-4}$–$10^{-5}$) do not undergo hydrolytic decomposition.

In contrast with alkyloxides, unsolvated phenoxides are soluble in liquid ammonia [47], they readily crystallise and have a definite melting point, which suggests that their crystal lattice is of a molecular nature. Sodium phenoxides (except for the first member of the series) melt considerably above their potassium analogues (see Table 10). In ammoniacal solutions, phenoxides exhibit appreciable electrical conductivity [164].

According to Fischer's results [312], the pyrolysis of derivatives of $C_6H_5OH$, independently of the nature of the metal, takes place at 450–500°. Under these conditions the aromatic nucleus gives small fragments — $CH_4$, CO, $CO_2$, $H_2$, the formation of which does not enable the mechanism of the thermal decomposition and the nature of the intermediate products to be established.

In 1958 Krüger [313] observed that association is peculiar to the alkali metal phenoxides. For example, $NaOC_6H_5$ exists as dimers in a melt with magnesium sulphate (at 1 M concentration).

Phenoxides crystallise from aqueous solutions as hydrates, and in the presence of phenol as $MOAr.xArOH.yH_2O$. Mixed molecular compounds of this type were observed also in studying solubility in the reciprocal systems $M(OAr)_n$–ArOH–$H_2O$. A detailed investigation was first completed by van Meurs [314] and alkali and alkaline earth metal phenoxides and resorcinolates were dealt with. Lichtenstein and coworkers [320,325] studied the solubility polytherms in systems containing sodium phenoxide or *o*-cresyl oxide, which are of technological importance (in the process for separating phenols in treating lignites). The equilibrium diagram of the $C_6H_5ONa$–$C_6H_5OH$–$H_2O$ system [320] at 25° is shown in Fig. 4. Table 11 lists the solid phases observed in the systems mentioned above.

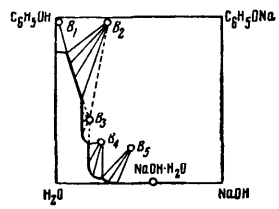



Fig. 4. Equilibrium diagram of the $C_6H_5ONa$–$C_6H_5OH$–$H_2O$ system at 25°. [320]

TABLE 11. Solid phases existing in the $M(OAr)_n$–ArOH–$H_2O$ systems.

| Phenol | Li | Na | K | Ca | Sr, Ba |
|---|---|---|---|---|---|
| $C_6H_5OH$ | ArOH<br><br>$LiOAr\cdot 2H_2O$<br><br>$LiOH\cdot H_2O$<br>25° [314] | ArOH ($B_1$)<br>$NaOAr\cdot 2ArOH$ ($B_2$)<br>$NaOAr\cdot ArOH\cdot 3,5H_2O$ ($B_3$)<br>$NaOAr\cdot 3H_2O$ ($B_4$)<br>$NaOAr\cdot NaOH\cdot 2.5H_2O$ ($B_5$)<br>$NaOAr\cdot ArOH\cdot 8H_2O$<br>$NaOAr\cdot ArOH\cdot 7H_2O$<br>0 — 50° [320] | ArOH<br>$KOAr\cdot 3ArOH$<br>$KOAr\cdot 2H_2O$<br><br>$KOH\cdot 2H_2O$<br>25° [314] | ArOH<br>$Ca(OAr)_2\cdot 3\cdot H_2O$<br><br>$Ca(OH)_2$<br>25° [314] | ArOH<br>$M(OAr)_2.4H_2O$<br><br>$M(OH)_2.8H_2O$<br>25° [314] |
| *o*-$CH_3C_6H_4OH$ | | ArOH<br>$NaOAr\cdot 3ArOH$<br>$NaOAr\cdot H_2O$<br>$NaOAr\cdot 3NaOH\cdot 6H_2O$<br>$NaOAr\cdot ArOH\cdot 6H_2O$<br>$NaOAr\cdot 2ArOH\cdot 6H_2O$<br>$NaOH\cdot H_2O$<br>$NaOH\cdot 4H_2O$<br>0 — 50° [325] | | | |
| *p*-$C_6H_4(OH)_2$ | | | $Ar(OH)_2$<br>$KOArOH\cdot 2H_2O$<br>$KOArOH\cdot 4H_2O$<br>30° [314] | | $Ar(OH)_2$<br>$Ba(ArO)_2\cdot 2H_2O$ *<br>$Ba(OH)_2\cdot 8H_2O$<br>30° [314] |

* This compound should obviously be given the formula $Ba(OArOH)_2.Ba(OH)_2$.

TABLE 12. Magnesium and alkaline earth metal phenoxides.

| ArOH | Mg.Ca | Sr, Ba |
|---|---|---|
| $C_6H_5OH$ | $Ca(OAr)_2 \cdot nArOH \cdot 2 \cdot H_2O$ ($n = 2,4$, etc.)<br>$Ca(OAr)_2 \cdot 5.5H_2O$ ($< 0°$)<br>$Ca(OAr)_2 \cdot 3H_2O$<br>$Ca(OAr)_2 \cdot 2H_2O$ (?), decomp. 105°<br>$Ca(OAr)_2$; V[311, 312, 314] | $Sr(OAr)_2 \cdot 4H_2O$ V[314]<br>$Ba(OAr)_2 \cdot 4H_2O$<br>$Ba(OAr)_2$, decomp. 450°; V[314] |
| α-$C_{10}H_7OH$ | $Ca(OAr)_2$, [346] | |
| β-$C_{10}H_7OH$ | $BrMgOAr \cdot (C_2H_5)_2O$, III [218]; $Ca(OAr)_2$ [346] | |
| $C_6H_4(OH)_2$-1,2 | $Ca[OAr/OH/]_2$, V[347] | $Ba[OAr(OH)]_2$, V[348]<br>$BaO_2Ar \cdot 3.5H_2O$, decomp. 240°<br>$BaO_2Ar$, V[349] |
| $C_6H_4(OH)_2$-1,3 | | $BaO_2Ar \cdot 2H_2O$, V[314, 349] |
| $C_6H_4(OH)_2$-1,4 | | $BaO_2Ar \cdot xH_2O$, V[349] |
| 3-CHO—$C_6H_3(OH)_2$-1,2 | | $BaO_2Ar \cdot 4H_2O$, decomp. 105°<br>$BaO_2Ar \cdot 2H_2O$, decomp. 170°, V[348] |
| 4-CHO—$C_6H_3(OH)_2$-1,2 | | $Ba[OAr/OH/]_2 \cdot 3H_2O$, $BaO_2Ar \cdot 4H_2O$, decomp. 120°<br>$BaO_2Ar \cdot 2H_2O$, decomp. 160°, V[348] |
| 2,4,6-$Br_3C_6H_2OH$ | $Ca(OAr)_2$, [50] | |
| $Cl_5C_6OH$ | $Mg(OAr)_2 \cdot 10H_2O$ IV[335] $Ca(OAr)_2$ IV[335] | $Sr(OAr)_2 \cdot 2H_2O$ IV[335] $Ba(OAr)_2 \cdot 2H_2O$ IV[335] |

As is evident from the data in Table 11, the formation of molecular compounds with phenols is characteristic only for sodium and potassium phenoxides. The lithium and alkaline earth phenoxides only form hydrates, whose solubility in water falls in the sequences: K > Na > Li; Sr > Ba > Ca. [314]

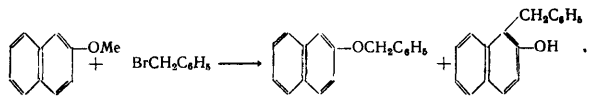
The "crystal phenolates", $MOAr.nArOH$, are readily soluble in water, alcohol, acetone, and can be recrystallised from hot benzene. They all crystallise well and melt without decomposition.

The problem of the structure of the phenoxide hydrates is interesting. For a long time they, like the products of the partial hydrolysis of alkoxides, were considered to be molecular compounds of hydroxides with phenols [311]. However, Forcrand [341] showed that on careful dehydration of these compounds anhydrous phenoxides could be obtained (and not hydroxides, which are formed in those cases when hydrolysis is carried to the limit).

In comparison with alkoxides, there have been many fewer investigations of the reactions of phenoxides; we will note only the most important of them. The action of $CO_2$ at room temperature on dry sodium phenoxide forms the sodium salt of phenylcarbonic acid (by analogy with alkoxides), and on further heating it isomerises into sodium salicylate [342]. This reaction forms the basis of industrial methods of preparing aromatic hydroxy-acids (Kolbe and Schmidt). In alcoholic solution, evidently a mixture of two acids is formed as a result of partial substitution: phenyl- and ethyl-carbonic [342]. In aqueous solution, according to Meyer [323], the decomposition of phenoxides by carbonic acid sometimes does not go to completion (although $K_{diss}$ of phenol is six orders of magnitude below the first $K_{diss}$ of $H_2CO_3$) owing to the formation of stable "acid phenoxides" (MOAr.ArOH) between unreacted phenoxide and the phenol liberated in the reaction. The equilibrium constant of the reaction: $NaOC_6H_5 + H_2CO_3 \rightleftharpoons C_6H_5OH + NaHCO_3$ is 1.05 at 20°. [343] Wesseley and coworkers [315] found that in the Kolbe reaction of lithium and potassium phenoxides lead mainly to the synthesis of salicylic acid but the potassium and caesium phenoxides to the formation of the *p*-hydroxy--acids.

Sulphur dioxide forms with phenoxides (unlike alkoxides) salts of the phenylsulphinic acid $MSO_2OC_6H_5$ (and not of phenylsulphurous acid) [344].

The reaction of phenoxides with halogen-substituted hydrocarbons, leads, by analogy with other Williamson syntheses, to the formation of ethers. However, owing to conjugation in the system Me–O–C=C–, phenoxides are here characterised by a dual reactivity, due to the formation of not only *O*-derivatives, but also *C*-derivatives. Thus the reaction of 2-naphthyl oxides with benzyl bromide leads according to Zagorevskii's results [218], depending on the nature of the metal, to different proportions of the products of alkoxylation and alkylation:




The maximum yield of esters is reached with silver or tetramethylammonium phenoxide.

The metallation of sodium and potassium phenoxides (by *n*-pentylsodium) leads to the replacement of one or two atoms of hydrogen in the nucleus, which in the case of $NaOC_6H_5$ results in *ortho*-substitution whereas the –OK group proved to be more strongly *meta*-orientating [345].

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# CHEMISTRY OF UNSTABLE OXYGEN--CONTAINING RADICALS

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## INTRODUCTION

In recent years there has been particular interest in unstable free radicals having an unpaired electron on an oxygen atom. A recent review[1] described the production, thermochemistry, and reactions of a large group of alkoxy--radicals, but the four years since its publication have seen a considerable increase of work on these radicals, and this has persuaded us to write the present article.

We shall consider the gas- and liquid-phase reactions most typical of RO· radicals, but not those of stable oxygen-containing radicals such as the substituted phenoxy--radicals, nor heterogeneous reactions involving hydroperoxides.

## REACTIONS OF RO· RADICALS

Oxygen-containing radicals with an unpaired electron on the oxygen atom are produced as unstable intermediates in many chemical processes. We indicate below only the main ones; a detailed list was given in the above review[1].

RO· radicals are produced in the light- and heat-induced decomposition of alkyl and aralkyl

nitrites: $RONO \rightarrow RO\cdot + NO$,

nitrates: $RONO_2 \rightarrow RO\cdot + NO_2$,

hyponitrites: $RONNOR \rightarrow 2RO\cdot + N_2$,

hypochlorites: $ROCl \rightarrow RO\cdot + Cl$,

and peroxides: $ROOR \rightarrow 2RO\cdot$,

and in the decomposition, in solution, of dialkyl and diaralkyl peroxodicarbonates:

$$ROCOOCOR \rightarrow 2ROCO\cdot \rightarrow 2RO\cdot + 2CO_2,$$

dialkyl diperoxocarbonates:

$$ROOCOOR \rightarrow ROOCO\cdot + RO\cdot \rightarrow ROO\cdot + CO_2 + RO,$$

and dialkyl monoperoxocarbonates:

$$ROCOOR \rightarrow ROC\cdot + RO\cdot.$$

The formation of RO· radicals in the photolysis of organic esters and ethers has been described.

The RO· radicals are usually identified by indirect kinetic and analytical methods. Direct mass-spectrometric determination of free RO· radicals has been described only for the phenoxy-radicals produced in the pyrolysis of anisole[2] and the methoxy-radicals produced in the decomposition of methanol and dimethyl ether light-sensitised by mercury[3]. The RO· radicals produced by thermal or photo-decomposition undergo various reactions, the main ones being decomposition, hydrogen abstraction, and disproportionation, depending on the structure of the radicals and the chemical and physical properties of the medium. Moreover, the RO· radicals may isomerise or react with other active particles or radicals present, or with compounds containing double bonds.

Below we list the main reactions of RO· radicals in the gaseous and liquid phases. Since liquid-phase reactions have attracted most attention in recent years, we shall give them more attention here also.

1. Decomposition of RO· radicals. Alkoxy--radicals can decompose by two reactions: with the elimination of a hydrogen atom:

$$RCH_2O\cdot \rightarrow H\cdot + RC\!\!<\!\!\begin{matrix}O\\H\end{matrix},$$

or the alkyl radical:

$$RCH_2O\cdot \rightarrow R\cdot + CH_2O.$$

Of these two the second is more favourable thermodynamically[4] (see Table 1), and experimental observations support this.

The decomposition of methoxy-radicals has been observed in the photolysis of methyl nitrate[6]:

$$CH_3O\cdot \rightarrow CH_2O + H\cdot,$$

and decomposition of ethoxy-radicals at a carbon–hydrogen bond in the pyrolysis[7] and photolysis[8] of ethyl nitrate.

TABLE 1. Enthalpy required for decomposition of radicals.

| Radical | Required enthalpy, kcal mole$^{-1}$ | |
|---|---|---|
| | for elimination of an H-atom | for elimination of an R-radical |
| $CH_3O^{\cdot}$ | 25 | — |
| $C_2H_5O^{\cdot}$ | 21 | 13 |
| n-$C_3H_7O^{\cdot}$ | 19 | 11 |
| n-$C_4H_9O^{\cdot}$ | 23 | 11 |
| $(CH_3)_2CHO^{\cdot}$ | 18 | 6.4 |
| cyclo-$C_6H_{11}O^{\cdot}$ | 16 | 1.1 * (ring opening) |

* A different value has more recently been given[5].

Decomposition of the ethoxy-radical at the carbon–carbon bond with formation of formaldehyde and a methyl radical is much more frequently met with, for example, in the pyrolysis of ethyl nitrite[9,10] or nitrate[11,12]:

$$C_2H_5ONO \rightarrow C_2H_5O^{\cdot} + NO,$$
$$C_2H_5O^{\cdot} \rightarrow CH_3^{\cdot} + CH_2O.$$

Ethane and methane have been found in the decomposition of diethyl peroxide[13–15], ethyl hydroperoxide[14], and ethyl t-butyl peroxide[16], showing that the ethoxy-radicals decompose with the formation of methyl radicals.

The n-propoxy-radicals obtained from di-n-propyl peroxide[14], n-propyl nitrate[17], and n-propyl nitrite[10,18] decompose in this way:

$$CH_3CH_2CH_2O^{\cdot} \rightarrow C_2H_5^{\cdot} + CH_2O.$$

The isopropoxy-radical[10,19] is less stable; even in the presence of cyclohexene, which readily loses an $\alpha$-hydrogen atom, the isopropoxy-radicals are 48% decomposed[16]:

$$\text{iso-}C_3H_7O^{\cdot} \rightarrow CH_3^{\cdot} + CH_3CHO.$$

Under the same conditions, n-butoxy-radicals are 29% decomposed with the formation of formaldehyde and n-propyl radicals:

$$CH_3CH_2CH_2CH_2O^{\cdot} \rightarrow CH_2O + CH_3CH_2CH_2^{\cdot},$$

and in the presence of cyclohexene isobutoxy-radicals are 67% decomposed by the reaction[16]:

$$(CH_3)_2CHCH_2O^{\cdot} \rightarrow (CH_3)_2CH^{\cdot} + CH_2O.$$

The decomposition products of isobutyl nitrite contained formaldehyde and 2-nitrosopropane[10,18].

The s-butoxy-radical decomposes to form acetaldehyde and the ethyl radical[10,18]:

$$CH_3CH_2CH(CH_3)O^{\cdot} \rightarrow CH_3CH_2^{\cdot} + CH_3CHO.$$

Decomposition of the t-butoxy-radical to acetone and the methyl radical has been observed in the pyrolysis of di-t-butyl peroxide[7,20–29], t-butyl nitrite[24,31,32], and t-butyl hydroperoxide[7,30]:

$$(CH_3)_3CO^{\cdot} \rightarrow CH_3^{\cdot} + CH_3COCH_3.$$

The activation energy for the decomposition of the t-butoxy-radical is 11–13 kcal mole$^{-1}$.[33–38] Other t-alkoxy-radicals decompose similarly. At 250°, triethylmethoxyl radicals are 61% decomposed into butane and diethyl ketone[39]:

$$(C_2H_5)_3CO^{\cdot} \rightarrow C_2H_5^{\cdot} + (C_2H_5)_2CO.$$

In the decomposition of mixed t-alkoxy-radicals it is the largest hydrocarbon radical which is the more likely to be produced; for example, the decomposition of the t-pentyloxy-radical is 87–88% by the mechanism producing acetone with elimination of the ethyl radical[22]:

$$CH_3CH_2C(CH_3)_2O^{\cdot} \rightarrow CH_3CH_2^{\cdot} + (CH_3)_2CO.$$

Data obtained in the decomposition of a series of unsymmetrical alkoxy t-butyl peroxides in the presence of cyclohexene have been used to establish the following order of stability for simple alkoxy-radicals[40]:

$$CH_3O^{\cdot} > CH_3CH_2O^{\cdot} > CH_3CH_2CH_2CH_2O^{\cdot} > CH_3CH(CH_3)O^{\cdot} > (CH_3)_2CHCH_2O^{\cdot} > (CH_3)_3CO^{\cdot}.$$

This experimental order is in good agreement with thermochemical data: the alkoxy-radicals which decompose more readily have a lower enthalpy requirement for decomposition[4]. The elimination of a radical with formation of a carbonyl compound in a series of alicyclic oxy-radicals $C_5H_{10}\rangle C\langle^{R}_{O^{\cdot}}$ is thermochemically favourable only with certain substituents, for example, when R is t-butyl, benzyl, or 2-allyl; in most cases the oxy-radical decomposes with ring rupture, which in the case of cyclohexyloxy-radicals requires less energy than loss of a radical[5] (Table 2).

In fact, in the decomposition of cyclohexyl nitrite at 80–225° approximately 40% of the cyclohexyloxy-radicals decompose by ring opening with formation of a new radical. It is probably because of this radical that adipic acid is obtained in the presence of oxygen.

In the liquid phase the decomposition reactions are less characteristic of RO$^{\cdot}$ radicals. The isopropoxy- and cyclohexyloxy-radicals remain undecomposed at 40–70° in certain solvents[41,42], and methoxy-, ethoxy-, n-propoxy-, isopropoxy-, and n-butoxy-radicals generated in various solvents have not decomposed even at 120–155°.[43–45] Tertiary RO$^{\cdot}$ radicals decompose in solvents in which hydrogen abstraction is difficult; the relative yields of products from decomposition of t-butoxy-radicals in more than 30 hydrocarbons have been investigated[18,46], and Table 3 gives the relative rates of reaction of hydrocarbons with t-butoxy-radicals at 135° for 25 h. Decomposition of the t-butoxy-radicals is greatest in benzene and t-butylbenzene, in which hydrogen abstraction is difficult (Table 3).

TABLE 2. Enthalpy required for decomposition of substituted cyclohexyloxy-radicals.

| Aloxy | Group lost | Carbonyl compound | $\Delta H$ required, kcal mole$^{-1}$ |
|---|---|---|---|
| Cyclohexyloxy | H | cyclohexanone | 16 |
| | ring opening | $\cdot CH_2(CH_2)_4CHO$ | 0 |
| 1-Methylcyclohexyloxy | $CH_3$ | cyclohexanone | 4 |
| | ring opening | $\cdot CH_2(CH_2)_4COMe$ | 2 |
| 1-Phenylcyclohexyloxy | $C_6H_5$ | cyclohexanone | 9 |
| | ring opening | $\cdot CH_2(CH_2)_4COC_6H_5$ | 2 |
| 1-Butylcyclohexyloxy | $C_4H_9$ | cyclohexanone | −5 |
| | ring opening | $\cdot CH_2(CH_2)_4COC_4H_9$ | +1.2 |
| Decalyl-9-oxy | 1–9 ring opening | monocyclic radical | −1 |
| | 9–10 ring opening | ditto | 0 |
| 1-Hydroxycyclohexyloxy | OH | cyclohexanone | 20 |
| | ring opening | $\cdot CH_2(CH_2)_3CH{=}CHCHO$ | 1 |
| Tetrahydropyranyl-1-oxy | H | 1-hydroxytetrahydropyran | 16 |
| | ring opening | $\cdot CH_2(CH_2)_3OCHO$ | 0 |
| 1-Ethylcyclohexyl hydroperoxide | H | cyclohex-1-enol | −3 |
| | ring opening | $\cdot CH_2(CH_2)_2CH{=}CHCHO$ | 1 |

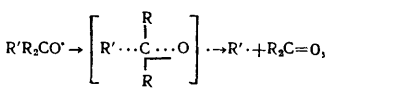
TABLE 3. Relative rates of reaction of t-butoxy-radicals with hydrocarbons.

| Hydrocarbon | Butanol / acetone | Hydrocarbon | Butanol / acetone |
|---|---|---|---|
| Benzene | 0.015 | Cyclohexane | 18 |
| t-Butylbenzene | 0.48 | Ethylbenzene | 4.5 |
| Mesitylene | 7.4 | Tetralin | 24 |
| 1-Methylnaphthalene | 3.2 | 2,3-Dimethylpentane | 4.6 |
| 2-Methylnaphthalene | 1.8 | Decalin | 18 |
| n-Hexadecane | 5.8 | Isopropylbenzene | 3.4 |

It has recently been shown that the isotope effect is fairly large in the decomposition of the t-butoxy-radical[47]; when $^{14}C$ is introduced the rate of decomposition of the radical $(CH_3)_3{}^{14}CO^{\cdot}$ decreases by 7%.

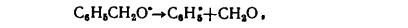
In the decomposition of tertiary alkoxy-radicals the rate of loss of n-alkyl is ten times that for methyl, and the rate for secondary alkyl is 20 times that for ethyl[48].

An important factor in the decomposition of alkoxy--radicals is the nature of the alkyl radical generated, and especially its stability[49]. It is thought that the decomposition includes a transition state, the free energy of activation of which decreases with increasing stability of the radical which is produced:



and in fact the stable benzyl radical is very readily eliminated from the $\alpha\alpha$-dimethylphenethoxy-radical; dimethylbenzylmethanol, produced by abstraction of hydrogen from the solvent by the undecomposed radical, is only formed in small amounts (less than 5%).

Aralkyloxy-radicals show the same features as the simple oxygen-containing radicals. The first member of this series, the benzyloxy-radical, is exceptionally stable[50-52]. In reactions of benzyl nitrite, dibenzyl hyponitrite, or *p*-nitrobenzyl nitrite in solution, no formaldehyde or phenol derivatives, such as would be formed in decomposition of the benzyloxy-radical:

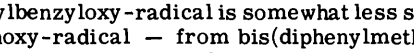


are observed. The benzyloxy-radicals produced in the thermal decomposition of dibenzyl peroxodicarbonate in benzene, carbon tetrachloride, chloroform, or isopropyl alcohol[41,42,53,54] at 40–70° also do not decompose.

The $\alpha$-phenylethoxy-radical does not decompose at temperatures up to 132°.[55]

The $\alpha$-methylbenzyloxy-radical is somewhat less stable[16]. The phenylmethoxy-radical — from bis(diphenylmethyl) peroxide — decomposes in bromobenzene, isopropylbenzene, or nitrobenzene with the formation of benzophenone. At 210° a phenyl radical is also eliminated (0.03 mole per mole of peroxide)[56,57]. The triphenylmethoxy-radical (from triphenylmethyl nitrate) decomposes with the formation of benzophenone and a phenyl radical[58].

The cumyloxy-radical also decomposes readily[59]:

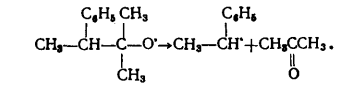


but no elimination of a phenyl radical is observed. At approximately 160° decomposition of the radical completely suppresses the abstraction of hydrogen from the solvent[60].

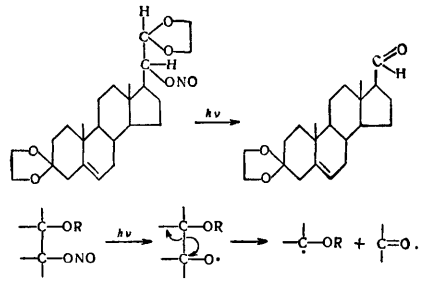
The ease of intramolecular fragmentation in $C_6H_5R_2CO^{\cdot}$ radicals thus decreases in the series $CH_3 > C_6H_5 > H$.

The following order of stability of aralkyloxy-radicals in the liquid phase has been suggested, based on experimental results and thermochemical calculations[50] (Table 4).

Decomposition of the *L*-(+)-2-methyl-3-phenylbutoxy--radical has been observed in the thermal decomposition of *L*-(+)-2-methyl-3-phenyl-2-butyl hypochlorite[61] in anhydrous solvents:



An interesting example of decomposition of an alkoxy--radical has been observed in the photolysis of steroidal nitrites[62]. The main photolysis products are carbonyl compounds and acids produced by the scission of oxygen--containing groups adjacent to the active centre, for example:



or[63]



2. Hydrogen abstraction. In all their reactions, particularly in the gas phase, RO$^{\cdot}$ radicals decompose into a carbonyl compound and an alkyl radical, so that in the presence of reagents with an easily broken carbon–hydrogen bond, the hydrogen may be abstracted either by the RO$^{\cdot}$ radical with the formation of an alcohol, or by the R$^{\cdot}$ radical with the formation of the corresponding hydrocarbon RH. We shall consider only reactions involving direct abstraction of hydrogen by RO$^{\cdot}$ radicals.

Gray has estimated the exothermicity of hydrogen abstraction from various hydrocarbons (Table 5).[4] It is seen that hydrogen abstraction should take place least readily from saturated hydrocarbons and most readily from the $\alpha$-methylene group of unsaturated hydrocarbons, and in fact with cyclohexene hydrogen abstraction completely suppresses addition of RO$^{\cdot}$ radicals to the double bond[64].

TABLE 4. Order of stability of aralkyloxy--radicals.

| Radical | Atom or radical lost | Residual carbonyl compound | Increase in enthalpy, kcal mole$^{-1}$ | Stability, decreasing from most (1) to least (6) |
|---|---|---|---|---|
| $C_6H_5CH_2O^{\cdot}$ | $C_6H_5^{\cdot}$ | $CH_2O$ | 16.3 | 1 |
| | $H^{\cdot}$ | $C_6H_5CHO$ | 19.9 | |
| $(C_6H_5)_2CHO^{\cdot}$ | $C_6H_5^{\cdot}$ | $C_6H_5CHO$ | 15.8 | 2 |
| | $H^{\cdot}$ | $(C_6H_5)_2CO$ | 19.4 | |
| $(C_6H_5)_3CO^{\cdot}$ | $C_6H_5^{\cdot}$ | $(C_6H_5)_2CO$ | 11.5 | 3 |
| $C_6H_5CH(CH_3)O^{\cdot}$ | $CH_3^{\cdot}$ | $C_6H_5CHO$ | 6.8 | 4 |
| | $C_6H_5^{\cdot}$ | $CH_3CHO$ | 10.7 | |
| $(C_6H_5)_2CH_3CO^{\cdot}$ | $H^{\cdot}$ | $C_6H_5COCH_3$ | 9.6 | |
| | $CH_3^{\cdot}$ | $(C_6H_5)_2CO$ | 2.4 | 5 |
| | $C_6H_5^{\cdot}$ | $C_6H_5COCH_3$ | 5.6 | |
| | $CH_3^{\cdot}$ | $C_6H_5COCH_3$ | 0.3 | 6 |
| $C_6H_5C(CH_3)_2O^{\cdot}$ | $C_6H_5^{\cdot}$ | $(CH_3)_2CO$ | 8.0 | |

TABLE 5. Enthalpy change for hydrogen abstraction: $RO^{\cdot} + XH \rightarrow ROH + X^{\cdot}$, assuming $D_{(RO-H)} = 102$ kcal mole$^{-1}$.

| XH | Compound | $D_{X-H}$ | Exothermicity, $-\Delta H$, kcal mole$^{-1}$ |
|---|---|---|---|
| *Aliphatic compounds* | methane | 101 | 1 |
| Primary | ethane | 96 | 6 |
| Secondary | propane | 94 | 8 |
| Tertiary | isobutane | 89 | 13 |
| *Unsaturated* | | | |
| Primary | propene | 77 | 25 |
| | toluene | 77 | 25 |
| Secondary | cyclohexene | 73 | 27 |
| Tertiary | cumene | 74 | 26 |
| *Aldehydes* | | | |
| Aliphatic | acetaldehyde | 80 | 22 |
| Aromatic | benzaldehyde | 78 | 24 |

In the gas phase hydrogen abstraction depends to a large extent on the stability of the RO$^{\cdot}$ radicals[40]; in the presence of the same hydrocarbon the relative yields of hydrogen abstraction and radical decomposition products differ according to the structure of the radicals.

Methoxy-radicals are the most stable, and in the gas phase they remove hydrogen from cyclohexene [16,40] to produce methanol (76% yield). In the photolysis of methyl acetate[65] the methoxy-radicals abstract hydrogen from acetate molecules; the energy of activation for the abstraction of hydrogen from the acetate by the methoxy-radical (5 kcal mole$^{-1}$) is one-half the energy of activation for hydrogen abstraction by the methyl radical (10 kcal × × mole$^{-1}$) [66,67]. The $CH_3O^{\cdot}$ radicals produced by the thermal decomposition of dimethyl peroxide[68] disproportionate to give methanol and formaldehyde, and the latter then loses hydrogen by reaction with further $CH_3O^{\cdot}$ radicals, so that the final reaction products are methanol and carbon monoxide only. On the other hand, in the decomposition of dimethyl peroxide in methanol[69], the methoxy-radicals abstract hydrogen from the alcohol, and the resulting $^{\cdot}CH_2OH$ radical dimerises to produce ethylene glycol.

The methoxy-radicals produced in the decomposition of dimethyl peroxide[70] and methyl nitrite[70,71] abstract hydrogen from ethane, propane, n-butane, isobutane, neopentane, and cyclopropane.

The ethoxy-radical is somewhat less stable, so that the yield of ethanol by reaction with cyclohexene [16,40] is lower (65%) than the yield of methanol in the corresponding reaction of methoxy-radicals.

In the gas phase the ethoxy-radicals produced in the photolysis of ethyl propionate[71] abstract hydrogen from the parent ester molecule; the energy of activation for this process (5.5 kcal mole$^{-1}$) is in good agreement with the value previously obtained for the methoxy-radical [65-67].

The pyrolysis of ethyl nitrite or nitrate would also be expected to show reaction of ethoxy-radicals with unreacted molecules of the starting material [11,19], but addition of diethyl peroxide to the pyrolysis zone has shown [72,73] that the ethoxy-radicals derived from the peroxide do not abstract hydrogen from ethyl nitrite or nitrate.

The extent of hydrogen abstraction from cyclohexene at 195° by propoxy- and butoxy-radicals [16,40] is shown in Table 6.

TABLE 6. Yield of products from the abstraction of hydrogen from cyclohexene at 195° in the gas phase by RO$^{\cdot}$ radicals obtained by the decomposition of unsymmetrical alkyl t-butyl peroxides.

| RO$^{\cdot}$ | ROH, % | RO$^{\cdot}$ | ROH, % |
|---|---|---|---|
| n-$C_4H_9O^{\cdot}$ | 30 | $(CH_3)_3CO^{\cdot}$ | 8 |
| iso-$C_3H_7O^{\cdot}$ | 19 | | |
| $(CH_3)_2CHCH_2O^{\cdot}$ | 6 | | |

t-Butoxy-radicals are unstable and only rarely abstract hydrogen in gas-phase reactions. Their reaction with aziridine at 129-154° is known [33], and photolysis of di-t-butyl peroxide at 30° has produced a small quantity of t-butyl alcohol [22].

t-Butyl alcohol has been identified in reactions with aldehydes [26,74]. The energy of activation for abstraction of hydrogen from isobutane by t-butoxy-radicals is ~ 4 kcal × × mole$^{-1}$. [38]

Hydrogen abstraction is more typical of RO$^{\cdot}$ radicals in the liquid phase.

In the same solvent under the same temperature conditions, hydrogen abstraction from the solvent by alkyloxy-radicals decreases in the series [43,44]:

$$^{\cdot}OCH_3 > {}^{\cdot}OC_2H_5 > {}^{\cdot}OC_3H_7 > {}^{\cdot}OC_4H_9 > {}^{\cdot}OCH(CH_3)_2.$$

The methoxy-radical abstracts hydrogen from toluene at 155° to give a 100% yield of methanol; the yield of methanol is somewhat lower (70-80%) in diphenylmethane or diphenylethane. The yields of the corresponding alcohols in the reaction of ethoxy- and chloroethoxy-radicals with isopropylbenzene at 125° are of the same order, while n-propoxy- and n-butoxy-radicals give a 60% yield of alcohol and isopropoxy-radicals give only a 50% yield.

Hydrogen abstraction by t-butoxy-radicals has been the most investigated reaction, including abstraction from saturated and alkyl-aromatic hydrocarbons [35,46].

Table 7 shows the relative velocity constants for hydrogen abstraction from various hydrocarbons by $CH_3^{\cdot}$, $CCl_3^{\cdot}$, t-$C_4H_9O^{\cdot}$, and ROO$^{\cdot}$ radicals [75], the rate of abstraction of hydrogen from the methyl group of toluene being taken as the unit.

The decomposition of di-t-butyl peroxide in cyclohexene has produced almost 100% butanol [64]:

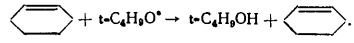


TABLE 7. Relative rates of hydrogen abstraction by radicals.

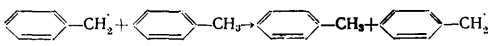
| Substance | ROO$^{\cdot}$ | $^{\cdot}CCl_3$ | Polystyryl | t-Butoxy | $CH_3^{\cdot}$ | |
|---|---|---|---|---|---|---|
| | 90° | 91.5% | 100° | 135° | 80° | 65° |
| Toluene | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| *o*-Xylene | — | — | — | 1.2 | — | 0.99 |
| *m*-Xylene | 1.15 | 1.0 | — | 1.25 | — | 1.0 |
| *p*-Xylene | 1.6 | 1.13 | — | 1.52 | — | 1.19 |
| Mesitylene | 1.9 | 1.0 | — | 1.22 | — | 0.94 |
| Ethylbenzene | 7.75 | 4.6 | 3.7 | 3.2 | 3.5 | 4.14 |
| Cumene | 13.3 | 12.5 | 9.0 | 5.1 | 10 | 12.9 |
| Indane | 37 | 7.1 | — | — | — | 8.3 |
| Tetralin | 134 | 25.6 | — | 15.2 | — | 2.3 |
| Diphenylmethane | 16 | 11.9 | 9.5 | — | — | — |

The dimers and trimers of the radicals from the solvent, which are obtained in high yield, retain the initial unsaturation.

The formation of chlorine-substituted alkenes in the reaction of various alkenes with t-butyl hypochlorite demonstrates that the reaction occurs by hydrogen abstraction from the alkene, and not by addition of a t-butoxy-radical to the double bond[57]; in the light-induced reaction of but-2-ene with t-butyl hypochlorite at 40° the double-bond addition product makes up only 3–4% of the total, 96 ± 3% being chlorobutene isomers.

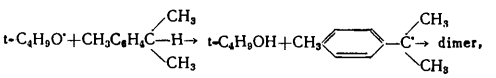
t-Butoxy-radicals react with substituted cycloalkanes by hydrogen abstraction from a side-chain, without affecting the ring[76], and the reaction with ethylene and propene oxides proceeds analogously: with t-butyl hypochlorite, the corresponding chlorocyclopropanes or chloro-epoxides are produced in high yield. On the other hand, the liquid-phase chlorination of these compounds with chlorine gives large amounts of acyclic chlorinated products. The selectivity of hydrogen abstraction by RO· radicals in this case has provided a convenient preparative procedure.

In alkyl-aromatic solvents t-butoxy-radicals abstract hydrogen from the $\alpha$-carbon atom, producing a stabilised benzyl-type radical, which then dimerises. The hydrogen transfer reaction



does not occur in these reactions[77]. The reaction with isopropylbenzene produces 2,3-dimethyl-2,3-diphenylbutane[20]. Hydrogen abstraction from cumene by t-butoxy-radicals is also observed in the decomposition of di-t-butyl diperoxycarbonate[78], and analogous products are found with ethylbenzene and toluene[64]. t-Butoxy-radicals only abstract hydrogen from the side-chains of alkylbenzenes, unlike the radicals obtained in the decomposition of acetyl or benzoyl peroxide, which can also react with the aromatic nucleus[79].

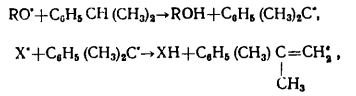
The reaction of RO· radicals with $p$-chlorotoluene has given 1,2-di-($p$-chlorophenyl)ethane[80], and dehydro-dimers are obtained in the reaction of di-t-butyl peroxide with diphenylmethane; 4-methylbiphenyl; $o$-, $m$-, and $p$-chloro-, $p$-bromo-, and $p$-iodo-toluene; $\beta$- and $\gamma$-picolines; and $p$-methylanisole[81,82]. The hydrogen atom of tertiary groups is readily abstracted[36]; in $p$-methylcumene hydrogen is abstracted from the isopropyl-group, and only one dimer is obtained:



no 1,2-di-($p$-isopropylphenyl)ethane, the dimerisation product of radicals which might be obtained by hydrogen abstraction from the $p$-methyl-group, being found[81,82]. When the peroxide is decomposed in anisole, the dimer, as expected, is not formed.

The reactivity of these alkylbenzenes towards t-butoxy-radicals, measured by the relative rate of formation of the dimer, depends on the substituent groups, and the influence of these is not due solely to their stabilising effect on the benzyl radicals produced by hydrogen abstraction, but also by their polar character, since the results obtained in the decomposition of di-t-butyl peroxide in a series of alkyl-aromatic solvents with various substituents are in accordance with the Hammett $\sigma$ and $\rho$ parameters[83]. For the reaction of t-butoxy-radicals with alkyl-aromatic solvents the value $\sigma$ = -0.5 was found.

In some cases the abstraction of hydrogen from alkyl-aromatic solvents is not accompanied by formation of the corresponding dimers[5]. It is thought that the solvent radicals react with oxy-radicals, giving up hydrogen to them, or combine with other active particles in the system, for example, nitric oxide if the reaction occurs by decomposition of nitrites:



where X· = NO or RO·.

Hydrogen abstraction from benzaldehyde by t-butoxy-radicals produces t-butyl alcohol in 100% yield[84]; the radicals from the solvent give complex association products. Tertiary benzylamines $C_6H_5CH_2NRR'$ are dehydrogenated by t-butoxy-radicals to $C_6H_5\dot{C}HNRR'$ radicals, which then dimerise or disproportionate, depending on R and R'.[85] Analogous reactions are observed with benzyl ethers $C_6H_5CH_2OH$.[86,87]

In dimethylformamide[88] the products of the thermal decomposition of di-t-butyl peroxide are t-butyl alcohol and a mixture which indicates that hydrogen is abstracted both from a methyl and the formyl group of the solvent.

At 140° t-butoxy-radicals abstract an $\alpha$-hydrogen atom from primary and secondary alcohols, forming RR'C·–OH radicals, which then dimerise to a glycol. A mixture of alcohols produces mixed glycols[89].

In the decomposition of di-t-butyl peroxide in n-butyric acid at 116° hydrogen is abstracted by the t-butoxy-radicals from the $\alpha$-carbon atom, and the resulting radical dimerises. In the decomposition of the peroxide in ethyl butyrate, hydrogen abstraction from the acid residue of the ester is six times as rapid as from the alcoholic residue, and is ten times as rapid in the $\alpha$-position as in the $\beta$-position[90].

In the decomposition of cyclohexyl or 1-methylcyclohexyl nitrite in cumene[5] the yield of the corresponding alcohol is 0.90–0.97 mole per mole of initial nitrite. In chlorobenzene, as in pyrolysis of the pure nitrites, the yield of alcohol does not exceed 0.6 mole.

The benzyloxy-radical abstracts hydrogen from cumene[91], and the $\alpha$-methylbenzyloxy-radical abstracts hydrogen from benzenethiol, producing 1-phenylethanol in 55% yield[92]; this alcohol is formed in 20–26% yield in the thermal decomposition of phenethyl nitrite[55].

In cumene, the diphenylmethoxy-radical produces 15–24% of 2,2-diphenylethanol[56]. Hydrogen abstraction by the cumenyloxy-radical from cumene decreases rapidly as the temperature is raised from 110° to 160°.[93]

Isopropoxy-, cyclohexyloxy-, and benzyloxy-radicals abstract hydrogen from isopropyl alcohol, dehydrogenating it to acetone[53,94].

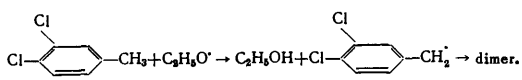
The reactions of R· and RO· radicals can be compared by investigating the decomposition of dialkyl peroxodicarbonates and acetyl peroxide in various solvents[43–45]. In solvents whose molecules contain a labile readily removed hydrogen atom, this is abstracted by R· and RO· radicals at approximately the same rate. In solvents without such hydrogen atoms, RO· radicals undergo disproportionation more than they participate in hydrogen abstraction (Table 8).

TABLE 8. Comparison of the reactions of free alkyl and alkoxy--radicals.

| Free radical | | Solvent: isopropylbenzene (A) hydrogen abstraction from solvent, % | isopropylbenzene (A) disproportionation, % | p-isopropylmethylbenzene (A') hydrogen abstraction from solvent, % | p-isopropylmethylbenzene (A') disproportionation, % | trimethylacetic acid (B) hydrogen abstraction from solvent, % | trimethylacetic acid (B) disproportionation, % |
|---|---|---|---|---|---|---|---|
| $\cdot CH_3$ | (125°) A'<br>(125°) A<br>(125°) B<br>(110°) A | 100<br>61 | 0<br>0 | 100<br>73.3 | 0<br>0 | 71.0<br>28.9 | 0<br>68.1 |
| $\cdot OCH_3$ | (130°) B<br>(110°) A | | | | | | |
| $\cdot OC_2H_5$ | (130°) A'<br>(110°) A<br>(140°) B | 70.4 | 18.8 | 58.7 | 13.7 | 5.3 | 95 |
| $\cdot C_3H_7$ | (125°) A<br>(135°) B | 78 | 22 | | | 0—3 | 20.0 (50% dimerisation) |
| $\cdot OC_3H_7$ | (145°) A<br>(140°) B | 51.7 | 33.3 | | | 5.6 | 92.5 |
| $\cdot O(CH_3)_3$ | (135°) A | 0 | 84.0 | | | | |
| $\cdot OC_4H_9$-iso | (130°) A | 83.5 | 9.5 | | | | |
| $\cdot OC_4H_9$ | (135°) A | 61.8 | 3.7 | | | | |

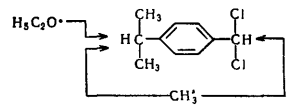
In some cases intramolecular hydrogen abstraction is observed; for example, in the decomposition of bis-(1-methylperoxocarbonatocyclohexyl) peroxide [95] the main products are methanol and the saturated $CH_2(CH_2)_4C(=O)O$ and unsaturated $CH_2(CH_2)_2CH{=}CHC(=O)O$ lactones, the latter being formed when hydrogen abstraction by the RO· radicals from the solvent is difficult. In isopropyl alcohol the yield of unsaturated lactone is 13 mole %, and in cyclohexane and benzene 39–46 mole %, of the total amount of lactones. At the same time there is almost complete absence of reaction between methoxy-radicals and the solvents, which shows that the formation of methanol in solvents with a difficultly removable hydrogen atom proceeds by an intramolecular reaction, the dehydrogenation product being the unsaturated lactone.

Alkoxy-radicals show an interesting selectivity in hydrogen abstraction from the solvent [44,45]: in chloro-substituted aralkyls the position of the chlorine with respect to the supposed point of attack by the alkoxy-radicals has a substantial influence on the course of the reaction. Thus in the reaction of $C_2H_5O\cdot$ radicals with 3,4-dichlorotoluene the dimer 1,2-bis-(3,4-dichlorophenyl)ethane is formed in 61% yield, the disproportionation of the $C_2H_5O\cdot$ radicals in this solvent occurring to no more than 11%:

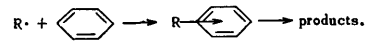


In 2,6-dichlorotoluene the corresponding dimer, produced from the radicals of the solvent by hydrogen abstraction from the α-position, is formed in only 21% yield, disproportionation of the ethoxy-radicals in this solvent occurring to the extent of 27%; and in benzal chloride there is no attack at the α-position at all, practically no tetrachlorotolane being formed [tolane is diphenylacetylene (Ed. of Translation)].

These results are explained by the so-called "repulsion effect", which is suffered by the approaching alkoxy-radical if chlorine atoms or methoxycarbonyl groups are close to the most probable point of attack. In some cases this effect causes a change in the point of attack. In their reaction with p-isopropylbenzylidene dichloride $(CH_3)_2CHC_6H_4CHCl_2$, ethoxy-radicals abstract only the α-hydrogen of the isopropyl group, giving a symmetrical dimer, while methyl radicals react equally with both α-hydrogen atoms, giving a mixture of isomers of the dimer:



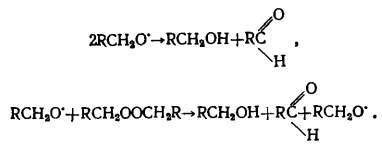
The absence of reaction products of RO· radicals with benzene can apparently be explained in an analogous manner [41,54]. The free electron on the electronegative oxygen atom hinders the formation of the transitional π complex, the existence of which has been clearly demonstrated in the reaction of R· radicals with aromatic compounds:



The selectivity of hydrogen abstraction by the t-butoxy--radical is due to its polar properties, which are equal to those of the chlorine atom [96], but unlike chlorine, t-butoxy--radicals are considerably more sensitive to the strength of the carbon–hydrogen bond; their reactivity towards primary, secondary, and tertiary hydrogen atoms is in the proportion 1 : 8 : 44, as against 1 : 3 : 4.5 for chlorine.

3. Disproportionation. The disproportionation of alkoxy-radicals is considerably more exothermic than hydrogen abstraction. According to Gray [1,4] $\Delta H$ for disproportionation is -70 (-90) kcal mole$^{-1}$.

In many cases it is difficult to distinguish between disproportionation and reaction of the radical with the starting material, since the products are the same:



Clearly, this matter can only be resolved kinetically, by showing the presence or absence of the initiated decomposition.

Such special investigations have not been carried out (with certain exceptions [51,53]), so that by the term "disproportionation" is generally understood both reaction between two RO· radicals, and reaction between an RO· radical and the starting material.

Disproportionation in the gas phase is uncommon. For methyl radicals produced in the pyrolysis of dimethyl peroxide [68] disproportionation is observed at 113–143°. The methoxy- and ethoxy-radicals formed in the photolysis of methyl acetate [65] and ethyl propionate [97] and the $CD_3O\cdot$ radicals produced in the photolysis of [$D_3$]methyl acetate [66,67] also disproportionate.

The reaction products obtained in the slow decomposition of di-n-propyl peroxide [14] in the gas phase at 146–175° contain propionaldehyde and propanol, which may be formed by disproportionation of $CH_3CH_2CH_2O\cdot$ radicals; however, initiated decomposition of the peroxide is more probable in this case:

$$CH_3CH_2CH_2O\cdot+(CH_3CH_2CH_2O)_2\rightarrow CH_3CH_2CH_2OH+$$
$$+CH_3CH_2CHO+CH_3CH_2CH_2O\cdot.$$

Disproportionation of $CH_3O^{\cdot}$, $C_2H_5O^{\cdot}$, n-$C_3H_7O^{\cdot}$, iso-$C_3H_7O^{\cdot}$, and n-$C_4H_9O^{\cdot}$ radicals in the liquid phase is observed when they are formed in solvents in which hydrogen abstraction is difficult, for example, in trimethylacetic acid or methyl trimethylacetate [43]. 100% disproportionation of the ethoxy-radicals takes place in dimethyl succinate or dimethyl malonate [44], or 2,6-dichlorotoluene or benzaldehyde [45]. Isopropyloxy-radical disproportionation products have been found in the pyrolysis of diisopropyl peroxocarbonates [98]. With t-butoxy-radicals the reaction is observed to a slight degree, and produces acetone and the t-butyl methyl ether [99]:

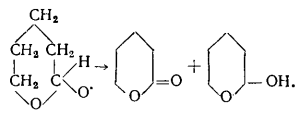
$$2\,(CH_3)_3CO^{\cdot} \rightarrow (CH_3)_2C{=}O + CH_3OC\,(CH_3)_3.$$

Disproportionation of benzyloxy- and cyclohexyloxy-radicals occurs in the decomposition of dibenzyl and dicyclohexyl peroxodicarbonates in benzene, carbon tetrachloride, or acetic acid [41,42]. The rate of decomposition of these peroxocarbonates in benzene and carbon tetrachloride is not affected by the presence of 2,2-diphenyl-1-(2,4,6-trinitrophenyl)hydrazino-radicals [53], which shows the absence of initiated decomposition of the peroxides, so that the formation of the corresponding alcohol and ketone in the reaction of the RO$^{\cdot}$ radicals must be due exclusively to their disproportionation.

Disproportionation is also observed when peroxodicarbonates are decomposed in the presence of various metals. Here direct attack of the RO$^{\cdot}$ radicals on the metal with formation of the corresponding alkoxides does not occur [100]. The formation of octanone and (+)-octan-2-ol in the thermal decomposition of optically active (+)-oct-2-yl nitrite [101] is due to disproportionation:

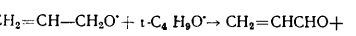
$$2(+)\text{-}C_6H_{13}CH\,(CH_3)\,O^{\cdot} \rightarrow C_6H_{13}COCH_3 + (+)\text{-}C_6H_{13}CH\,(CH_3)\,OH,$$

and similarly for 2-hydroxytetrahydropyran and δ-valerolactone in the thermal decomposition of t-butyl tetrahydropyran-2-yl peroxide [102]:



Disproportionation between two different RO$^{\cdot}$ radicals has been observed in the pyrolysis of allyl t-butyl and t-butyl cyclohexyl peroxides [103]:

$$CH_2{=}CH{-}CH_2O^{\cdot} + t\text{-}C_4H_9O^{\cdot} \rightarrow CH_2{=}CHCHO + t\text{-}C_4H_9OH,$$



The benzyloxy-radicals produced in the decomposition of benzyl nitrite [50] and benzyl hyponitrite [51,104] undergo disproportionation. In the latter case the disproportionation occurs in a "cage" of solvent, since dilution of the hyponitrite solution from 0.1 M to 0.0001 M had practically no effect on the yield of benzaldehyde [104]. The possibility is not excluded of a mechanism whereby two radicals formed in the solvent "cage" first dimerise to dibenzyl peroxide, and then are re-formed by its decomposition and disproportionate. However, dimerisation of two alkoxy-radicals, as will be shown below, is a rare event, and is only found with cumenyloxy-radicals [1]:

$$2C_6H_5C\,(CH_3)_2O^{\cdot} \rightarrow [C_6H_5C\,(CH_3)_2O]_2.$$

Disproportionation has been invoked to explain the formation of 1-phenylethanol in the thermal decomposition of pure 1-phenylethyl nitrite [55].

It is seen from the above that disproportionation is one of the most typical reactions of RO$^{\cdot}$ radicals in the liquid phase. Even in solvents which readily give up hydrogen, in many cases there is parallel formation of disproportionation products [41]. In this connection it is an interesting fact that isopropyloxy-*C* radicals $(CH_3)_2CHOH$ do not disproportionate [53].

4. Reactions with other radicals. RO$^{\cdot}$ radicals can interact with other radicals present in the system.

The methoxy-radicals produced in the thermal decomposition of methyl t-pentyl peroxide combine with methyl radicals to give a considerable quantity of dimethyl ether [105].

In the photolysis of methyl acetate [106] and [$D_3$]methyl acetate [66,67] the $CH_3O^{\cdot}$ and $CH_3^{\cdot}$ radicals are found to disproportionate and also to recombine, the ratio of the two rates of reaction $K_{dis}/K_{recom}$ being 1.4 and independent of the temperature, indicating the zero energy of activation for the disproportionation.

In the photolysis of ethyl propionate [97] the ratio $K_{dis}/K_{recom}$ for the ethoxy- and ethyl radicals is 2.3. Ethyl methyl ether has been found in the decomposition of t-butyl ethyl peroxide [73].

The formation of 1,2-epoxy-2-methylpropane in the decomposition of di-t-butyl peroxide may be due to the reaction [60]:

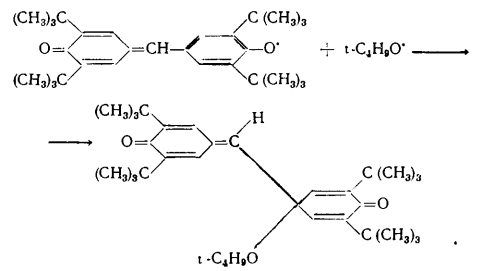
$$(CH_3)_3CO^{\cdot} + R^{\cdot} \rightarrow RH + CH_2{-}C\,(CH_3)_2.$$

The reaction between RO$^{\cdot}$ radicals and nitrogen monoxide or dioxide is of this type. Methoxy-radicals can combine with nitrogen monoxide to give methyl nitrite [38], or disproportionation may occur [107]:

$$CH_2O^{\cdot} + NO \rightarrow CH_2O + HNO, \qquad 2HNO \rightarrow H_2O + N_2O.$$

An analogous reaction is known for ethoxy-radicals [31,108]. Such reactions are less characteristic of t-butoxy-radicals. At 160° the rate of combination of nitrogen monoxide with $(CH_3)_3CO^{\cdot}$ is ~0.7 that of decomposition of the radical [34].

The combination of t-butoxy-radicals with the stable galvinoxyl† free radical has been described [109]:



No dimerisation with the formation of oxygen–oxygen bonds occurs, and in general this dimerisation is not a characteristic of RO$^{\cdot}$ radicals; according to approximate calculations [109] the activation barrier for this reaction is fairly high: 5 kcal. Investigation of the thermal decomposition of di-t-butyl monoperoxocarbonate [110] has also shown that there is no recombination of RO$^{\cdot}$ radicals in the solvent "cage".

The products of the reaction of RO$^{\cdot}$ radicals with another stable free radical, the 2,2-diphenyl-1-(2,4,6-trinitrophenyl)hydrazino-radical, have not been described,

† See Ref.109 for a derivation of this name (Ed. of Translation)].

but it is known that the (2,4,6-trinitrophenyl)hydrazino--radical is an active acceptor of RO· radicals, and may be used to study the kinetics of their formation in solution [111].

5. Isomerisation. Gray and Williams [1,4] found that the isomerisation of RO· radicals is thermodynamically favourable (Table 9).

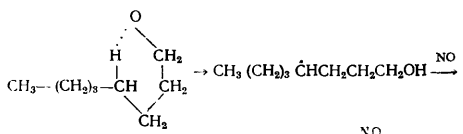
Isomerisation of alkoxy-radicals has been observed in the light-induced reaction of a number of tertiary alkyl hypochlorites [112], a free-radical chain reaction producing the corresponding chlorohydrins:

$$RCH_2(CH_2)_nC(CH_3)_2O \rightarrow R\dot{C}H(CH_2)_nC(CH_3)_2OH \xrightarrow{\text{hypochlorite}}$$
$$\xrightarrow{\text{hypochlorite}} RCHCl(CH_2)_nC(CH_3)_2OH + RCH_2(CH_2)_nC(CH_3)_2O\cdot, \text{ etc.}$$

The yield of the isomerisation product increases with the number of carbon atoms in the t-alkoxy-radical. The intramolecular nature of the hydrogen abstraction step in the rearrangement is demonstrated by the constant yield of isomerisation product as the concentration of hypochlorite in the solution is increased from 1.7 to 6.7 M. No isomerisation of primary or secondary alkoxy-radicals was detected [112], but it was later shown that intramolecular hydrogen abstraction occurs in the light-induced and thermal decomposition of n-butyl hypochlorite, with subsequent formation of the chlorohydrin [113].

The isomerisation of the alkoxy-radical in the light--induced decomposition of an alkyl nitrite leads to formation of nitroso-alcohol dimers [114]; the isomerisation passes through an intermediate six-membered ring, so that the yield of nitroso-dimer is directly dependent on the structure of the alkoxy-radical.

In the decomposition of n-octyl nitrite the main reaction product is the dimer of 4-nitrosooctan-1-ol:

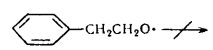


$$\xrightarrow{NO} CH_3(CH_2)_3CHCH_2CH_2CH_2OH \rightarrow \text{dimer},$$
$$NO$$

but with alkyl nitrites having less than five carbon atoms no intermediate six-membered ring compound can be formed, and the yield of nitroso-dimers is very much less. The same effect is observed with substituted alkylaromatic [115] and cyclohexyloxy-radicals [116]. Cyclohexyl nitrite itself gives a very low yield (4%) of nitroso-dimer, while 2-cyclohexylcyclohexyl nitrite gives a 30% yield of the dimer [116].

No dimer has been detected in the photolysis of benzyl nitrite, but 4-phenylbutyl and 5-phenylpentyl nitrites give up to 35% yields of nitroso-dimer.

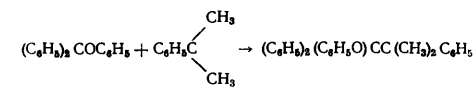
There is no evidence for the migration of hydrogen from the benzene nucleus [115]:



Other cases are known of the isomerisation of aryl-substituted alkoxy-radicals. Triphenylmethoxy isomerises into the phenyl ether [117]:

$$(C_6H_5)_2CO\cdot \rightarrow (C_6H_5)_2\dot{C}OC_6H_5 \rightarrow \text{dimer}.$$

In solution in cumene at 120–140° the isomerised triphenylmethoxy-radical combines with the α-cumenyl-radical [91]:



The diphenyl-*p*-tolylmethoxy-radical can isomerise in two ways, with migration of either the *p*-tolyl or a phenyl group [91]:

$$p\text{-}CH_3C_6H_4(C_6H_5)_2CO\cdot \rightarrow (C_6H_5)_2COC_6H_4CH_3 \text{ or } p\text{-}CH_3C_6H_4(C_6H_5)COC_6H_5.$$

The 1-naphthyldiphenylmethoxy- and biphenylylmethoxy--radicals can also isomerise in two ways in solution in cumene, but the rate of migration of the 1-naphthyl or biphenylyl group is six times that of the phenyl [91].

The *p*-nitrophenyldiphenylmethoxy-radical isomerises by migration of the *p*-nitrophenyl group; the resulting radical then decomposes [118]:

$$p\text{-}NO_2C_6H_4(C_6H_5)_2CO \rightarrow (C_6H_5)_2COC_6H_4NO_2 \rightarrow C_6H_5\cdot + C_6H_5COC_6H_4NO_2.$$

The use of optically active compounds has shown that the 1-phenylethoxy-radical does not isomerise in solution [92], and the absence of isomerisation has been demonstrated for gas-phase reactions of $CH_3O\cdot$ radicals [3] and for reactions of $(CH_3)_2CHO\cdot$ radicals in solvents [94].

6. Addition to a double bond. The addition of RO· radicals to a double bond has been demonstrated in the reaction of di-t-butyl or di-α-cumenyl peroxide with butadiene, isoprene, and chloroprene [119,120]:

$$t\text{-}C_4H_9O\cdot + CH_2{=}CH{-}CH{=}CH_2 \rightarrow t\text{-}C_4H_9OCH_2{-}CH{=}CH{-}CH_2 \rightarrow \text{dimer}.$$

An oxygen-containing polymer is obtained in the decomposition of di-t-butyl peroxide in hex-1-ene, which shows the addition of the RO· radicals to the double bond of the hexene [113]. Benzyloxy-radicals initiate the polymerisation of methyl methacrylate [29].

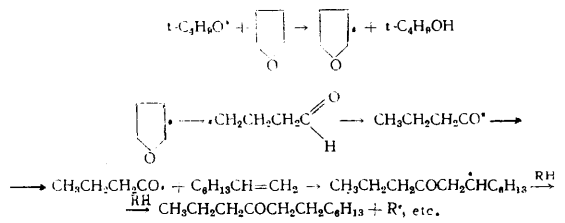
$^{14}C$-labelled di-t-butyl peroxide has been used to demonstrate that in the polymerisation of styrene the initiation is caused mainly by t-butoxy-radicals [47]. At low concentrations of styrene in the solution and at high temperatures the polymerisation is initiated by the methyl radicals produced in the decomposition of the t-butoxy-radicals.

The complex light-induced decomposition of steroidal nitrites has been explained by the intramolecular reaction of the resulting alkoxy-radical with a double bond [121].

TABLE 9. Thermochemistry of isomerisation of alkoxy--radicals.

| Type of isomerisation | Initial radical | Radical obtained | $\Delta H$, kcal × × mole$^{-1}$ |
|---|---|---|---|
| Migration of a hydrogen atom from carbon | $CH_3O\cdot$ | $\cdot CH_2OH$ | −7.5 |
| | $C_2H_5O\cdot$ | $\cdot CH(CH_3)OH$ | −9.5 |
| | $(CH_3)_2CHO\cdot$ | $\cdot C(CH_3)_2OH$ | −12 |
| | $C_6H_5CH_2O\cdot$ | $\cdot CH(C_6H_5)OH$ | −11 |
| | cyclo-$C_6H_{11}O\cdot$ | cyclo-$\dot{C}_6H_{10}OH$ | −14 |
| Migration of hydrogen atoms from distant $CH_2$--groups | $RCH_2(CH_2)_nO\cdot$ | $RCHCH_2OH$ | −8.5 |
| | $CH_3CH_2O\cdot$ | $\cdot CH_2OCH_3$ | 5 |
| Migration of a methyl group | $(CH_3)_2CHO\cdot$ | $\cdot CH(CH_3)OCH_3$ | 0.5 |
| | $(CH_3)_3CO\cdot$ | $\cdot C(CH_3)_2OCH_3$ | 0.5 |
| | $C_6H_5C(CH_3)_2O\cdot$ | $\cdot CCH_3C_6H_5(OCH_3)$ | −1.5 |
| Ring opening | cyclo-$C_6H_{11}O\cdot$ | — | 4 |
| Migration of an aryl group | $(C_6H_5)_3CO\cdot$ | $\cdot C(C_6H_5)_2OC_6H_5$ | −1.5 |
| | $C_6H_5(CH_3)_2CO\cdot$ | $\cdot C(CH_3)_2OC_6H_5$ | −1.5 |

The products obtained from di-t-butyl peroxide and tetrahydrofuran in the presence of oct-1-ene indicate the following reactions to occur [122]:



In other cases there is no direct evidence of addition of RO· radicals to double bonds. For example, in the polymerisation of styrene in the presence of cyclohexyl hydroperoxide the initiators may be other radicals present in the system [123].

The infrared spectra of the polymer obtained from ethylene in the presence of diethyl peroxodicarbonate exhibit the characteristic carbonate group absorption bands [124], and hence the initiation is due mainly to ROC(=O)O· radicals [125-127]. The polymerisation of other monomers in the presence of peroxocarbonates presumably proceeds analogously.

C-radicals and O-oxyradicals behave differently towards double bonds. By $^{14}C$-labelling, investigation of the decomposition of diisopropyl peroxodicarbonate in isopropyl alcohol in the presence of maleic acid has shown that the isopropyloxy O-radical $(CH_3)_2CHO\cdot$ does not add to the double bond of maleic acid, while the isomeric C-radical $(CH_3)_2C(\cdot)OH$ adds to the maleic acid to give a high yield of terebic acid [94,128] [3-carboxy-4-methylpentan--4-olide (Ed. of Translation)].

The t-butoxy-radical may react with alkenes not by addition at the double bond, but by abstraction of $\alpha$-hydrogen [26,57,129].


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U.D.C. 541.6

# BLOCK COPOLYMERS

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## I. INTRODUCTION

Until recently, the properties of polymeric materials were varied chiefly by altering the chemical composition and structure of the original monomers, the mean molecular weight of the polymer, the cross-linking of the polymer chain, the molecular-weight distribution, etc. Various methods for modifying macromolecular compounds are now becoming increasingly important. We think that one of the most promising methods, as far as industry is concerned, for modifying polymeric materials involves block and graft copolymerisation.

Block copolymers are macromolecular compounds whose main chain consists of two or more polymer blocks with different chemical composition or spatial configuration, joined to one another either directly or by means of low-molecular bifunctional compounds. The properties of block copolymers are generally determined by the properties of the individual homopolymeric sections in the main chain, but block copolymers also exhibit a number of properties which are not shown by the polymer fragments composing the main chain. An example is the block copolymer, of the diphilic type, consisting of blocks of aliphatic polyester and poly(methacrylic acid). This block copolymer, unlike poly(methacrylic acid), can be melted and is soluble in a mixture of acetone and alcohol, but is insoluble in water. The possibility of using familiar monomers to prepare polymeric materials exhibiting new properties fundamentally different from those of the corresponding homopolymers has led to the recent publication of a large number of papers and reviews [1-29] dealing with the synthesis and study of block copolymers. A classification of block copolymers has now become necessary. We suggest that the most rational basis for a classification of block copolymers is provided by the structural-chemical principle proposed by Korshak[30] for macromolecular compounds. This principle makes it possible to show directly in the name of the block copolymer the chemical character and structural features of its component blocks, their interconnection, and also the position occupied by the given block copolymer in a series of other macromolecular compounds. By analogy with the previously-proposed classification for graft copolymers [31,32], we propose a classification according to which block copolymers can be divided into three types:

1. Homochain block copolymers (main chain consisting of polymeric homochain blocks).
2. Heterochain block copolymers (main chain consisting of polymeric heterochain blocks).
3. Homo-heterochain block copolymers (main chain consisting of polymeric homochain and heterochain blocks).

In the synthesis of block copolymers, the polymer fragments of the main chain may form either highly-ordered (crystalline) or disordered (amorphous) regions in the structure of the block copolymer. To reflect these structural features of block copolymers, the above types of block copolymer can in turn be subdivided into the following three groups: (a) amorphous block copolymers (all polymer fragments of the main chain amorphous); (b) crystalline block copolymers (all polymer fragments of the main chain crystalline); and (c) crystalline-amorphous block copolymers (polymer fragments of the main chain having structures with different degrees of order).

The classification of a block copolymer in a given type and group is independent of whether the polymer blocks making up the block copolymer are joined to one another directly or by means of bifunctional low-molecular compounds.

The proposed classification covers all possible types of block copolymer, including block copolymers consisting of organic and inorganic polymer fragments, natural and synthetic block copolymers, and also the so-called stereo-block copolymers and optically active block copolymers.

Block copolymers are prepared by mechanochemical, radiochemical, and other chemical methods. The first two methods give not only block copolymers but also graft copolymers, and the final product is a mechanical mixture of homopolymers with block and graft copolymers. The separation of this mixture is not always possible. It is

not the aim of the present review to examine in detail the synthesis of block copolymers by all known methods, and we shall restrict ourselves to chemical methods of synthesis.

## II. HOMOCHAIN (CARBOCHAIN) BLOCK COPOLYMERS

The greatest number of papers has been devoted to block copolymers of this type, evidently because of the possibility of synthesising carbochain block copolymers by the usual methods for the homopolymerisation of vinyl monomers. All the methods described for the preparation of carbochain block copolymers are variants of vinyl monomer polymerisation, taking place by a free-radical or ionic mechanism. Irrespective of the nature of the original materials, the block copolymers obtained by the first mechanism are generally amorphous copolymers, whereas those obtained by the second mechanism are crystalline or crystalline-amorphous block copolymers.

### 1. Synthesis of Block Copolymers by Radical Polymerisation

This method has found the widest application in the synthesis of carbochain block copolymers. Since there are many methods for preparing macroradicals capable of initiating carbochain block copolymerisation, this method is extending considerably the range of utilisation of polymerisation for the synthesis of polymers. The production of polymeric radicals and subsequent block copolymerisation can be carried out by a mechanochemical method involving the application of mechanical stress to the polymer chains by means of ultrasonic vibrations[33-36], rolling[37-43], vibration milling[44,45], the electrohydraulic effect[46,47], etc.[48-58] in the presence of a given monomer. Carbochain block copolymers can also be obtained by the action of various forms of high-energy ionising radiation on a polymer chain in the presence of the corresponding monomer[59-68]. The synthesis of carbochain block copolymers by chemical means can be achieved by the addition of "live" macroradicals to the monomer, by the initiation of the block copolymerisation reaction by macroradicals which retain their activity, or by macroradicals formed as a result of the decomposition of peroxide groups in the main chain of the homopolymer. The most complete studies have been made of the method for the synthesis of block copolymers based on the introduction, into the homopolymer block, of terminal groups which, depending on their chemical character, are capable of forming macroradicals and initiating subsequent block copolymerisation.

#### A. Methods based on the presence, in the polymer block, of active terminal groups capable of forming macroradicals initiating the polymerisation of monomers with the formation of block copolymers.

In this method, as in all other methods for the preparation of block copolymers, particular attention is paid, in the synthesis of the block copolymers, to the maximum or complete elimination of the simultaneous formation of graft copolymers and homopolymers. This task is complicated by the fact that the probability of side reactions leading to the formation of undesirable products is much greater under the conditions of synthesis of block copolymers than in homopolymerisation, since the process takes place in two stages.

Depending on the chemical character of the active terminal group introduced into the homopolymer block, the mechanisms of the formation of macroinitiators and the direct formation of block copolymers differ considerably, and it is impossible to give a general scheme for the preparation of block copolymers by this method.

Block copolymerisation initiated by terminal hydroperoxide groups. Homopolymer fragments containing terminal hydroperoxide groups are obtained by polymerising monomers in the presence of dihydroperoxides under conditions ensuring the homolytic decomposition of only one hydroperoxide group, to avoid the formation of an inactive homopolymer[69]. Some patents recommend for this purpose the use of polyfunctional hydroperoxides containing two or more hydroperoxide groups with different reactivities[70]; it is believed that this reduces the formation of homopolymer to a minimum. Most frequently, however, the dihydroperoxides of *p*- and *m*-diisopropylbenzene are used to obtain the polymeric hydroperoxide. To avoid initiation of the homopolymerisation of the primary monomer by the hydroxyl radical, the reaction is carried out in the presence of $Fe^{2+}$ ions[71-73]. It has been suggested[74] that the formation of homopolymer blocks with terminal hydroperoxide groups should be regarded as a series of competing reactions whose kinetics can be examined by the method of Frost and Schwemer[75] with the condition that $[Fe^{2+}]_0 = 2[HOOROOH]_0$.

On the basis of the proposed mechanism for the reaction of the dihydroperoxide, monomer, and $Fe^{2+}$, it was found theoretically that the ratio

$$\frac{\text{Fe}^{2+}\text{ consumed as a result of oxidation by radicals}}{\text{monomer consumed as a result of initiation of polymerisation}} = \frac{[Fe^{2+}]}{[\bar{M}]}\left\{\frac{K_{10}[HOORO^{\cdot}] + K_{20}[\cdot OROM_n^{\cdot}] + K_{30}[\cdot ORO^{-}]}{K_{1i}[HOORO^{\cdot}] + K_{2i}[\cdot OROM_n^{\cdot}] + K_{3i}[\cdot ORO^{-}]}\right\}.$$

An analogous relationship in the form

$$\frac{\Delta Fe^{2+}_{total}\,\Delta^{*}Fe^{2+}}{2\Delta^{*}Fe^{2+} - \Delta Fe^{2+}_{total}} \quad \text{or} \quad \frac{\frac{1}{\Delta Fe^{2+}_{total}}}{\Delta Fe^{2+}_{total} - \Delta^{*}Fe^{2+}} - 2$$

can also be found experimentally, with the condition that the total quantity of $Fe^{2+}$ used up in the course of the reaction ($\Delta Fe^{2+}_{total}$), and the proportion which has reacted with the hydroperoxide ($\Delta^{*}Fe^{2+}$) are known. $[Fe^{2+}]$ is calculated from the experimental data and $[\bar{M}]$ is taken as equal to the concentration of the polymerising monomer.

In the second stage of the synthesis — the synthesis of the actual block copolymer — an effort is made to carry out the reaction under conditions ensuring the minimum possibility of chain-transfer reactions[76]. The method described for the preparation of block copolymers was studied in detail by Molyneux[77] for the case of the block copolymer of styrene with methyl methacrylate. In the first stage of the synthesis, thermal polymerisation of styrene was carried out at 70° in the presence of a dihydroperoxide *m*-diisopropylbenzene to give polystyrene with terminal hydroperoxide groups.

The block copolymer was prepared by suspension polymerisation at 0–25° in the presence of $Fe^{2+}$ ions and sodium pyrophosphate. The reaction products contain polymethyl methacrylate blocks in numbers either equal to or double

the number of original polystyrene blocks. Turbidimetric titration with subsequent extraction showed that the concentration of block copolymers in these products is ~ 10%. This low yield of block copolymers is due to the absence of terminal hydroperoxide groups from a considerable proportion of the polystyrene blocks (~ 25%) and to homopolymerisation of methyl methacrylate. It is assumed that the latter is due to chain transfer to benzene from polymeric radicals, which are localised in the droplets and have a long life time, and also to the reaction of monomer with radicals formed in the organic or aqueous phases of the suspension as a result of the decomposition of hydroperoxide remaining in the polystyrene. The marked non-uniformity of the block copolymer composition (a mixture of block copolymers of two types $A_nB_m$ and $B_mA_nB_m$ is formed) is apparently due to the fact that the original hydroperoxide derivatives of polystyrene contain either one or two hydroperoxide groups.

The chain-transfer reaction can also be used to obtain a homopolymer block with a terminal hydroperoxide group. It has been reported[78] that polymers or statistical copolymers of alkenes, containing terminal hydroperoxide groups, are obtained by polymerising alkenes or their mixtures at 0–35° in an aqueous emulsion containing 0.05–20 wt.% of monomer, in the presence of diisopropylphenyl dihydroperoxide as initiator and a chain-terminating reagent. The polymeric derivatives formed in this way are isolated and used as initiators for block copolymerisation with vinyl monomers. It is recommended that these polymers be stored at a temperature not exceeding 30°, to avoid decomposition of the terminal hydroperoxide groups.

Block copolymerisation initiated by terminal peroxide groups. Terminal peroxide groups are introduced into homopolymer fragments using phthaloyl peroxide[79]. Smets[80] showed that if styrene is kept for 5–6 h at 75° in the presence of 0.5% phthaloyl peroxide, polystyrene containing terminal peroxide groups is formed. This polymeric peroxide, dissolved in a benzene solution of methyl methacrylate, initiates a block copolymerisation reaction at 100°; after treatment for 5 h, the quantity of methyl methacrylate converted amounts to 40%. More detailed study of polymeric derivatives of phthaloyl peroxide[81,82] showed that to obtain a block copolymer in good yield it is necessary to take account of the relative reactivity and ability to undergo chain-transfer reactions shown by the monomeric components taking part in the block copolymer formation. For example, polystyrene containing terminal phthaloyl peroxide groups readily initiates the polymerisation of methyl methacrylate and ethyl $\alpha$-chloroacrylate at 100° but does not initiate the polymerisation of vinyl acetate or vinylpyrrolidone, whereas the analogous peroxide derivative of poly(vinyl acetate) readily initiates the polymerisation of styrene and ethyl $\alpha$-chloroacrylate under the same conditions. The solubility of the block copolymers obtained in this way differed significantly from that of the corresponding homopolymers, and this made it possible to isolate them in pure form. Analysis of the infrared spectra of the block copolymer of styrene with methyl methacrylate showed that the concentration of styrene units in the block copolymer varies from 22% to 30%.

Another method for introducing terminal peroxide groups into homopolymer blocks involves the polymerisation of styrene in the presence of t-butyl hydroperoxide and $Cu^{2+}$ ions[83,84]. The decomposition of t-butyl hydroperoxide in the presence of $Cu^{2+}$ ions evidently leads to the formation of $(CH_3)_3COO^{\cdot}$ and $(CH_3)_3CO^{\cdot}$ radicals, the first of which, probably as a result of recombination with the growing polystyrene macroradical, form active terminal peroxide groups capable of initiating subsequent block copolymerisation.

$$(CH_3)_3COO^{\cdot}+\dot{C}H(C_6H_5)CH_2CH(C_6H_5)CH_2-\cdots\longrightarrow$$

$$\longrightarrow(CH_3)_3COOCH(C_6H_5)CH_2-CH(C_6H_5)CH_2-\cdots.$$

An interesting property of this polymeric peroxide is its relatively high thermal stability; it does not decompose below 60°, even when exposed to ultraviolet light.

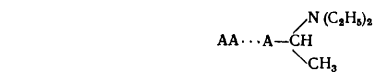
Study of the kinetics of formation of these macroperoxides[85,86] showed that the order of the reaction involved in the initiation of the primary monomers by t-butoxy- and t-butylperoxy-radicals decreases with increase in their concentration, since the primary radicals take part in a chain-termination reaction. In the block copolymerisation of these macroradicals with methyl methacrylate and vinyl acetate, it was observed that increase in the viscosity of the reaction medium decreased the yield of block copolymer.

The use of 2–8 mole % $(CH_3)_3COOOC(CH_2)_4COOOC(CH_3)_3$ has been recommended for the initiation of the polymerisation of the primary monomer in the synthesis of analogous polymeric peroxide derivatives[87]. The polymerisation is carried out homogeneously or heterogeneously at 70–90°. This method has been used to prepare homopolymer blocks of styrene, vinyl chloride, methyl methacrylate, and vinyl acetate, containing one terminal peroxide group. The absence of macromolecules containing no terminal peroxide groups is apparently due to the extremely low initiating power of the $(CH_3)_3CO^{\cdot}$ formed in the decomposition of the initiator

$$(CH_3)_3COOOC(CH_2)_4COOOC(CH_3)_3\longrightarrow(CH_3)_3COOOC(CH_2)_4^{\cdot}+CO_2+{}^{\cdot}OC(CH_3)_3.$$

Satisfactory results were obtained in the block copolymerisation of polystyrene with acrylonitrile, of poly(vinyl acetate) with styrene, and of poly(vinyl chloride) with styrene, although the block copolymers obtained had a low polymerisation coefficient. Block copolymers with vinyl chloride could not be obtained, because of the high rate constant of the chain-transfer reaction via the monomer.

Block copolymerisation initiated by terminal amino-groups. In the synthesis of carbochain block copolymers by chain-transfer reactions[88], the use of terminal amino-groups in homopolymer blocks as macromolecular chain-transfer reagent has been proposed[89]. The rate constants for chain transfer were determined for the radical polymerisation of styrene and vinyl acetate in the presence of primary, secondary, and tertiary amines[90]. The highest values of the rate constant for chain transfer were observed for the polymerisation of acrylonitrile and methyl methacrylate in the presence of triethylamine[91]; this is attributed to the formation of ionic structures in the transition state. Bamford and coworkers[92] showed that to obtain block copolymers of the type $A_nB_m$ it is best to carry out the homopolymerisation of the monomer A in the presence of triethylamine; chain transfer takes place through the latter with the formation of a compound of the type



This polymeric product was used as macromolecular chain-transfer agent in the homopolymerisation of the monomer

under conditions ensuring a high degree of chain transfer by the growing radical.

To reduce the formation of homopolymer to a minimum, it is recommended that the second stage of the synthesis of the block copolymer be carried out using monomers for which the life time of the kinetic chain during polymerisation is appreciable. A series of equations for calculating kinetics of block copolymerisation were proposed for the case of the block copolymer of methyl methacrylate with acrylonitrile. In the derivation of the equation, which makes it possible to determine the number of transfer acts (n.t.) through each polymeric molecule formed, it was postulated that chain transfer takes place only through the polymer chain. The equation is

$$\text{n.t.} = (k_3'[S_A] + k_3''[E])\{k_3'[S_A] + k_3''[E] + (Ik_4)^{1/2}\}^{-1},$$

where $[S_A]$ is the concentration of poly(methyl methacrylate), $[E]$ the concentration of terminal groups, $I$ the rate of initiation, $k_3'$ and $k_3''$ the rate constants for the chain-transfer reaction through the elementary units of the polymer chain and through the terminal amino-groups respectively, and $k_4$ the mean rate constant for the chain-termination reaction resulting from disproportionation.

The weight-average concentration of poly(methyl methacrylate) fragments ($m$) is calculated from the equation

$$m = a(k_3'[S_A] + k_3''[E])\{k_3'[S_A] + k_3''[E] + (Ik_4)^{1/2}\}^{-1},$$

where $a$ is the polymerisation coefficient for poly(methyl methacrylate) with terminal amino-groups.

The following equation was proposed for the number-average polymerisation coefficient of polyacrylonitrile $\bar{P}$ for a low degree of conversion

$$\bar{P} = k_2[B]\{k_3'[S_A] + k_3''[E] + (Ik_4)^{1/2}\}^{-1},$$

where $k_2$ is the rate constant for the reaction of chain growth and $[B]$ the acrylonitrile concentration.

Bamford and White [93] found that the dependence of the concentration of block copolymer molecules of the type $A_nB_m$, containing $a$ units of monomer A and $b$ units of monomer B, $[P_{ab}]$, on the quantities $a$ and $b$ is given by the equation

$$[P_{ab}] = [S_B]\alpha^{a-1}(1-\alpha)^2\beta^b(1-\beta)k_3'[S_A]/k_2[B],$$

where $[S_A]$ and $[S_B]$ are the concentrations of the homopolymer blocks $A_n$ and $B_m$ respectively, $\alpha$ and $\beta$ the probability factors for growth of the homopolymer chains of monomers A and B, $[B]$ is the concentration of monomer B, and $k_3'$ and $k_2$ are the rate constants for the reactions of chain transfer and chain growth respectively. These equations were used to find the block copolymer distribution with respect to chain length ($r = a + b$) for a given composition ($a/b = c$) and the distribution with respect to composition for a given chain length. It was shown that the quantity of graft copolymer formed as side product is $[k'/k''(1 - \alpha)]$ times the concentration of block copolymers, where $k'$ and $k''$ are the rate constants for the reactions of chain transfer by any unit of the polymer chain and by the terminal amino-group of the polymer formed by the polymerisation of monomer A. From this it follows that with increase in the polymerisation coefficient of the original monomer, equal to $1/(1 - \alpha)$, the concentration of impurity increases, although this is also accompanied by the formation of a block copolymer with greater molecular weight. Since the block copolymer synthesised by means of terminal amino-groups is non-uniform with respect to composition and dimensions of the homopolymer fragments, it was considered advisable either to fractionate the macromolecular chain-transfer agent thoroughly before the synthesis of the actual block copolymer or to extract the low-molecular fractions from it with a suitable solvent.

A polymer containing a terminal aromatic amino-group is obtained by a polymerisation reaction initiated by a diazonium salt and an aromatic acid containing a free amino-group or a group from which a free aromatic amino-group can be prepared by subsequent reactions. This reaction was used to obtain an acrylonitrile homopolymer with a terminal amino-group, and after diazotisation this was used as macromolecular initiator for block copolymerisation with acrylonitrile and 2-methyl-5-vinylpyridine [94,95].

Block copolymerisation initiated by terminal groups containing halogen. Homopolymeric blocks with terminal halogen atoms absorb light with wavelength 2880–3500 Å, are raised to an excited state, and dissociate into free reactive polymeric radicals which are used as macromolecular initiators in block copolymerisation. The macromolecular halides are usually prepared by the thermal or photolytic polymerisation of styrene [96,97] or methyl methacrylate [98] in the presence of $CBr_4$ or $CBrCl_3$ which terminate the chain by a chain-transfer reaction.

In the second stage of the synthesis of the block copolymer, the macrohalide obtained is irradiated with ultraviolet light in the presence of a vinyl monomer, for example, methyl methacrylate, styrene, acrylonitrile, etc. The macroradical formed as a result of irradiation initiates the secondary polymerisation with the formation of the block copolymer, which can be isolated by fractionation on a column using the method developed by Baker and Williams [99].

The centres initiating block copolymerisation are formed only by decomposition of the C–Br group, since $CCl_3$ groups do not undergo photolytic decomposition under the conditions of the synthesis, whereas $CBr_3$ groups undergo further photolysis and are converted into centres initiating block copolymerisation. Chlorine-containing block copolymers are obtained in analogous fashion [100]. Hydrophilic block copolymers are obtained by polymerising acrylic acid in the presence of organic bromine-containing compounds with three or four carbon atoms and three bromine atoms. The resulting bromine-containing acrylic acid homopolymer is dissolved in an inert aqueous medium with another vinyl monomer, for example acrylamide, and the mixture is irradiated with ultraviolet light to give the block copolymer [101,102].

Block copolymerisation initiated by terminal groups containing sulphur. In the polymerisation of vinyl monomers in the presence of organic compounds containing sulphur atoms, it was found that the latter take part in chain-transfer reactions with the formation of homopolymeric blocks containing terminal SH groups [98,103]. These polymers are capable of undergoing photolytic decomposition at the terminal group, so that they may initiate block copolymerisation when irradiated with ultraviolet light in the presence of vinyl monomers. An analogous ability to undergo chain-transfer reactions is shown by various organic disulphides [104], and disulphides such as tetraethylthiuram disulphide† are used

† Bis(diethylthiocarbamoyl) disulphide (Ed. of Translation).

simultaneously to initiate the polymerisation of the primary monomer.

The polymerisation of styrene using tetraethylthiuram disulphide as initiator leads to the formation of polymer blocks with terminal sulphur-containing groups capable of undergoing photolysis with the formation of macroradicals which initiate block copolymerisation. A block copolymer of styrene with methyl methacrylate was prepared in this way [105]. Analysis showed that the product of this block copolymerisation consisted of 40% pure block copolymer, 30% styrene homopolymer, and 30% methyl methacrylate homopolymer [106]. Block copolymers of styrene with vinyl acetate were synthesised in analogous fashion in yields of more than 70%. [107] These block copolymers are soluble in most hydrocarbons and ketones, and are insoluble in methanol. The poly(vinyl acetate) block of this block copolymer can then be hydrolysed with a methanol solution of alkali to give the block copolymer of styrene with vinyl alcohol [108]. This block copolymer is insoluble in benzene, methanol, and water, and merely swells in these solvents; it is partly soluble in phenol and cresol. Another method of using sulphur-containing organic compounds in the synthesis of block copolymers involves the polymerisation of styrene (initiator diisopropylphenyl monohydroperoxide) in the presence of cumenethiol as chain-transfer agent. Chain transfer leads to the formation of polystyrene with molecular weight 28 000 (compared with 83 000 for control specimens of polystyrene), from which it is concluded that about 25% of the polystyrene blocks contain terminal isopropyl groups. These terminal groups are readily oxidised to hydroperoxide groups to give polystyrene blocks with terminal hydroperoxide groups which are capable, in the presence of $Fe^{3+}$ ions, of initiating the block copolymerisation of polystyrene with various vinyl monomers [109].

Block copolymerisation initiated by terminal groups consisting of acid hydrazides. Acrylonitrile is capable of undergoing polymerisation in the presence of the redox system consisting of acid hydrazides and $Fe^{3+}$ ions. The initial rate of polymerisation of acrylonitrile in 1 *N* acetic acid solution at 40° is almost linearly dependent on the concentration product $[\text{acid hydrazide}]^{1/2}[Fe^{3+}]^{1/2}$. The polymerisation of acrylonitrile can be initiated in analogous fashion by using, instead of the monomeric acid hydrazides, polymeric blocks containing acid hydrazides as terminal groups. This method has been used to prepare block copolymers of polyaminotriazole with polyacrolein, exhibiting a high affinity for acid dyes [110].

B. Methods based on the presence, in the main chain of the polymeric block, of active groups capable of forming macroradicals which initiate the polymerisation of monomers with the formation of block copolymers.

Block copolymerisation initiated by dye molecules present in the leuco-form in the main chain of the polymeric block. On the basis of spectroscopic data obtained by Oster's method [111] in studies of the products of the photopolymerisation of vinyl compounds, in the presence of dyes (eosin, safranine, Acridine Orange), reducing agents (ascorbic acid, thiourea), and oxygen, it has been established that the dye molecules are incorporated in the polymer molecule in the leuco-form. The photosensitising effect of the dyes present in the polymer molecule can be used for the initiation of block copolymerisation [112]. The irradiation, with visible light, of ω-*N*-(aminoeosin)-poly(methyl methacrylate) containing 1 eosin group for every 48 methyl methacrylate groups, in acetic acid in the presence of thiourea and acrylamide gave a block copolymer of methyl methacrylate and acrylamide, with a concentration of second monomer residues equal to 40%. A block copolymer of methyl methacrylate with styrene was obtained in analogous fashion but in higher yield (concentration of second monomer 79%); hydrolysis of this block copolymer showed that the homopolymer blocks are joined to one another by leuco-groups.

Block copolymerisation initiated by peroxide groups present in the main chain of the polymer block. Peroxides formed in the polymer during storage are capable of decomposing to form macroradicals which initiate block copolymerisation [113]. To obtain block copolymers using these polymeric peroxides, specimens of poly(methyl methacrylate), polystyrene, and poly(vinyl acetate) are kept in the vapours of styrene, acrylonitrile, vinylidene chloride, vinyl acetate, and methyl methacrylate [114]. Despite the heterogeneity of the process, which decreases considerably the rate of the block copolymerisation, analysis of the product showed an appreciable concentration of block copolymers. In the bulk copolymerisation of methyl methacrylate, styrene, and vinyl acetate in the presence of oxygen, peroxide bonds are formed in the main chain of the polymer [115]. If this polymeric peroxide is swollen in monomer and then heated, the macroradicals formed in the thermal decomposition of the peroxide groups begin to initiate polymerisation of the monomer adsorbed on the particles of polymeric peroxide, with the formation of a block copolymer.

Peroxide groups can also be introduced into the main chain of a polymer by a variety of chemical methods. For example, the partial dehydrochlorination of poly(vinyl chloride) gives a polymer with a main chain containing double bonds, ozonisation of which gives peroxide groups capable of initiating the block copolymerisation of vinyl monomers [116].

C. Methods based on the presence, in the main chain of the polymeric block, of side branches capable of undergoing photolytic degradation with the formation of macroradicals which initiate the polymerisation of monomers with the formation of block copolymers.

Block copolymerisation initiated by macroradicals formed by the photolytic degradation of keto-groups present in the polymer in the form of side branches. Irradiation of poly(vinyl methyl ketone) with ultraviolet light of wavelength 3130 Å leads to decomposition of the polymer by photolytic degradation according to a scheme analogous to that for the decomposition of monomeric aliphatic ketones under identical conditions [117-119]. The resulting macroradicals are capable of initiating the homopolymerisation and block or graft copolymerisation of monomers such as methyl methacrylate and vinyl acetate. As in the case of simple radical polymerisation, the rate of the block or graft copolymerisation depends on the concentration of keto-groups and is proportional to the square root of the intensity of irradiation.

D. Methods based on the introduction, into the monomer, of a mixture of polymer-homologues containing free active radicals capable of initiating the polymerisation of monomers with the formation of block copolymers.

Block copolymerisation initiated by radicals which have not lost their activity. In a study of the photopolymerisation of methyl methacrylate, Melville [120] observed that growth of the polymer chains continues after irradiation has stopped, and that this "growing polymer" may initiate the polymerisation of chloroprene without irradiation. Thomas [121] suggested that polymeric chains capable of growth may be preserved in a solid polymer. These macroradicals may initiate block copolymerisation when brought into contact with vinyl monomers. In the block polymerisation of acrylonitrile or acrylamide, the polymer formed is insoluble in the original monomer and is precipitated; this precipitate retains a large quantity of free macroradicals capable of further growth. With increase in temperature or the addition of solvents, the radicals occluded in the polymer are liberated due to the unwinding of the coiled polymer molecules, and may become centres for the initiation of the polymerisation of a second monomer [122]. The yield of block copolymers in this block copolymerisation is generally low — less than 5% in the case of poly(acrylonitrile) and less than 8% in the case of poly(acrylamide). This low yield of block copolymer is due to the incomplete liberation of the radicals during the block copolymerisation; this was confirmed by electron paramagnetic resonance studies. A block copolymer of methyl methacrylate with styrene was synthesised in analogous fashion [123].

The products of the emulsion polymerisation of styrene and methyl methacrylate, under the conditions of micro-gel formation, also contain radicals capable of initiating block copolymerisation. It has been established by electron microscopy [124] that the block copolymerisation is accompanied by an increase in the dimensions of the particles of the micro-gel; no new particles are formed. It is not clear whether the block copolymerisation centres are situated inside the micro-gel particles or on their surface. No homopolymer is formed under these conditions. These radicals can be used to prepare the block copolymer of vinyl acetate with methyl methacrylate [35]. For this purpose vinyl acetate is emulsion polymerised under the influence of $\gamma$-radiation; the macroradicals thus formed initiate the polymerisation of the second monomer.

Block copolymerisation initiated by long-lived macroradicals. In the suspension polymerisation of a water-insoluble monomer in the presence of an aqueous solution of another monomer, the macroradicals formed may diffuse through the phase boundary and initiate the polymerisation of the second monomer with the formation of a block copolymer. Block copolymers of methacrylic acid with styrene and vinyl acetate were prepared in this way [125-127]. Because of the complex mutual solubility of the monomers in one phase, however, the resulting block copolymer has an extremely indefinite composition and is formed in low yield. Block copolymers of *N*-vinylpyrrolidone with styrene [128] and vinyl chloride [129] are obtained in analogous fashion. A slightly different method was proposed for the preparation of block copolymers soluble in water and capable of being used as settling agents and filter aids [130]. One or several vinyl compounds forming water-soluble polymers (for example, acrylic or methacrylic acids or their salts or amides) are polymerised in aqueous solution and a further 0.5–30 wt.% of a vinyl monomer containing sulphonic or phosphoric acid residues in the molecule is added to polymerise with the still active primary monomer, which is not removed from the polymerisation medium.

Another example of block copolymerisation initiated by macroradicals with relatively long lifetime is the so-called "dynamic" method of block copolymer synthesis proposed by Hicks and Melville [131-134]. The essential features of the method are as follows. Monomer A, containing a photosensitiser, passes through a capillary, a small section of which is irradiated with a powerful quartz mercury lamp, into a reservoir containing monomer B. Decomposition of the sensitiser in the irradiated section produces free radicals (up to $10^{-4}$ mole) which react with the molecules of monomer A and form polymeric radicals of the type AA... A$^{\cdot}$. When they enter the reservoir containing monomer B, these radicals continue to grow, with the attachment of molecules of monomer B. The polymer molecules formed in this way have the structure ...AAABBB... or ...AAABBBBBAAA..., depending on the mechanism of the chain-termination reaction. Calculation shows that at an appropriate rate of flow of monomer A through the capillary, the main bulk of the free radicals formed during the irradiation are not deactivated in the time taken for the reaction mixture to pass through the capillary and enter the reservoir containing monomer B. The results of the theoretical calculations are confirmed by direct determination of the quantity of polymer formed only in the capillary and the quantity of polymer formed in the reservoir containing monomer B. This method has been used to synthesise block copolymers of butyl acrylate and acrylonitrile (monomers A) with styrene, using as sensitiser the dinitrile of azocyclohexanecarboxylic acid. The structure of the polymers obtained was studied by ultraviolet spectroscopy. Block copolymers of n-butyl acrylate with 2-vinylpyridine were synthesised in analogous fashion [135]; study of these block copolymers showed that their molecules consist of a poly(vinyl pyridine) block and a block of a statistical copolymer of both monomers used for the synthesis, situated between blocks consisting of units of the first monomer. This structure in the products obtained is due to the presence of both monomers in the second stage of the synthesis of the block copolymer.

E. Methods based on inter-chain exchange reactions during radical polymerisation, leading to the formation of block copolymers.

In the radical polymerisation of vinyl monomers to appreciable degree of conversion, secondary processes take place [136] involving reaction between the macroradicals formed. These reactions are of two types: (1) inter-chain exchange — a process of repeated degradation and recombination of macroradicals, and (2) the cross-linking of chain macromolecules without the formation of a gel. As a model system for the synthesis of a block copolymer, in which inter-chain reactions might take place in more or less "pure" form, use has been made of mixed solutions of polymers, in which thermal decomposition of the initiators — the sources of the primary free radicals — was carried out. The formation of block copolymers, confirmed by ultraviolet spectroscopy, was observed in mixed solutions

of polystyrene and polyisobutene in toluene in the presence of benzoyl peroxide and methylphenyltriazole. A method based on sedimentation in a density gradient was used for the quantitative analysis of the products obtained.

As mentioned above, the properties of block copolymers show not only the properties of their component homopolymers but also, as a rule, new properties differing sharply from those of the homopolymer. Some block copolymers exhibit properties which are so unique that the isolation of the pure block copolymers and the study of their properties is of considerable practical and theoretical interest. A number of reviews have been devoted to methods of studying block copolymers [137,138]. In our opinion, the most promising qualitative methods for the identification of block copolymers are nephelometric [139] and turbidimetric [140] titration. An apparatus has been described [141] for automatic turbidimetric titration, which makes it possible to determine the presence of a block copolymer in its mixtures with homopolymers.

The applicability of X-ray structural analysis to the study of block copolymers was confirmed for the block copolymer of methyl methacrylate with acrylonitrile [142]. The X-ray diffraction patterns for the block copolymers are similar to those for a mechanical mixture of the homopolymers, but there are certain differences in the scattering of X-rays by the block copolymers. The weight-average molecular weight of the block copolymers can be determined by light-scattering methods. The applicability of Stockmayer's equation

$$(I_0/k'c)_{c\to 0} = (dn/dc)_0^2\,\overline{M}\omega + 2b\,(dn/dc)_0\,\{M\Delta x\} + b^2\{M\,(\Delta x)^2\},$$

to the determination of the weight-average molecular weight of block copolymers from the values of the reduced intensity of the scattering of light in three different solvents has been studied experimentally for the block copolymer of styrene with methyl methacrylate. The parameters for the polydispersity of composition $M\Delta x$ and $M(\Delta x)^2$ show satisfactory agreement with one another when any three measurements in different solvents are chosen [143].

The thermodynamic equations for solutions of homopolymers have been used to calculate the Hildebrand solubility parameters for statistical, block, and graft copolymers $\delta_i = \sqrt{(\Lambda_i - RT)/V_i}$, where $\Lambda_i$ is the molar heat of volatilisation and $V_i$ the molar volume of the $i$th component of the mixture. Using the subscripts A and B to denote the values of $\delta$ for the corresponding homopolymers, and the subscript 0 for the solvent, and taking $(\delta_A - \delta_B) = p$ (with the condition that $\delta_A > \delta_B$), $|\delta_0 - \delta_A| = \Delta\delta_A$, $RT$ = = 600 cal, and $V_0 = 100$ cm$^3$, the authors obtained the following condition for the solubility of the statistical copolymers:

$$\Delta\delta_A + p(1-\beta) \leqslant {}^1/_6, \qquad (1)$$

where the solubility parameter $\delta_p = \delta_A\beta + \delta_B(1-\beta)$. This result was obtained from an analysis of the systems by the Flory–Huggins method. The derivation of this equation was based on the fact that the entropy ($S$) of the statistical copolymer is the same as the entropy of the homopolymer with the same polymerisation coefficient, whereas the heat of mixing $\Delta H$ depends on the interaction of the solvent with the main units of A and B. In the case of the block copolymers, it is necessary, in the calculation of the entropy, to make allowance for the fact that the volumes of the statistical segments are different for the homopolymers A and B. In the calculation of $\Delta H$ for the block copolymers, in the case of comparable homopolymers, the solubility condition is described by Eqn. (1), whereas for non-comparable homopolymers the solubility condition is described by the quadratic relation $(\Delta\delta_A)^2 - 2p(1-\beta)\Delta\delta_A + p^2(1-\beta) \leqslant (2^{-1} - z^{-1})RT/V_0$, where $z$ is the coordination number of the Flory–Huggins quasi-lattice and $\beta$ the volume fraction of monomer A in the statistical copolymer [144].

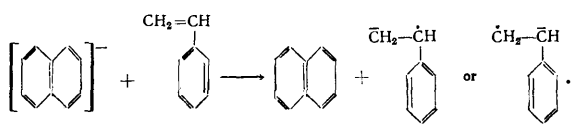
In the study of solutions of block copolymers of styrene with methyl methacrylate, containing 50–74% styrene, it was shown [145] that the dependence of the main thermodynamic properties of solutions, in toluene and ethyl methyl ketone, of fractionated specimens of these block copolymers, on the composition of the fractions, passes through a maximum at a styrene concentration of ~60%. In particular, the entropy of dissolution, heat of dilution, molecular dimensions, and the unperturbed length of the molecules of the block copolymers, calculated from viscosimetric data, have maximum values for the specimens containing 60% styrene. This phenomenon was related to the limiting intramolecular "separation into layers" of the homopolymeric sections of the block copolymer molecule as a result of their low compatibility in the given proportions. At the same time the values of the second virial coefficient and the Huggins constant are unaffected by change in the composition of the block copolymer, and this in turn can be attributed to the mutually cancelling influence of the two homopolymeric blocks of the same block copolymer molecule. The apparent dissociation constants of the block copolymers of acrylic acid with acrylamide were determined by electrometric titration [146] in 0.1 $N$ carbonate-free sodium chloride solution, with 0.1 $N$ sodium hydroxide solution. It was found that the acidity of this block copolymer is the same as that of polyacrylic acid.

In the study of the viscosity and light scattering of solutions of block copolymers of acrylonitrile and methyl methacrylate in mixed solvents [147], it was found that when benzene is added to a solution of the block copolymer in dimethylformamide there is a sharp decrease in viscosity and an increase in turbidity, continuing over a definite time interval. An analogous effect is produced by the addition of other precipitants to this solution. The critical concentration increases in the order $H_2O < CH_3COOH <$ $< C_2H_5OH < C_6H_6 < CCl_4 < (CH_3)_2CO$. The subsequent addition of dimethylformamide restores the viscosity of the system and decreases the turbidity, with considerable hysteresis. This change in the properties of the block copolymer solutions is due to the repeated formation of aggregates as a result of electrostatic interaction between the acrylonitrile units in the block copolymer chains. The use of the viscosity and light scattering of solutions of block copolymers in mixed solvents has been proposed for the determination of the composition and structure of block copolymers. The addition of acetonitrile to a benzene solution of the block copolymer of styrene with methyl methacrylate gives stable colloidal dispersions of the polymer as a result of the partial displacement of the chains of the polystyrene block while the chains of the polymethyl methacrylate block remain as it were dissolved in the solvent–precipitant mixture. Analogous dispersions can be obtained by peptising dry block copolymer; in this case it is found that the dimensions of the particles in the dispersion are related to the molecular weight of the block copolymer. A model has been proposed [148] relating the dimensions of the particles, the mean-square distance between the ends of the chains, and the molecular weight of the block copolymer.

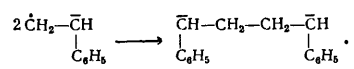
In a study of the vitrification temperature of block copolymers of acrylonitrile with methyl methacrylate [149], it was found that the value is intermediate between the vitrification temperatures of poly(acrylonitrile) and poly(methyl methacrylate), and depends to a marked extent on the structural arrangement of the monomer units in the polymer chain. This confirms the general hypothesis that the vitrification temperature of polymers is sensitive to the degree of structural order. The results of the studies showed that in this block copolymer the poly(acrylonitrile) block has a much greater influence on the properties of the block copolymer than the poly(methyl methacrylate) block.

## 2. Synthesis of Block Copolymers by Anionic Polymerisation

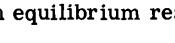
The simplest carbochain block copolymers can be synthesised by the "live" chain method proposed by Szwarc [150,151] and others [152]. In the case of styrene, anionic polymerisation can be carried out in the presence of the products of the addition of alkali metals to aromatic compounds in tetrahydrofuran. The resulting polymer molecule remains "live" during polymerisation until all the monomer is used up, as a result of which the "live" end may undergo polymerisation with new units of another monomer, added to the polymerisation system. Champetier [153] proposed the following mechanism for this block copolymerisation: naphthalene reacts with sodium or lithium to form a compound with component ratio close to 1. In tetrahydrofuran, capture of the electron of the sodium by naphthalene leads to dissociation of this compound to the $Na^+$ cation and the naphthalene radical-anion. In the presence of styrene, this radical-anion can act as an agent for the transfer of the negative charge to the styrene, with the formation of the styrene radical-carbanion.



Theoretically, there are two possible ways in which the polymerisation of styrene may begin under the influence of the styrene radical-carbanion — radical and anionic. Since in a medium of tetrahydrofuran the rate of anion polymerisation is much greater than that of radical polymerisation, however, and the styrene radical-carbanions have a tendency to combine at low temperatures by means of their radical ends with the formation of doubly-charged carbanions, in practice only anionic polymerisation takes place.



In the same paper Champetier states that the initiation of the polymerisation of the first monomer A by initiator is possible when the reduction potential of the initiator is higher or only slightly lower than the reduction potential of the monomer, since an equilibrium reaction of the type



takes place.

Initiation does not take place if the reduction potential of the initiator is appreciably lower than the reduction potential of the monomer. This also applies to the second stage of the synthesis of the block copolymer, that is, in order to obtain a block copolymer, it is necessary that the reduction potential of the polymer block be greater or only slightly less than the reduction potential of the second monomer. The block copolymers obtained with this condition usually consist of a central homopolymeric block (AAA), bounded on both sides by two different polymer blocks (BBB). If, however, the two monomers have fairly similar reduction potentials, it is possible to obtain a block copolymer whose main chain consists of several successive alternating homopolymer blocks AAA and BBB. A block copolymer with this structure was synthesised from styrene and isoprene [154] in tetrahydrofuran in the presence of the sodium naphthalenide as catalyst. Two series of block copolymers were obtained, with molecular weights 15 800 and 158 000 and the same molar ratio of homopolymeric blocks of styrene (A) to homopolymeric blocks of isoprene (B), but with different numbers and lengths of alternating blocks (A... AB... BA... AB... B). It was found that when the first (original) monomer is isoprene, the polydispersity of the block copolymers is greater, evidently due to the fact that the life of the polyisoprene chain is longer than that of the polystyrene chain.

Block copolymers of styrene with methyl methacrylate [155-157], containing about 46% styrene and 54% methyl methacrylate, are obtained by initiating the polymerisation of methyl methacrylate with "live" polystyrene at -70° in solution in tetrahydrofuran. To determine the molecular weight of the polystyrene blocks in these block copolymers, the growth of the "live" polystyrene chain in control experiments was terminated before the addition of methyl methacrylate and the light scattering of benzene solutions of the block copolymer was compared with that of solutions of the control specimen of homopolystyrene [158]. A combination of these methods and chemical analysis showed that the molecular weight of the polystyrene blocks is the same as that of the control homopolystyrene. When block copolymerisation was complete, no homopoly(methyl methacrylate) was detected, although about 50% of the polystyrene does not react; this is evidently due to the influence of deactivating impurities. Block copolymers of styrene and acrylonitrile were synthesised in analogous fashion [156,159]. Here it was found that acrylonitrile cannot form either a "live" polymer or a homopolymer. The solubility of these block copolymers in dimethylformamide increases with increase in their styrene content.

In the presence of sodium-naphthalene or sodium–biphenylide in tetrahydrofuran, "live" polymers may also be formed by 1,2-dihydronaphthalene and 2-vinylpyridine, and block copolymers of these compounds with styrene [160], containing up to five segments of homopolymer blocks, have been prepared. The viscosity of the resulting block copolymers is anomalously low, evidently due to the mutual incompatibility of the segments.

On the basis of the electron affinity of the monomers, Franta [161] studied the ability of monomers to form block copolymers under the influence of phenylisopropylpotassium of the "live" disodium tetramer of $\alpha$-methyl-styrene in tetrahydrofuran in an atmosphere of argon at -80°. The monomers studied were arranged in the following order of increasing carbanion stability and ability to initiate the polymerisation of all subsequent monomers, with the formation of block copolymers: $\alpha$-methylstyrene (1), styrene (2), isoprene (3), 2-vinylpyridine (4), 4-vinylpyridine (5), $\alpha$-vinylnaphthalene (6), $p$-bromostyrene (7), methyl methacrylate (8), methacrylonitrile (9), methyl acrylate (10), acrylonitrile (11), and ethylene oxide (12). Block copolymers are formed in good yield by the reaction of "live"

polymers of (2) with (3)–(9) and (12), (3) with (12), (5) with (8), and (7) with (8). The polymerisation of styrene is not initiated by the carbanions of (7), (8), and (9), and the polymerisation of 4-vinylpyridine is not initiated by the carbanions of (8).

Other catalysts which are often used in anion polymerisation to obtain carbochain block copolymers are the alkyllithiums: methyllithium, ethyllithium, n-propyllithium, n-butyllithium, n-pentyllithium, and their mixtures[162], and also compounds of lithium with alicyclic or aromatic radicals[163]. These have been used to prepare block copolymers of styrene with methacrylonitrile and of styrene with acrylonitrile. Block copolymers of butadiene or piperylene [penta-1,3-diene (Ed. of Translation)] with styrene, or of piperylene with isoprene, were prepared in analogous fashion[164]. Of the block copolymers obtained in the presence of alkyllithiums, the block copolymer of styrene with isoprene has been studied in most details[165]. Comparison of the curves for the nephelometric titration of the block copolymer and a mechanical mixture of the homopolymers of styrene and isoprene, with the same composition as the block copolymer, together with comparison of their ultraviolet spectra, showed that the copolymer is a block copolymer. The quantitative composition of the block copolymer was studied by measuring the partial specific volumes, by measuring the refractive indices of films of the block copolymer, and by ultraviolet spectroscopy. The equilibrium sedimentation of the block copolymer in a density gradient was also studied[166]; for this purpose a solution of the block copolymer in a mixture of butyl chloride and dichloroethane was placed in the centrifugal field of an ultracentrifuge. When equilibrium was established, the traces of homopolymers were concentrated at the foot of the cell and at the meniscus, and the block copolymer, which has an intermediate density, collected in a narrow band at a certain distance $x$ from the axis of rotation. The integral block copolymer concentration distribution close to $x$ has the form of a gaussian curve, whose width is determined by diffusion and the polydispersity of the composition.

Anionic block copolymerisation can also be carried out in the presence of metallic lithium[167,168]. The reaction is carried out in tetrahydrofuran. An interesting feature is that the reaction appears to take place as a result of instantaneous growth of the radical-ion. Metallic sodium can also be used as catalyst for this polymerisation[169,170]. A method has been described[171] for preparing block copolymers using metallic sodium; a film of sodium is treated successively with the vapours of styrene and $\alpha$-methylstyrene. The latter polymerises at the anionic end of the polystyrene with the formation of a live block copolymer radical. By repeating this operation it is possible to obtain a block copolymer with the required number of blocks. The softening temperature of the block copolymers is intermediate between that of a mixture of the homopolymers and that of a statistical copolymer of the same components, and decreases with increase in the number of blocks.

A method has been described[172] for preparing a block copolymer of ethylene with propene in the presence of a catalytic metal–Lewis acid ($TiCl_4$, $VOCl_3$) system. In this case also, polymerisation takes place by an anionic mechanism.

Stereospecific Ziegler–Natta catalysts[173] have also found extensive application in anionic block copolymerisation. For the most part these catalysts are used to obtain block copolymers of alkenes and their $\alpha$-substituted derivatives. The preparation of block copolymers of ethylene with propene with an unlimited number of homopolymer blocks of both monomers has been described[174]. To obtain these blocks of given length, it is recommended that each monomer be introduced into the polymerisation system alternately or after strictly defined time intervals[175] or until the vapour pressure of a given monomer decreases during polymerisation to a definite required value[176]. Another method for preparing these block copolymers[177] is based on the fact that the catalyst at the end of the growing chain does not lose its activity. In this method, as the polymerisation of ethylene is nearing completion, propene is added to the polymerisation system to undergo block copolymerisation with the polyethylene. This process may be repeated indefinitely to give block copolymers with a predetermined number of homopolymer blocks of both monomers. Increase in the total duration of the reaction gives block copolymers with a high characteristic viscosity, and increase in the propene content gives a polymer with higher density.

It has been shown possible[178] to apply rheological analysis to block copolymers of this type. Analogous methods may be used to obtain block copolymers of pent-1-ene, oct-1-ene, cyclohexene, butadiene, or isoprene with allyl bromide or chloride, methallyl chloride, isoprene, butadiene, styrene, but-1-ene, oct-1-ene, and chloroprene[179], and of ethylene with but-2-ene.[180] Infrared spectroscopy and X-ray diffraction showed[181] that block copolymers of acrylonitrile with vinyl acetate, methyl methacrylate, or styrene have a lower crystallinity than the homopolymers of these monomers, obtained under analogous conditions. A number of published facts[182] indicate that when certain catalytic systems such as $TiCl_4 + LiAlR_4$ or $VOCl_3 + AlR_2Cl$ are used, growth of the macromolecules continues for several days. These "long-lived" macromolecules were used for the synthesis of block copolymers of ethylene with propene and of ethylene with but-1-ene, with different types of distribution of the monomer units in the blocks. By varying the method of preparing the block copolymers, it was possible to obtain polymers with different structures, from crystalline to amorphous. The molecular conformation of the polymer and its hydrodynamic and mechanical properties were studied[183] for the case of the block copolymer of styrene with isoprene in the ratio 4 : 5. The molecular configuration of this block copolymer was investigated in the course of a study of the characteristic viscosity, diffusion, and sedimentation of the polymer in benzene, which is an effective solvent for both homopolymeric blocks, and also in ethyl methyl ketone and octane, which are selective solvents for the polystyrene and polyisoprene blocks respectively. It was shown that in the selective solvents, the insoluble blocks form globules but are retained in solution by the blocks which are "soluble" in the given solvent. This leads to a departure from the relationship connecting $\langle r^2 \rangle^{1/2}$ with $[\eta]$ and $D$, derived by Flory for flexible chain macromolecules, whereas this relationship is satisfied completely for the same block copolymer in benzene. Study of films of block copolymers obtained from selective solvents showed that the globular structure of the "insoluble" blocks is preserved completely after removal of the selective solvent, so that the film of block copolymer, obtained from solution in octane, behaves like rubber with a chemically bound filler, and the film obtained from solution in ethyl methyl ketone behaves like plasticised polystyrene.

The polymerisation of diazo-compounds in the presence of boron trifluoride or its derivatives takes place by a mechanism identical with that of the polymerisation of alkenes in the presence of Ziegler–Natta catalysts.

The macromolecules of the type $X_2B-(CHR)_n-X$ formed as a result of polymerisation are able in turn to initiate the polymerisation of freshly prepared diazo-compounds with the formation of block copolymers of the type $X_2B-(CHR)_n-(CHR')_m-X$. A polymerisation mechanism has been proposed[184], similar to that of the polymerisation of ethylene in the presence of alkylaluminiums, involving coordination of the diazoalkanes with the boron catalyst and subsequent migration of the groups initially bound to the boron atom. Analogous derivatives containing boron were observed in the reactions of diboranes with dialdehydes and ketones. Alkylene oxides can also react with diborane with the formation of products of the type $H_2B(OCH_2CHR)_nH$ and $HB\begin{smallmatrix}(OCH_2CHR)_xH\\(OCH_2CHR)_yH\end{smallmatrix}$. These reactions, as noted above, are similar to the polymerisation of alkenes, catalysed by alkylaluminiums, since both reactions include the stepwise anionic growth of the metal–alkyl chain. Since the diazoalkane has much higher nucleophilic activity than ethylene, it can, unlike ethylene, react with alkylborons. Alkylaluminiums in turn have a higher electrophilic activity than the corresponding alkylborons, so that it is to be expected that diazo-compounds will undergo block copolymerisation when initiated with alkylaluminiums more readily than the corresponding alkenes.

An ionic mechanism involving anionic and cationic polymerisation stages was proposed[185] for the preparation of block copolymers of $\alpha$-methylstyrene and isobutene with acrylonitrile and with acrylates. The $\alpha$-methylstyrene or isobutene is polymerised by a cationic mechanism with the formation of positive ions at the ends of the growing chains. Acrylonitrile or acrylates in turn polymerise by an anionic mechanism to give macromolecules containing terminal negative ions. The reaction of these growing macromolecules with ions of opposite sign at the ends of the chains gives the corresponding block copolymers.

Anionic polymerisation is also used to prepare the so-called stereo-block copolymers, consisting of polymeric molecules containing alternating, relatively long polymeric fragments with different spatial configurations, formed from the same monomer. These macromolecules may consist of isotactic and atactic segments, or of isotactic segments alone, with different spatial configurations. The mechanism of their formation was examined by Natta[186] on the basis of the assumption that two processes take place simultaneously — chain growth and a process in which inversion of configuration takes place. In practice, amorphous polymers, regarded as atactic, may contain very short stereo-blocks[187], which have not yet been isolated in pure form. The stereo-block copolymers of $\alpha$-alkenes, with relatively long segments with definite spatial configurations, are usually isolated from a mixture of the amorphous and crystalline polymers by extraction with selective solvents[188,189] with increasing solvent power for the given polymer. In this way it is possible to separate the amorphous polymer and stereo-block copolymers with different crystallinities[190-193]. Natta[194] showed, however, that the fractionation method is not always applicable to the separation of stereo-block copolymers of propene, since the solubility of the polymer usually depends not only on the degree of crystallinity but also on its molecular weight and structure. The separation of stereo-block copolymers differing only in their degree of crystallinity can be carried out successfully on a chromatographic column with a substrate of isotactic polypropene. In a study of the mechanical properties of the stereo-block copolymer of propene[195], it was found that at a high degree of isotactic character, when the macromolecule contains very small atactic segments, the fibres obtained from a melt of the block copolymer have a high strength.

A stereo-block copolymer of methyl methacrylate, consisting of alternating isotactic and atactic or syndiotactic and atactic polymeric blocks is obtained by the radical and anionic polymerisation of methyl methacrylate at low temperatures[196-198]. The isotactic-syndiotactic stereo-block copolymer of methyl methacrylate is obtained by polymerising methyl methacrylate in the presence of 9-fluorenyllithium at -70° in a medium of toluene[199]. This type of stereo-block copolymer crystallises readily[200,201] from pentyl acetate, heptan-4-one, and octan-3-one. The stereo-block copolymer of styrene can be isolated by extracting polystyrene synthesised in the presence of titanium-containing organometallic catalysts and washed beforehand with dry diethyl ether[202]. A method has been described for preparing linear stereo-block copolymers of propene, but-1-ene, and pent-1-ene, with macromolecules containing isotactic crystallising sections with asymmetric carbon atoms with the same spatial configuration, and also non-isotactic non-crystallising sections[203,204]. In the isolation of these stereo-block copolymers, the resulting mixture of polymers is separated by extraction with selective solvents, which dissolve first the non-isotactic polymers and then the stereo-block copolymers with gradually-increasing degrees of crystallinity. It has been reported that stereo-block copolymers can also be obtained from the dialkenes butadiene and isoprene[205]. It was suggested[206] that under the conditions of the stereospecific polymerisation of isobutyl vinyl ether[207,208], a stereo-block copolymer whose macromolecule consists of *d*- and *l*-isotactic segments and several atactic segments, distributed along the polymer chain, is also formed.

In the study of stereo-block copolymers, the proportion of isotactic and syndiotactic fragments can be determined by infrared spectrocopy[209,210] and the three-dimensional structure as a whole can be determined by measuring the heats of fusion[211,212] or by nuclear magnetic resonance studied on instruments with a high resolving power[213,214]. The three-dimensional structure of the stereo-block copolymer of styrene can also be determined from the difference in the rates of hydrolysis of the benzanilides of the atactic and isotactic segments of the polymer[215], which are readily obtainable from polystyrene and consist of the polyvinyl benzanilides with the corresponding spatial configurations.

### 3. Synthesis of Carbochain Block Copolymers by the Combination of Polymer Blocks, Containing Chemically Active Terminal Groups, by Means of Low-Molecular Bifunctional Compounds

To obtain homochain polymer blocks containing chemically active terminal groups, Bamford and Jenkins[216] proposed that the polymerisation of the original monomer be initiated using organic compounds containing two azo-groups and a functional group capable of reacting with hydroxyl or carboxyl groups. By initiating the polymerisation of styrene, acrylonitrile, and methyl methacrylate with $\gamma,\gamma'$-azo-$\gamma$-cyanovaleric acid or $\delta,\delta$-azo-$\delta$-cyano-n-pentanol, they prepared[217] homopolymeric blocks of styrene, acrylonitrile, and methyl methacrylate containing carboxyl or hydroxyl groups. To obtain macromolecules with a relatively low molecular weight and relatively high concentration of active terminal groups in the mixture of poly-

mer homologues, they suggested the use of an apparatus which makes it possible to carry out this process continuously. Block copolymers can be synthesised from the macromolecules with active terminal groups prepared in this way, by two methods: (1) by direct combination of two macromolecules, or (2) by the combination of two macromolecules by means of low-molecular bifunctional compounds such as decamethylene glycol.

In a study of the resulting block copolymers, Bamford and Jenkins[218] found that the molecular-weight distribution of these block copolymers is a function of the molecular-weight distribution of the original homopolymer blocks, the duration of the reaction, and the chemical properties of the reactive terminal groups. Using the method of Laplace transformations, they derived a general equation which makes it possible to use the measured characteristic viscosity to reach conclusions regarding the ratio of the final and initial mean polymerisation coefficients.

## III. CARBO-HETEROCHAIN BLOCK COPOLYMERS

Carbo-heterochain block copolymers, like carbochain block copolymers, can be obtained by various mechanochemical methods. The degradation of the polymer chains for the formation of reactive macroradicals is achieved using various grinding assemblies[219-222], by means of the electrohydraulic effect[46,47,223], and also by the freezing and subsequent melting of aqueous solutions of the polymers[224-226].

Carbo-heterochain block copolymers can also be obtained by anionic or radical polymerisation, by polycondensation, and by combining carbochain blocks with heterochain homopolymeric blocks.

### 1. Synthesis of Carbo-Heterochain Block Copolymers by Ionic Polymerisation

By analogy with the synthesis of carbochain block copolymers, carbo-heterochain block copolymers can be synthesised by Szwarc's "live" chain method. This method has been used to synthesise block copolymers of isoprene with ethylene oxide[161], of styrene with ethylene oxide, and of styrene with propene oxide[227]. This gives block copolymers of two types: polystyrene–poly(alkylene oxide) and poly(alkylene oxide)–polystyrene–poly(alkylene oxide). The polymeric products formed in the reaction always contain the alkylene oxide homopolymer in quantities corresponding to 46.4–73.6% of the total poly(alkylene oxide) content[228], probable due to the presence, in the polymerisation system, of traces of moisture, alkali, or oxygen, which terminate the growth of the block copolymer chain. In a study of the block copolymer of the second type in the block copolymer–water–ethylbenzene system[229], it was found that in these systems the block copolymers form mesomorphic gels resembling the nematic structures in the systems formed by water with low-molecular soaps. Study of the resulting birefringent structures by means of X-rays and the polarisation microscope showed that the hydrophobic polystyrene blocks, in the mixture with ethylbenzene, are localised with the formation of a hexagonal liquid-crystalline lattice in cylindrical regions with parallel orientation; the space between these regions is filled with a mixture of the hydrophilic poly(ethylene oxide) blocks and water. Each of the separate homopolymer blocks of the block copolymer has the configuration of a statistical coil. The equilibrium diagram shows clearly an immiscibility zone in which the gel is present in equilibrium with the isotropic liquid. At low concentrations of block copolymer, separation of the phases also takes place, and the aqueous and ethylbenzene layers can be separated by centrifuging. Mesomorphic gels are also formed in binary systems if the solvent is an effective solvent for the poly(alkylene oxide) blocks and an ineffective solvent for the polystyrene blocks, or vice versa. The gels may be nematic or smectic, depending on the nature of the solvent, but in both cases they are extremely stable.

The influence of the nature of the solvent on the structure of the mesomorphic gels of the block copolymers of styrene with ethylene oxide have also been studied by the method involving the scattering of X-rays at small angles in nitromethane, which is a solvent for the poly(ethylene oxide) and a precipitant for polystyrene, and in butyl phthalate, which is a solvent for polystyrene and a precipitant for poly(ethylene oxide)[230]. Mesomorphic gels of the block copolymer of styrene with ethylene oxide are formed in solutions in acrylic acid, which is a solvent for poly(ethylene oxide) and a precipitant for polystyrene, and in methyl methacrylate, which is a solvent for polystyrene and a precipitant for poly(ethylene oxide). When these systems are iradiated with ultraviolet light[231], the monomer present in the system polymerises in the presence of the mesomorphic phase, ensuring the production of a solid protective mesomorphic gel structure and forming a copolymer with an ordered structure. The irradiation of the "block copolymer of styrene with ethylene oxide–acrylic acid" system gives a copolymer of acrylic acid, whose gel has a cylindrical structure up to a concentration of block copolymer in the system equal to 90%, and a lamellar structure at other concentrations. The "block copolymer of styrene with ethylene oxide–methyl methacrylate" system under analogous conditions forms only a lamellar structure. The cylindrical structures were evidently formed by the aggregation of "cylinders" of polystyrene blocks surrounded by a solution of the poly(ethylene oxide) blocks, and the lamellar structure by a combination of alternating layers of "crystalline" poly(ethylene oxide) blocks and a polystyrene blocks in solution respectively.

Anion polymerisation can also be used to prepare carbo-heterochain block copolymers with general formula:

$$CH_3(C_2H_4)_n C(R')(R'')O[CH_2CH(R''')O]_m CH_2CH(R''')OH,$$

where R′ and R″ are alkyl groups with 1–4 carbon atoms, R‴ = H, $CH_3$, or $C_6H_5$, $n$ = 30–250, and $m$ = 1–70. These block copolymers are obtained by the reaction of polyethylene telomers, modified by monohydrie aliphatic alcohols or dialkyl ketones, with alkylene oxides in the presence of Na, Ce, Li, K, $NaOCH_3$, NaOH, or KOH in the molten state at 110–200° or in aqueous emulsion[232]. The block copolymer of acrylonitrile with ethylene oxide is obtained by polymerising acrylonitrile under the influence of the sodium salt of polyethylene glycol[233]. The composition of this block copolymer can be studied by infrared spectroscopy.

### 2. Synthesis of Carbo-Heterochain Block Copolymers by the Combination of Polymer Blocks, Containing Chemically Active Terminal Groups, by Means of Low-Molecular Bifunctional Compounds

Carbo-heterochain block copolymers of the polystyrene–poly(ethylene oxide)–polystyrene and polystyrene–poly(ethylene oxide) types are prepared by the combination of

polyhydroxyéthylene glycol with polystyrene containing one or two terminal acid chloride groups and prepared by the reaction of "live" polystyrene with phosgene[228].

It is also possible to synthesise carbo-heterochain block copolymers based on 2,2-di-(4-hydroxyphenyl)propane polycarbonate. These are prepared by linking polystyrene with low-molecular 2,2-di-(4-hydroxyphenyl)propane polycarbonate containing terminal hydroxyl groups[234]. Polycarbonate blocks with low molecular weight, controllable within narrow limits, are obtained by varying the concentration of the original substances and the reaction temperature, and polystyrene blocks with terminal hydroxyl groups are prepared by hydrolysing a polymer obtained in the presence of benzoyl peroxide and containing terminal benzoxy-groups. The presence of flexible blocks in the block copolymer chain facilitates ordering of the polycarbonate, which forms flexible polymers with a high melting point. It was found[235] that during the bulk polymerisation of a mixture of styrene with $\beta$-propiolactone in the presence of an initiator of the radical type, the product is a copolymer, hydrolysis of which, followed by treatment with poly(ethylene oxide), gives a carbo-heterochain block copolymer.

### 3. Synthesis of Carbo-Heterochain Block Copolymers by Radical Polymerisation

A method was recently developed for preparing polymeric peroxide initiators[236], making it possible to carry out carbo-heterochain block copolymerisation by the radical-polymerisation method. These initiators are prepared by polymer-analogue transformations from aliphatic or aromatic polyesters containing terminal carboxyl or acid chloride groups at the surface of separation between the two phases. On thermal decomposition, these initiators form macroradicals capable of initiating the block copolymerisation of vinyl monomers, which polymerise by a radical mechanism. This method has been used to synthesise a block copolymer of a polyester of hydroxyheptanoic acid with poly(methacrylic acid). Unlike poly(methacrylic acid), the resulting block copolymer is fusible, soluble in a mixture of acetone and methanol, and insoluble in water.

An extremely promising method for the production of fibres involves the use of carbo-heterochain block copolymers which may be partly or completely crystalline according to the crystallising ability of the homopolymer fragments which alternate regularly in the main chain of the block copolymer. The carbo-heterochain block copolymer of acrylonitrile with 10–40% of compounds such as poly(vinyl alcohol), poly(ethylene oxide), starch, cellulose, and poly(acrylic acid) can be used[237] to prepare readily dyed fibres using ordinary shaping methods.

## IV. HETEROCHAIN BLOCK COPOLYMERS

Heterochain block copolymers were first found in natural macromolecular compounds. In a study of silk fibroin, consisting of a polypeptide chain[238], it was found that the amino-acids are arranged in the chain in an ordered fashion. X-Ray diffraction study of the same silk fibroin[239] established that its molecule, with molecular weight ~30 000, consists of three segments of an ordered structure with molecular weight ~7000, separated by amorphous segments with molecular weight ~5000. This indicated that silk fibroin is a natural heterochain stereo-block copolymer. A number of block copolymers of cellulose were prepared by synthesis[240]. It was found[241] that substitution in cellulose under heterogeneous conditions in most cases gives heterochain block copolymers containing large segments of unchanged glucose residues, located chiefly in crystalline regions. The glucose residues in the amorphous regions are very sensitive to the action of substituents. X-Ray structural analysis shows that up to a degree of substituion in the cellulose equal to 25–35%, no changes are observed in the crystalline regions. The resulting block copolymer combines the properties of rigidity and strength, associated with the crystalline regions, with elasticity and flexibility, asociated with the substitution in the amorphous regions.

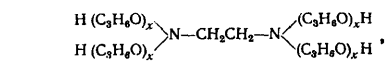
Synthetic heterochain block copolymers can be obtained by ionic polymerisation, polycondensation, the combination of heterochain polymeric blocks containing chemically active terminal groups, inter-phase polycondensation, and exchange reactions.

### 1. Synthesis of Heterochain Block Copolymers by Ionic Polymerisation

This method has been used to prepare heterochain block copolymers of formaldehyde with various polymeric blocks containing active terminal hydroxyl, sulphydryl, carboxyl, or primary amino-groups[242]. For example, the polymerisation of 99% pure formaldehyde in the presence of dimethyldialkylammonium hydroxide and poly(tetramethylene glycol) with molecular weight ~7000 gives a block copolymer containing 73% poly(methylene oxide) units. This block copolymer is less crystalline but has a higher impact strength than the formaldehyde homopolymer[243]. The preparation of block copolymers of diisocyanates or bisepoxy compounds with linear polyesters containing terminal hydroxyl groups has been described[244]. X-Ray structural analysis of these block copolymers indicates the presence of crystalline regions with structures identical with that of the crystallites of the homopolymers. Some block copolymers with low glass points and low degrees of crystallinity, such as poly(ethylene terephthalate)–poly(ethylene adipate), are rubberlike materials with high strength. The block copolymers of ethylene oxide with propene oxide[245] have found extensive application as non-ionic detergents. A poly(propene oxide) block containing a terminal hydroxyl group is used as the original hydrophobic fragment of the block copolymer chain[246–248]. When ethylene oxide is added to this macromolecular glycol, its terminal groups initiate block copolymerisation with the formation of a block copolymer with general formula:

$$HO-(CH_2CH_2O)_x-(C_3H_6O)_y-(CH_2CH_2O)_xH.$$

The physical properties of these block copolymers may be varied over a wide range to give mobile liquids (40% ethylene oxide), waxy products (50% ethylene oxide), and hard solids (70% ethylene oxide). Analogous methods can be used to prepare block copolymers of propene oxide and ethylene oxide with ethylenediamine[249], since the reaction of propene oxide with ethylenediamine gives a macromolecular compound with general formula



whose terminal groups are able to initiate the polymerisation of ethylene oxide with the formation of a block copolymer.

Block copolymers of alkene 1,2-oxides, with general formula $R''(RCHRCHO)_n-(R'CHR'CHO)_mH$, where R and R' represent the H atom or a hydrocarbon radical, and R'' the radical in the catalyst molecule, are obtained in two stages[250]. In the first stage, the polymerisation of the alkylene oxide $\overrightarrow{RCHRCRO}$ is initiated by organometallic catalysts, and in the second stage the polymerisation of the other alkene oxide $R'\overrightarrow{CHR'CHO}$ is initiated by the primary polymer block containing active terminal groups. When alkaline or acidic catalysts are used in the first stage of the block copolymerisation, it is possible in analogous fashion to obtain block copolymers of alkyl glycidyl esters with ethylene oxide. Block copolymers of this type have found application as surface-active agents[251]. It was found that the surface-active properties of these block copolymers deteriorate sharply with increase in the length of the lateral groups.

In a study of block copolymers of the poly(ethylene oxide)–poly(propene oxide)–poly(ethylene oxide) type[252], it was found that in benzene solution these copolymers form inclusion compounds with urea and thiourea. Viscosimetric determination of the molecular weights of these inclusion compounds showed that there is an appreciable fractionating effect.

The ion polymerisation method was also used to prepare heterochain stereo-block copolymers[253]. For example, the polymerisation of acetaldehyde in the presence of partly hydrolysed aluminium alkoxide gave a stereo-block copolymer of acetaldehyde, whose structure was confirmed by solubility data, infrared spectroscopy, and X-ray structural analysis. This stereo-block copolymer is less elastic than atactic amorphous polyacetaldehyde. Its solubility is intermediate between the solubilities of the crystalline and amorphous polymers[254].

### 2. Synthesis of Heterochain Block Copolymers by Polycondensation

This method for preparing the heterochain block copolymers has been very little studied, and is used chiefly for modifying the properties of polyesters used in the production of synthetic fibres. It has been used to prepare block copolymers of ethylene terephthalate with poly(ethylene oxide) by heating a mixture of dimethyl terephthalate, ethylene glycol, and poly(ethylene oxide) at 200–275°, in the presence of PbO. Study of the properties of this block copolymer[255] showed that the introduction of poly(ethylene oxide) blocks with molecular weight 1000–6000 into the polymer increases the hydrophilic character of the polymer, its flexibility, and the ease with which it can be dyed. The degree of crystallinity, strength, and ductility shown by this block copolymer, are almost the same as those for polyethylene terephthalate, but the stability to the action of ultraviolet light is much lower. At concentrations of poly(ethylene oxide) in the block copolymer up to 20%, the mechanical properties deteriorate[256] due to the decreased concentration of crystalline fraction in the fibre.

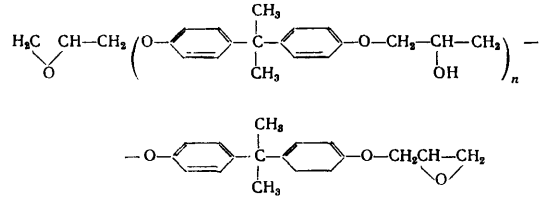
### 3. Synthesis of Heterochain Block Copolymers by the Combination of Polymer Blocks Containing Chemically Active Terminal Groups

This method, involving the introduction of flexible and elastic blocks of one polymer into the main chain of another polymer with a rigid structure, can be used to modify macromolecular compounds such as polycarbonates[257]. As a result of the presence of these blocks, which alternate regularly in the main chain of the block copolymer, the final product is also elastic. For example, the block copolymer formed by the combination of polycarbonate blocks with poly(tetramethylene oxide) is an elastomer[234]. More frequently, however, the polymeric blocks are joined by means of low-molecular bifunctional compounds such as diisocyanates, with the formation of heterochain polyester–urethane block copolymers[258,261].

The methods for preparing these block copolymers are varied. For example, a polyester with a molecular weight of several thousand, obtained by the polycondensation of adipic acid with ethylene glycol, is treated with an excess of diisocyanate to join the polyester blocks. The isocyanate groups formed at the ends of the chain are in turn capable of reacting with water, glycols, or diamines, with the formation of substituted ureas[262]. Analogous methods are used to prepare block copolymers of poly(ethylene terephthalate) with poly(ethylene succinate), poly(ethylene adipate), poly(ethylene azelaate), poly(ethylene sebacate), poly(ethylene phthalate), poly(ethylene isophthalate), and poly(diethylene adipate)[263]. Tetramethylene diisocyanate is used as linking agent. The properties of these block copolymers differ considerably, depending on the chemical nature of the original polyester blocks. The degree of crystallinity of the reactants and products can be determined by X-ray structural analysis and from the temperature of the second-order transformation.

It is possible to obtain a rubberlike elastic heterochain block copolymer suitable for the production of fibres and films[264] by using as the original polymer blocks, polyesters prepared by the polycondensation of glycol with an aliphatic dicarboxylic acid or with an asymmetric aromatic dicarboxylic acid and poly(ethylene terephthalate), and by using tetramethylene diisocyanate as linking agent. The preparation of block copolymers by the combination of statistically mixed polyesters using diisocyanates has also been described[262]. These block copolymers have a lower strength than the analogous block copolymers consisting of two components, evidently because of the irregularity of the polyester chain, resulting from the introduction of a third component into the polyester block[265]. The use[266] of symmetrical aromatic diisocyanates as linking agents instead of aliphatic diisocyanates improves the physical properties of the resulting block copolymer. With increase in the "diisocyanate : polyester" ratio, the molecular weight of the heterochain block copolymer increases, with a corresponding increase in the viscosity of the dilute solutions, the Mooney plasticity, and the softening temperature. It was found[267] that in order to obtain polyester-urethane block copolymers with increased elasticity it is best to link the original polyester blocks by means of diisocyanates with three alkyl substituents. The physical properties of these block copolymers are also influenced to a marked extent by the crystallinity of the original polyester blocks[268]. For example, polyethylene terephthalate and polyethylene adipate are crystalline, and the physical properties of block copolymers based on these compounds are almost identical with those of the homopolymers. If, however, the crystallinity of one of these blocks is broken down, for example, by the introduction of a non-crystalline segment such as poly(propene adipate), the impact strength of the block copolymer increases, but all the other mechanical properties deteriorate, in almost direct proportion to the concentration of added polymer block, which acts as an internal

plasticiser. Heterochain block copolymers can also be obtained from epoxide resins of the type



(synthesised by the usual methods and containing active terminal epoxy-groups[269]) by the reaction with phenol–formaldehyde and urea–formaldehyde resins, polyamides, etc. Block copolymers of this type, prepared by the reaction of ED-5 and ED-6 with dimethylresorcinol resin, are used to impregnate glass fibres for the production of glass-fibre-reinforced plastics. Lacquer from this block copolymer, and glass fabric impregnated with it, remain stable for 2–2.5 months[270]. The fusion of phenol–formaldehyde and other polycondensation resins with polyesters, and also the treatment of Novolaks first with a polyhydric alcohol and then with a polybasic acid, was used by Petrov to obtain a number of heterochain block copolymers, which he called joint resins[271].

### 4. Synthesis of Heterochain Block Copolymers by Inter-Phase Polycondensation

Study of inter-phase polycondensation showed that this method can be used to prepare macromolecular compounds for the synthesis of heterochain block copolymers[272].

The block copolymers are prepared by the reaction of polymeric blocks containing terminal acid chloride and hydroxyl groups[273] at the phase boundary between two immiscible solvents[274]. The preparation of analogous block copolymers by the reaction of polyester blocks containing terminal hydroxyl groups with a mixture of the acid chlorides of dicarboxylic acids and diphenols has been described[275]. Similar block copolyesters[276] can be prepared by the joint condensation of two polyesters, for example, poly(ethylene terephthalate) and poly(ethylene isophthalate)[277].

### 5. Method Based on Inter-Chain Exchange Reactions

When two homopolyesters are fused together, a statistical copolymer is obtained[278]. In a study of the inter-chain reaction between polyester macromolecules, Korshak and coworkers[279] established that the process involves degradation and intermolecular exchange, as a result of which block copolymers are formed as intermediate products. This work enabled a number of authors to prepare various block copolymers by exchange reactions[280]. The use of CaO as catalyst for the reaction was proposed[281]. In analogous fashion, Flori[273] prepared block copolyesters using macromolecules containing terminal acid chloride and hydroxyl groups as original homopolyester blocks. In this case the formation of the block copolyesters most probably takes place both by the interaction of the active terminal groups of the polyesters and by the inter-chain exchange reaction. To increase the ease with which the fibres based on poly(ethylene terephthalate) can be dyed, Kresse[282] used exchange reactions to synthesise a number of block copolyesters of poly(ethylene terephthalate). In a study of the reaction conditions, he found that one of the decisive factors influencing the rate of redistribution is the viscosity of the components of the block copolycondensation Beginning with the formation of macromolecules of definite magnitude, the exchange reactions proceed predominantly by an intermolecular exchange mechanism; the block copolyester formed at the start of the reaction is converted into a mixed polyester in the subsequent stages of the reaction. The formation of block copolyesters in the poly(ethylene terephthalate) macromolecule was proved by extracting the products of the joint polycondensation. A fibre capable of undergoing subsequent orientation was formed from the resulting block copolyesters.

Mixed polyamides have been prepared in analogous fashion by fusing two polyamides together[283]. It is possible that when two different polyamides are fused together, exchange reactions take place, and the formation of the mixed polymers passes through a stage involving the formation of block copolymers[284]. Experimental confirmation of this suggestion was found in work by Ayers[285]. In a study of the formation of the statistical copolyamide based on nylon-6,6 and nylon-6,10 by distribution chromatography on paper, Ayers showed that formation of the block copolymers begins approximately half an hour after the start of the reaction, and that in the subsequent reaction these block copolymers are completely converted into the mixed polyamide. More detailed study of this reaction[286] showed that as the mixture of polyamides is heated there is a decrease in the temperature of flow and an increase in the solubility and tensile strength. The block copolymers formed in the reaction have a comparatively short life, of the order of 3–5 h. Analogous results were obtained in a study of inter-chain reaction for the case of the preparation of a mixed polyamide from poly(hexamethylene adipamide) and poly(hexamethylene sebacamide)[287]. The rate of the inter-chain reaction is increased considerably by the addition of small quantities of hexamethylenediammonium adipate, which catalyses side reactions. This catalyst also accelerates the subsequent conversion of the intermediate block copolymer into the mixed polyamide[288]. Inter-chain reaction has also been used to prepare heterochain block copolymers of polyamides with various thermosetting resins[289]; for this purpose the mixture of polyamide and epoxide resin is heated at 240–290° in the presence of t-butyl peroxide. When poly(aminotriazole) blocks are heated[290], only very stable block copolymers are formed, and on subsequent heating these are converted into a mixed polymer. The authors attribute this to the fact that in this polymeric system there is no inter-chain exchange reaction and the block copolymers are formed only by the reaction of the terminal groups of the homopolymers. Inter-chain reaction was recently used[291] to give a new type of heterochain block copolymer, consisting of mixed polyamido-esters. Polymeric products of this type are of considerable practical interest, since they open up the possibility of preparing polymers with a new combination of properties, based on previously prepared polymers. The formation of these mixed polymers in the first stage of the process, as in the case of mixed polyamides, is said to pass through a stage involving the formation of block copolymers, which apparently can be isolated in pure form under suitable conditions.

Modern methods of organic synthesis are making it possible to extend considerably the number of block copolymers. In addition to the synthesis of new block copolymers, it is necessary to pay particular attention to the

study of the dependence of the properties of block copolymers on their composition, the magnitude and number of the blocks, the sequence of the blocks, etc. The elucidation of this dependence will make it possible to achieve deliberate control of the synthesis of block copolymes and to obtain polymers with a desired range of properties.


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# PROGRESS IN THE CHEMISTRY OF THE CARBODIIMIDES

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## 1. INTRODUCTION

The carbodiimides form a class of organic compounds the membership of which is determined by the presence of the carbodiimide grouping $-N=C=N-$. The general formula of the carbodiimides may be represented as follows:

$$R-N=C=N-R',$$

where R and R′ are alkyl or aryl groups.

Carbodiimides may be regarded as alkyl (aryl) derivatives of the simplest representative of the class HN=C=NH, which exists mainly as the tautomeric form of cyanamide, $H_2N-C\equiv N$.[1] Carbodiimides form one of several classes of organic compounds with cumulative double bonds (isocyanates, ketens, allenes, ketenimines). Although some aromatic carbodiimides were first synthesised 80 years ago, it is only in recent years that interest in them has been aroused[1]. Recently polymeric carbodiimides $(-R-N=C=N-)_x$ with fibre- and film-forming and other valuable practical properties have been obtained.

In Russian literature there are only references of the most general kind to the carbodiimides[2].

## 2. PREPARATION OF CARBODIIMIDES

Up to recently the method of synthesising carbodiimides by eliminating hydrogen sulphide from disubstituted thioureas had the most importance preparatively[3].

$$RNHCSNHR' \xrightarrow{-H_2S} RN=C=NR'.$$

The starting thioureas are obtained from amines or disulphides. Aliphatic amines first form the salt of a substituted dithiocarbamic acid:

$$RNHCS\overline{S}R'\overset{+}{N}H_3 \xrightarrow{t^\circ} RNHCSNHR'+H_2S.$$

The thioureas are treated with mercury(II) oxide, lead(II) oxide, or sodium hypochlorite, and carbodiimides are formed. A large number of aliphatic, aromatic, and mixed carbodiimides have been synthesised in this way. When thioureas are treated with mercury(II) oxide or sodium hypochlorite the yield of carbodiimides is fairly high: with dicyclohexylcarbodiimide the yield reaches 90%.[4-10]

In an original method of preparing dicyclohexylcarbodiimide developed by Amiard, water is eliminated from *NN'*-dicyclohexylurea with the aid of *p*-toluenesulphonyl chloride and pyridine[11]. The starting symmetrical dicyclohexylurea is obtained in good yield by heating urea with cyclohexylamine:

$$2C_6H_{11}NH_2 + NH_2CONH_2 \rightarrow C_6H_{11}NHCONHC_6H_{11} + 2NH_3,$$

$$C_6H_{11}NHCONHC_6H_{11} + 2p\text{-}CH_3C_6H_4SO_2Cl \longrightarrow$$

$$\longrightarrow C_6H_{11}N=C=NC_6H_{11} + (p\text{-}CH_3C_6H_4SO_2)_2O + 2HCl.$$

Diethylcarbodiimide was first synthesised by the interaction of ethyl isocyanate and tetraethylphosphine imide; the latter can be obtained from triethylphosphine and ethyl azide[12]:

$$(C_2H_5)_3P+C_2H_5N_3 \rightarrow (C_2H_5)_3P=NC_2H_5+N_2,$$

$$(C_2H_5)_3PNC_2H_5+C_2H_5NCO \rightarrow C_2H_5N=C=NC_2H_5+(C_2H_5)_3PO.$$

Some aromatic carbodiimides were first prepared by the prolonged heating of isocyanates. For example, diphenylcarbodiimide is prepared by heating phenylisocyanate for 24 h at 180° in the absence of air[13]:

$$2C_6H_5NCO \longrightarrow C_6H_5N=C=NC_6H_5+CO_2.$$

Prolonged heating converts diisocyanates into polycarbodiimides. Thus, when methylenebis-(4-phenylisocyanate) was heated at 220° in the absence of air, the content of isocyanate groups fell from 33.5 to 25.8% in 11 h and to 22.8% in 24 h and methylenediphenyl-4,4'-poly(carbodiimide) was formed. An empirical formula relating the degree of conversion of isocyanates into carbodiimides with the temperature and duration of the reaction has been derived from a study of the kinetics of the thermal conversion of a number of isocyanates into carbodiimides[14]:

$$g = 100 - at^2,$$

where $g$ is the amount of unreacted isocyanate groups expressed as a percentage of the initial quantity, $t$ the time of heating in hours, and $a$ an empirical temperature coefficient (at 220° this varies from 0.1 to 0.6, and at 180° it varies from 0.01 to 0.06).

It has been demonstrated that the thermal conversion of isocyanates into carbodiimides is autocatalytic.

The conversion of isocyanates into carbodiimides on heating presumably proceeds through intermediate unsymmetrical cyclic dimers. The decarboxylation of such dimers is greatly facilitated by the non-uniform distribution and displacement of electron density in the ring[15]:



The method of preparing carbodiimides by heating isocyanates has not been widely used because a large amount of by-products is formed in the reaction.

The method of preparing carbodiimides by the catalytic decarboxylation of isocyanates, which has been developed in recent years, is in practice the most important method[16-23]. Carbodiimides are prepared by this method by adding a decarboxylation catalyst to isocyanates, in the pure state or in an inert solvent; heating for several hours produces a vigorous evolution of carbon dioxide and carbodiimides are formed in high yield

$$2RNCO \xrightarrow[\text{catalyst}]{t^\circ} RN=C=NR+CO_2.$$

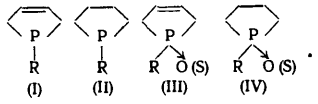
The following examples illustrate the method. *p*-Nitrophenylisocyanate is heated with catalyst (1-ethyl-3-methyl--3-phospholine-1-oxide) and there is a vigorous evolution of carbon dioxide; after 1–2 min the reaction mass solidifies and, after removal of the residual carbon dioxide, 4,4'-dinitrophenylcarbodiimide is obtained in 100% yield[19].

Aliphatic carbodiimides are formed in low yield by this method, but the yield of product can be increased, however, by selecting suitable conditions. Thus, when 50 g of butylisocyanate was boiled with 0.7 g of 3-methyl-1--phenylphospholen 1-oxide for 15 h only 6.2 g (15.5% yield) of dibutylcarbodiimide was obtained; when, however, the same amount of butyl isocyanate was heated in decahydronaphthalene with double the amount of catalyst, 24 g (60% yield) of dibutylcarbodiimide was obtained 15 min after the beginning of the reaction[20]. Diethylcarbodiimide has been obtained in 50% yield by heating a solution of ethyl isocyanate in toluene (1 : 1 by volume) in the presence of 3-methyl--1-phenylphospholen 1-oxide (3% of the weight of isocyanate) for 6 h at 100–105°.[17]

Polycarbodiimides are obtained from diisocyanates by the same method. The reaction is, as a rule, carried out in a solvent (light petroleum, benzene, toluene, xylene) in the presence of 2–3% of decarboxylation catalyst.

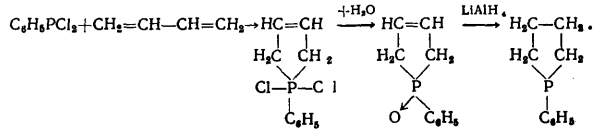
A great many compounds have been used as catalysts for the decarboxylation of isocyanates. However, the greatest catalytic activity is shown by substituted phosphocyclopentenes, phospholens (I), and their saturated analogues, the

phospholans (II), and also by the oxides and sulphides of the phospholens (III) and phospholans (IV):[24]

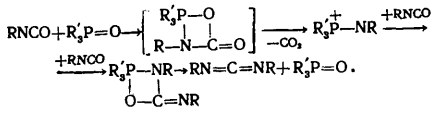


(I) (II) (III) (IV)

These organophosphorus catalysts are obtained by fairly simple methods, for example, by the reaction of alkyl- or aryl-dichlorophosphines with isoprene or butadiene, or in other ways[18,20,25]:



In addition to the phospholens, trialkylphosphine oxides have been proposed as catalysts for the decarboxylation of isocyanates. The mechanism of formation of carbodiimides when these catalysts are used is represented as follows[21-23]:



A number of other organophosphorus, and also organoarsenic, compounds, with a strongly polarised P=O or As=O bond have fairly high catalytic activity; examples are, the phosphates $(RO)_3PO$, the phosphonates $(RO)_2P(O)R'$, triarylarsine oxides $Ar_3AsO$, etc.[21,26] The activities of different catalysts have been compared by studying the kinetics of the decarboxylation of isocyanates[15,22].

## 3. PHYSICAL PROPERTIES OF CARBODIIMIDES

Aliphatic carbodiimides are colourless or slightly coloured distillable liquids with a characteristic odour. The aromatic carbodiimides are generally crystalline compounds that decompose or become partly polymerised on long storage or on being heated. For example, dicyclohexylcarbodiimide, which is widely used in laboratory practice, is a crystalline compound with m.p. 35–36° under normal conditions. It is fairly stable and can be kept for several months; it is readily soluble in inert organic solvents and in alcohol, with which it virtually does not react even on being heated; in this it differs from other carbodiimides. The stability of carbodiimides increases with increasing chain length and branch of side-chains.[27,28] For example, diethylcarbodiimide polymerises after a few days, but diisopropyl- or dicyclohexyl-carbodiimides are stable when stored for several months[12,28]. Unsaturated dialkenecarbodiimides with an unbranched chain (diallyl- and allylbromo-carbodiimides) are stable as monomers only when a polymerisation inhibitor has been added[29].

The aromatic carbodiimides differ considerably in their stability[10]. For example, di-*p*-iodophenylcarbodiimide polymerises very readily. The freshly prepared unsubstituted diphenylcarbodiimide is a mobile liquid, but after a few days it is converted to a solid pasty mass. Di-*p*-tolylcarbodiimide is a solid crystalline compound that remains stable for several months. Bis-(*p*-dimethylaminophenyl)-carbodiimide is stable for three years. Alcoholic solutions of aromatic carbodiimides are more sensitive to heat than solutions of aliphatic carbodiimides.

TABLE. Carbodiimides prepared by decarboxylation of isocyanates.

| Carbodiimide | B.p., °C/mmHg | Literature reference |
|---|---|---|
| Dipropyl | 56—58/11 | 18 |
| Diisopropyl | 36—37/10 | 33 |
| Diallyl | 58—60/10 | 18 |
| Diisopropenyl | 73/43 | |
| Diphenyl | 171/12 | 18 |
| Dicyclohexyl | 154/12 | 22 |
| 4,4′-Dinitrophenyl | m.p. 164—166 | 19 |

The decomposition and polymerisation products of carbodiimides are basic, but their composition and structure have not been sufficiently studied. The dimers and trimers of diphenyl- and di-*p*-tolyl-carbodiimides have been most studied[10].

The physical properties and stability of the poly(carbodiimides) depend on the methods by which they are prepared and the degree of polymerisation. Poly(carbodiimides) may be obtained as elastic vulcanisates, glasslike blocks, moulding powders, film, and fibres. They are soluble in organic solvents. The poly(carbodiimide) obtained from toluene-2,4-diisocyanate melts at 113–115°; the poly-(carbodiimide) of methylenebis-(4-phenylisocyanate), which melts at 250°, is similar to Nylon-6.[16]

An intense absorption band characteristic of the –N=C=N– group occurs in the 2100–2130 $cm^{-1}$ region of the infrared spectrum of carbodiimides[15,16,19]. It is interesting that allenes have a characteristic absorption band in the 1875–2000 $cm^{-1}$ region[25,30]; isocyanates have a band in the 2180–2270 $cm^{-1}$ region[31], and ketimines a band at about 2000 $cm^{-1}$.[32] Table 1 shows some carbodiimides obtained by the decarboxylation of isocyanates.

## 4. CHEMICAL PROPERTIES OF CARBODIIMIDES

The chemical properties of the carbodiimides are determined primarily by their unsaturation, and therefore by their tendency to enter into addition reactions. This refers in particular to reactions with compounds having an active hydrogen atom.

a. Reactions with weak acids. Carbodiimides combine with hydrogen sulphide to form *sym*-dialkyl(aryl)-thioureas[5,34]:

$$RN{=}C{=}NR + H_2S \rightarrow RNHCSNHR.$$

With hydrogen selenide the carbodiimides form the corresponding selenoureas[35]:

$$RN{=}C{=}NR + H_2Se \rightarrow RNHCSeNHR.$$

Carbodiimides react with hydrogen cyanide to form α-cyano-*NN′*-dialkyl(aryl)formamidines[36,37]:

$$RN{=}C{=}NR + HCN \rightarrow RNHC(=NR)CN.$$

b. Reactions with phenols. When carbodiimides are heated with phenols, crystalline ethers of pseudoureas are formed[3]:

$$RN{=}C{=}NR + ArOH \rightarrow RNHC(=NR)OAr.$$

c. Reactions with carboxylic acids. Carbodiimides react with carboxylic acids to form acyl ureas or

acid anhydrides and ureas, according to the reaction conditions [27,34]:

$$RN{=}C{=}NR + R'COOH \begin{cases} \rightarrow RNHCONHR + (R'CO)_2O \\ \rightarrow R'CONRCONHR \end{cases}.$$

Carbodiimides react analogously with dicarboxylic acids [38,39]. Oxalic acid forms disubstituted ureas with carbodiimides [10]. This reaction is used for the identification of carbodiimides. Carbodiimides are quantitatively determined in the following manner [40]. A known amount of oxalic acid dissolved in dioxan is added to the carbodiimide sample, the mixture is heated under reflux, and the solution is titrated against sodium methoxide dissolved in a mixture of benzene and methanol in the presence of Thymol Blue indicator.

The use of the reactions of carbodiimides with carboxylic acids is considered in greater detail below, in the Section dealing with applications of carbodiimides. This also applies to the reactions of carbodiimides with phosphoric acids.

d. Reactions with phosphoric acid. Carbodiimides react vigorously with esters of phosphoric acid to give esters of pyrophosphoric acid in quantitative yield [41]:

$$2(RO)_2POOH + RN{=}C{=}NR \longrightarrow R\overset{+}{N}H{=}\overset{\cdot}{C}{-}\overset{\cdot}{N}HR + \bar{O}P(OR)_2 \longrightarrow$$

$$\longrightarrow (RO)_2P(O)-O-P(O)(OR)_2 + RNHCONHR$$

The reaction with alkylsulphonic acids occurs in a similar manner with the formation of acid anhydrides and ureas [10]:

$$2R'SO_3OH + RN{=}C{=}NR \rightarrow R'SO_2{-}O{-}SO_2R' + RNHCONHR.$$

e. Reactions with alcohols. On being heated, alcohols combine with carbodiimides to form substituted ureas. The reaction goes best in the presence of acid catalysts [42,43]:

$$RN{=}C{=}NR \xrightarrow{H^+} R\overset{+}{N}H{=}C{=}NR \xrightarrow{+R'OH} RNHC(=NR)OR' + H^+.$$

f. Other addition reactions. In the presence of catalytic quantities of their sodium derivatives, malonic ester, acetoacetic ester, and acetylacetone form substituted amidines with carbodiimides [44], for example:

$$RN{=}C{=}NR + CH_2(COOC_2H_5)_2 \rightarrow RNHC(=NR)CH(COOC_2H_5)_2.$$

Substituted amidines are also formed by the reaction of carbodiimides with Grignard reagents [45]:

$$RN{=}C{=}NR + R'MgBr \rightarrow RNCR'{=}NRMgBr \xrightarrow{H_2O} RNHCR'{=}NR + MgOHBr.$$

Ammonia combines with carbodiimides to give disubstituted guanidines [5]:

$$RN{=}C{=}NR + NH_3 \rightarrow RNHC(=NR)NH_2.$$

Carbodiimides react with amines to form trisubstituted guanidines [5,6]:

$$RN{=}C{=}NR + R'NH_2 \rightarrow RNHC(=NR)NHR'.$$

With cyanamide they form disubstituted cyanoguanidines [46]:

$$RN{=}C{=}NR + H_2NC{\equiv}N \rightarrow RNHC(=NR)NHCN.$$

Aliphatic carbodiimides react with cyanamide in the presence of sodium ethoxide.

Diazomethane combines with aromatic carbodiimides to form triazole derivatives [47,48]:

$$ArN{=}C{=}NAr + CH_2N_2 \rightarrow ArNHC(=CH{-}N{=}N){-}NAr.$$

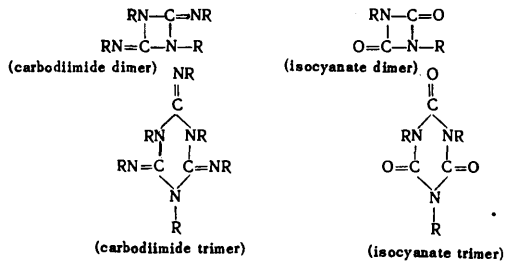
Derivatives of tetrazole are formed by the addition of hydrazoic acid to carbodiimides [49,50]:

$$ArN{=}C{=}NAr + HN_3 \rightarrow ArN{=}C(N_3){-}NHAr \rightarrow ArN{-}C(=N{-}N{=}N){-}NHAr.$$

Dry hydrogen chloride reacts vigorously with diphenylcarbodiimide [10]. The reaction proceeds with appreciable evolution of heat and leads to the addition of one or two molecules of hydrogen chloride, depending on the proportions of the reagents. In the presence of water this reaction leads to the formation of *sym*-diphenylurea

$$C_6H_5N{=}C{=}NC_6H_5 \begin{cases} \xrightarrow{HCl} C_6H_5NH{-}CCl{=}NC_6H_5 \\ \xrightarrow{2HCl} C_6H_5NH{-}CCl_2NHC_6H_5 \\ \xrightarrow[HCl]{H_2O} C_6H_5NHCONHC_6H_5 \end{cases}.$$

g. Formation of dimers and trimers. The carbodiimides form dimers and trimers similar in structure to isocyanate dimers and trimers [3,51]:

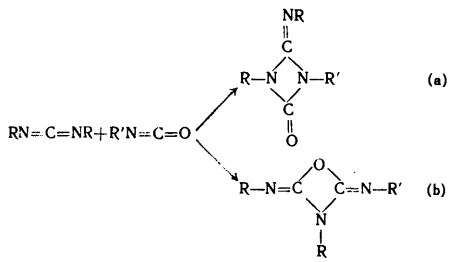



The chemical properties of the carbodiimides given above show that these are similar to those of other classes of compounds with cumulative double bonds, in particular to those of the isocyanates. However, under ordinary conditions the carbodiimides react less vigorously than the isocyanates with acids, alcohols, and amines [51]. The aliphatic carbodiimides are less reactive than the aromatic [15].

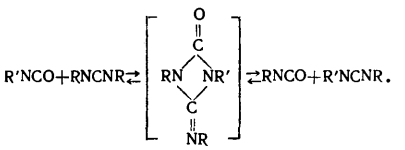
The chemical properties of the polycarbodiimides have been little studied up to now. Some of them, for example the polycarbodiimide obtained by decarboxylation of methylene-bis-(4-phenylisocyanate) react slowly with acids, alkalis, and amines, even on heating [15]. In contrast, the polycarbodiimide obtained from toluylenediisocyanate readily reacts with alcohols and ammonia [17,18].

## 5. REACTIONS OF CARBODIIMIDES WITH ISOCYANATES

Several years ago it was shown that carbodiimides react with isocyanates to form thermally unstable adducts [15]:



Compound with structure (a) was identified by infrared spectroscopy as the main product of the reaction. Compounds of this type are called uretonimines by analogy with uretdiones, the dimerisation products of isocyanates [15]. When heated, uretonimines decompose into the starting materials and products in which the radicals are completely or partially exchanged:



It is possible to exchange completely or partly the radicals of carbodiimides and isocyanates by suitable choice of reagents and reaction conditions.

Uretonimines are obtained from carbodiimides and isocyanates by heating them in the absence of air and moisture to 100–160°. Copper and copser salts are used as catalysts. Uretonimines are high-boiling liquids or solid compounds. For example, the uretonimine obtained from diisopropylcarbodiimide and phenyl isocyanate is a yellowish crystalline compound under ordinary conditions [52].

Diisocyanates react with carbodiimides to form two types of end-products [15]:

$$RNCNR+OCNR'NCO\rightarrow RNCNR'NCO+RNCO,$$
$$\text{(a)}\ RNCNR'NCO+RNCNR\rightarrow RNCNR'NCNR+RNCO,$$
$$\text{(b)}\ RNCNR'NCO+OCNR'NCO\rightarrow OCNR'NCNR'NCO+RNCO,$$

where $R = C_6H_{11}$; $R' = (CH_2)_6$.

In the last stage of the reaction, polymers of different chain length and with different end-groups can be obtained; the product depends on the proportions of the reagents used. Thus, if dicyclohexylcarbodiimide is added to an excess of hexamethylenediisocyanate, a poly(carbodiimide) of the following structure is obtained:

$$C_6H_{11}-[-(CH_2)_6-N=C=N-]_x-C_6H_{11}$$
$$(x=1, 2, 3).$$

If the diisocyanate is used in excess, the poly(carbodiimide) will have the isocyanate end-groupings:

$$O=C=N-(CH_2)_6-[-N=C=N-(CH_2)_6-]_x-N=C=O$$
$$(x=1, 2, 3).$$

In both cases, products of more branched structure are obtained along with these compounds. These products are formed by the direct reaction of carbodiimides with isocyanate groups according to the scheme given above for the formation of uretonimines [15].

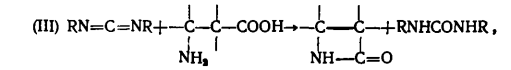
## 6. APPLICATIONS OF CARBODIIMIDES

As already mentioned, until a method of preparing carbodiimides by the catalytic decarboxylation of isocyanates was developed, they had no industrial applications and were used in laboratory synthesis and analysis for characterising carboxylic acids, identifying amino-acids in peptides, etc. [2]

Carbodiimides are also used as dehydrating agents for the production of ester (I), amide (II), lactam (III), and peptide (IV) bonds:

(I) $RN=C=NR+R'OH+R''COOH\rightarrow R''COOR'+RNHCONHR,$

(II) $RN=C=NR+R'NH_2+R''COOH\rightarrow R''CONHR'+RNHCONHR,$

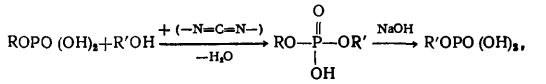
(III) 

(IV) $RN=C=NR+R'CHNH_2COOH+R''COOH\rightarrow R''CONHCHR'COOH+RNHCONHR.$

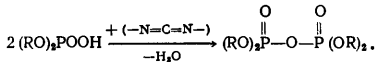
These reactions are quantitative with dicyclohexylcarbodiimide [2].

The β-lactam ring in penicillinoic acid was first closed to form penicillin by means of carbodiimides [2].

Other examples of the use of carbodiimides in dehydrating reactions are known in addition to the cases given above. Thus, carbodiimides have been used for phosphorylation reactions [2]:



and also for the preparation of pyrophosphoric acids:



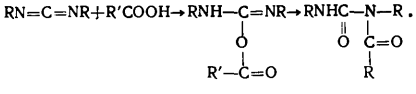
Peptides can be selectively degraded by means of carbodiimides:

$$CH_3CONHCH_2CONHCH_2COOH+RN=C=NR\rightarrow$$
$$\rightarrow CH_3CONHCH_2CONRCONHR \xrightarrow{NaOH} CH_3CONHCH_2COOH+NH_2CH_2CONRCONHR.$$

Carbodiimides have been successfully used in the synthesis of nucleotides, polynucleotides, coenzymes, etc. [43]

Polycarbodiimides have not yet found wide practical applications. But studies of the properties of polycarbodiimides give grounds for regarding them as promising polymer materials with film-forming and fibre-forming capabilities. Poly(carbodiimides) are outstandingly stable to heat and to the action of corrosive liquids [15,18,19,23].

The tendency of carbodiimides to form acylated substituted ureas by reaction with carboxylic acids has been utilised in employing them as anti-aging additives to polyurethanes. In these cases, the reaction of carbodiimides with acids goes according to the following scheme:



It is well known that when plastics containing ester groupings age, carboxylic compounds are formed that accelerate the reaction autocatalytically. It has been shown that poly-(carbodiimides) are effective inhibitors of this process. They are very compatible with plastics, stable on storage, non-volatile, etc.[15,53]

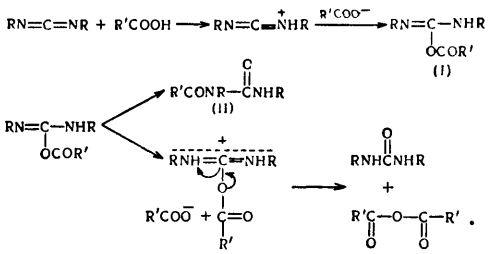
Carbodiimides can be used as anti-shrink additives in the treatment of textiles[54].

Some carbodiimides are physiologically active[54]. The toxicity of dicyclohexylcarbodiimide for the rat ($LD_{50}$) is 2.6 g $kg^{-1}$. Carbodiimides have herbicidal and fungicidal activity[55].

The use of carbodiimides in acylation reactions. The ability of carbodiimides to combine with carboxylic acids with the formation of *NN'*-diaryl- or *NN'*-dialkyl-ureides has been used for the identification of these acids[56]. The same reaction has been used for the detection of traces of acids in animal and vegetable oils[57]. In this reaction the best results are obtained with dicyclohexylcarbodiimide.

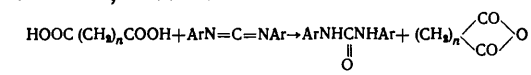
The nature of the end-products in this reaction depends on the structure of the carbodiimide and on the type of solvent. Ureides are the main products formed from diarylcarbodiimides; in those cases where dicyclohexylcarbodiimide was used, acid anhydrides and dicyclohexylurea were obtained as the main products. Zetzsche, using dicyclohexylcarbodiimide, obtained the anhydrides of butyric and stearic acids in 90% yield[56]. Ether, benzene, acetone, cyclohexane, and light petroleum were used as solvents in these reactions. Ureides of *NN'*-dicyclohexylurea were obtained in pyridine or alcohol solution.

According to Khorana[43], the mechanism of formation of acid anhydrides together with ureides may be represented as follows:



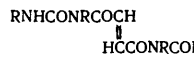
In accordance with the proposed scheme, a molecule of acid combines with one of the double bonds of carbodiimide to form an intermediate compound (I), which either rearranges to a more stable form with the formation of a ureide (II) or reacts with a second molecule of acid, if this is present in excess, to give an acid anhydride and a substituted urea. In alcoholic solution, compound (I) reacts with the alcohol to form an acid ester.

Khorana, who analysed the different directions the reactions of carbodiimides with carboxylic acids may take, has made the following observations[10]. With aromatic acids the reaction goes mainly in the direction of forming alkylureas. Ether, benzene, dioxan, and pyridine may be used as solvents; the use of alcohols is undesirable as they form polymeric by-products. Under very mild conditions an acyl urea is formed quantitatively. Since acylureas crystallise very well, this reaction may be used to characterise carboxylic acids. The most suitable carbodiimide for this purpose is *sym*-bis-(*p*-dimethylaminophenyl)carbodiimide. Malonic, succinic, and glutaric acids mainly form disubstituted ureas and cyclic anhydrides. Evidently, cyclisation occurs after 1,2-addition:



where $n$ = 1, 2, 3.

Similarly, phthalic acid and maleic acid form cyclic anhydrides, but fumaric acid gives the normal adduct:



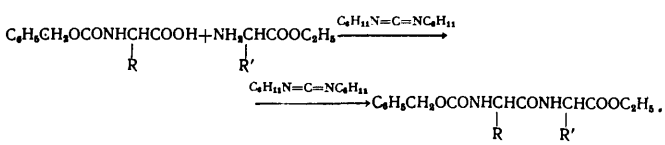
Adipic acid forms the monoacyl- and diacyl-ureas. The higher acids give normal derivatives, and each carboxylic group reacts independently.

Aliphatic carbodiimides, as a rule, form disubstituted ureas and anhydrides with carboxylic acids. However, by controlling the reaction an acylurea can be obtained. For example, when the reaction is carried out in hot pyridine and the carboxylic acid is added in portions to dicyclohexylcarbodiimide, the acylurea is obtained in satisfactory yield. Dicyclohexylurea is formed when dicyclohexylcarbodiimide reacts with an aqueous solution of acetic acid. To obtain diisopropylurea, the reaction between diisopropylcarbodiimide and acetic acid is carried out in acetone[58].

Methyl benzoate has been obtained from methanol and benzoic acid in the presence of dicyclohexylcarbodiimide[59]. A patent has also been obtained for the preparation of esters by the reaction of chloroacetic, phenoxyacetic, and salicyclic acids with methanol and 2-chloroethanol in the presence of dicyclohexylcarbodiimide. The desired products were obtained in 72–100% yield[60]. Butyranilide has been obtained by the reaction of butyric acid with aniline in the presence of dicyclohexylcarbodiimide[59]. This interesting observation was further applied in carrying out syntheses, with the use of amino-acids and carbodiimides. Like ordinary organic acids, in this reaction amino-acids form ureides, many of which have been prepared by Khorana[41].

Khorana noted that when the reaction was carried out with dicyclohexylcarbodiimide in pyridine solution cleavage of the ureide occurred[41]. When alcohol was used as a solvent, a certain amount of urea was formed in addition to the ureides. This suggests that in the course of the reaction dehydration of two molecules of amino-acid occurred with the possible formation of a peptide.

A new method of synthesising peptides has been developed[61], consisting in a reaction between a benzyloxycarbonylamino-acid, or a phthaloylamino-acid, and the ethyl ester of another amino-acid in the presence of dicyclohexylcarbodiimide:



In this way the ethyl ester of benzyloxycarbonylglycyl--*L*-phenylalanylglycine, benzyloxycarbonyl-*L*-serylglycine, phthaloyl-*L*-phenylalanylglycine, and phthaloyl-*L*--phenylalanyl-*L*-leucine have been obtained; the yield of peptide in these reactions was 70–90%.

Peptides were also obtained by Khorana, but in lower yield (20–50%)[62]. In addition to peptides, he isolated ureides

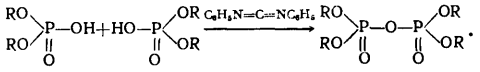
of *NN'*-dicyclohexylurea of the type $C_6H_{11}NHCONRC_6H_{11}$, where R = *N*-(*p*-toluenesulphonyl)-*DL*-phenylalanyl or *NN'*-phthaloyl-*DL*-phenylalanyl.

Using these methods, Amiard obtained a number of dipeptides of methionine, protecting the amino-groups with trityl groups $C(C_6H_5)_3$ and then condensing the protected methionine with esters of glycine and leucine[63]. The reaction was carried out in methyl chloride; the yield was 80–90%. Using the same method, Amiard[64] synthesised $\alpha$- and $\gamma$-glutamylpeptides, and Sheehan[65] synthesised di- and tri-peptides containing hydroxyamino-acids (serine and threonine).

The use of carbodiimides for the synthesis of peptides is of great preparative value. Previous methods were based on the activation of the carboxyl group taking part in the reaction, after which derivatives were obtained, for example acyl chlorides, azides, etc.[66] The use of cyclohexylcarbodiimide eliminated the necessity of using these derivatives, since in the presence of carbodiimides, peptides are formed directly as a result of the reaction of the free carboxyl group of one amino-acid molecule with the free amino-group of another molecule. The use of carbodiimides in the synthesis of peptides is dealt with in a number of original papers[67-70].

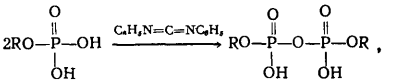
The use of carbodiimides in the synthesis of phosphorus-containing compounds. We have already noted that carbodiimides react with esters of phosphoric acid to form derivatives of pyrophosphoric acid[41]. In this way various esters and anhydrides of phosphoric acid can be obtained together with other compounds such as nucleotides, oligonucleotides, some coenzymes, etc.[66] Depending on the properties of the reagents, the phosphorylation reaction in the cold in aqueous pyridine solution, in anhydrous pyridine, or in dimethylformamide may take from several minutes to several hours[66].

*sym*-Tetrabenzyl-, tetraphenyl-, and tetra-*p*-nitrophenyl-pyrophosphate esters are obtained by condensing diesters of phosphoric acid[71]:



Adenosine diphosphate and adenosine triphosphate[72] and also a series of other important biochemical products[73-76] are obtained by the interaction of orthophosphoric acid with adenosine-5′ phosphoric acid in the presence of dicyclohexylcarbodiimide.

A symmetrical diester of pyrophosphoric acid is obtained by condensing two molecules of adenosine-5′ phosphoric acid in the presence of dicyclohexylcarbodiimide[77]:



where R is adenosine.

Todd and coworkers have synthesised nicotinamide–adenine dinucleotide in this way[78]. Another important coenzyme, flavin–adenine dinucleotide, was obtained in a similar way, but di-*p*-tolylcarbodiimide was used as a dehydrating and condensing agent[79]. Cytidine diphosphate choline and cytidine diphosphate ethanolamine were obtained with the aid of the same carbodiimide[80].

The use of carbodiimides in the synthesis of mixed acid anhydrides. Mixed acid anhydrides formed by the reaction of an amino-acid with adenosine-5′ phosphoric acid participate in the synthesis of protein, and interest in the synthesis of this type of compound is understandable[81]. The methods previously used for the synthesis of mixed acid anhydrides[82,83], for example the reaction of an acid chloride with the silver salt of adenosine-5′ phosphoric acid, or the action of amino-acid esters on the sodium salt of adenosine-5′ phosphoric acid, gave low yields.

The use of carbodiimides has enabled great progress to be made in this important field of synthesis. Berg[84] obtained derivatives of the anhydrides of *L*-serine, *L*-phenylalanine, *L*-tryptophan, and *D*-methionine by reaction of amino-acids with adenosine-5′ phosphoric acid in the presence of dicyclohexylcarbodiimide. Other important mixed anhydrides have been obtained with the aid of carbodiimides[84-86]. A mixed anhydride of adenylic and sulphuric acid (adenosine-5′ phosphosulphate), which is of biochemical interest, has been obtained in 40–50% yield by the action of concentrated sulphuric acid on adenosine-5′ phosphoric acid in the presence of dicyclohexylcarbodiimide in aqueous pyridine solution[87].

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In conclusion, it should be noted that the cases of the use of carbodiimides which we have considered are of great preparative value and primarily lead to a reduction in the number of intermediate stages and to an increased yield of the desired products compared with other methods. When carbodiimides are used, complicated multi-stage syntheses are reduced to one or two steps in the majority of cases. Another important advantage of syntheses with the use of carbodiimides is the simplicity of these compounds as condensing and water-removing agents. Reactions in which carbodiimides are used are usually carried out under mild conditions at room temperature, or at a slightly higher temperature, with the use of such accessible solvents as ether, pyridine, or dimethylformamide. Dicyclohexylurea, which is formed as a result of these reactions, is poorly soluble in these solvents, and this facilitates the purification and separation of the reaction products. Moreover, the course of the reaction can be followed by observing the amount of substituted urea precipitated. These reactions, as a rule, do not take more than a few hours.

Because of the development of new methods of synthesising carbodiimides by the catalytic decarboxylation of isocyanates, they have become more accessible and the range available has been extended. On the whole, the outlook for the wide use of carbodiimides and poly(carbodiimides) is very promising.


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# ELECTROMIGRATION IN LIQUID METALS

D. K. Belashchenko

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## I. INTRODUCTION

The concept of electromigration (or electrodiffusion, electrolytic migration, etc.) covers a range of phenomena associated with the directed displacement of the components of a solution when an electric current is passed through the solution. Since a real substance, even when chemically pure, in general consists of a solution either of different isotopes or of defects of different types in a matrix (vacancies, displaced atoms, etc.) and, moreover, contains activated complexes in a transition state, the phenomenon of electromigration may be and is observed even in pure substances.

The magnitude of the electromigration effect depends on various factors: the nature of the solution, the magnitude of the electric field, concentration, temperature, and other parameters. Since the directed displacement (migration) during electromigration (e.m.) takes place due to and by means of the random diffusion movements of individual particles, the direct relation between the elementary acts of diffusion and e.m. is obvious. If the external electric field applied to the system is weak compared with the atomic field, the role of the external field is merely a certain ordering of the individual elementary acts of diffusion but does not lead to a change in the mechanism of the acts themselves. This feature is related to the fact that a weak external field may be regarded as a perturbation which alters the number of particles undergoing migration with the field and against the field but does not influence the frequency of these displacements. The frequency of the displacements may depend on the external field when the change in potential energy associated with the displacement of a charged particle and its environment in the external field becomes comparable with the activation energy of the diffusion process. For this it is necessary to use a field with an intensity of $10^7$–$10^8$ V $cm^{-1}$, which is hardly possible.

The elementary act of diffusion is a fairly complex process, particularly in metals. A charge introduced into a metal should be screened by the conduction electrons. These screening electrons are usually not localised close to the central charge (impurity ion) and they cannot be regarded as moving behind the central charge like the rigid sheath of an ion. Thus the elementary act of diffusion in a metal involves not only the displacement of the charged impurity ion but also the redistribution of the conduction electrons in space, leading to more or less complete screening of the ion throughout the whole path of the displacement. In the case of electromigration, these processes take place together with the passage of current through the metal, so that the interaction of the ion itself and the screening charge with the stream of conduction electrons becomes significant. As a result of all these features, the electromigration effects characterise not only the charge of the ions of the components of the solution but also the state of the conduction electrons and the interaction of the former with the latter. Thus the study of electromigration makes it possible to investigate not only the electrical properties of the diffusing particles but also the mechanism and characteristic features of the elementary act of diffusion itself.

The phenomenon of e.m. has recently become one of the most widespread means of studying ionic crystals and semiconductors. In the case of ionic crystals this is due chiefly to the fact that in these crystals the e.m. (ionic conduction) is responsible for the electrical conductivity of the substance and is a property which is extremely sensitive to the formation of charged complexes, defects, etc., in the crystal. The study of e.m. in salts is facilitated by the possibility of producing intense electric fields ($10^4$–$10^5$ V $cm^{-1}$). The study of e.m. in semiconductors makes it possible to establish the sign and magnitude of the charge on the impurity, which determines its action as an alloying additive (donor or acceptor behaviour). In view of the importance of impurities in metallurgy and in semiconductor physics, the study of e.m. in these materials is being widely developed.

Unfortunately, insufficient attention is as yet being paid to the study of e.m. in metallic systems. This is due partly to the fact that the magnitude of e.m. in metals is relatively low (the transport numbers of ions in metallic solutions, in the most favourable case, amount to $10^{-4}$–$10^{-5}$ mole × × $faraday^{-1}$). In addition, the lack of a satisfactory theory of e.m. is hindering considerably the development of experimental work in this field. Only in recent years has interest in the study of e.m. increased, chiefly in connection with the discovery that it is possible to separate isotopes by means of e.m. in liquid metals. Work has also begun on the study of e.m in solid metallic solutions and pure metals, chiefly in the USSR. A characteristic feature is the effort to advance from qualitative on semi-quantitative studies to a precise quantitative characterisation of e.m. It should be noted, however, that until recently the interpretation of the results of e.m. measurements were oversimplified. Einstein's relationship between mobility and diffusion coefficient makes it possible to use the rate of movement of an impurity in an electric field to determine a certain characteristic with the dimensions of charge — "the effective charge" — whose magnitude is determined not only by the charge of the diffusing ion but also by all the interactions between this ion and the surrounding system of ions and electrons. In earlier work, however, this effective charge was identified with the "true charge" of the ion, and on this basis far-reaching conclusions were made regarding the nature of the interaction in solutions, etc. The position has recently changed somewhat. In the study of e.m., allowance is now being made for the so-called "electron wind", that is, the interaction of the stream of electrons (the electric current) with the impurity ions. These and other features complicate considerably the picture of diffusion migration in an electric field and make the interpretation of experimental data difficult. In particular, there is as yet no reliable method for calculating the "true charge" of an ion from the magnitude of the effective charge during electromigration in solid solutions.

In the study of e.m. in liquid metallic solutions, the position is even less satisfactory. Despite much work carried

out in this direction, there are very few trustworthy experimental data. This is due to the unreliability of the procedures used. The chief factor leading to incorrect results is apparently convection produced by the high current densities, heating of the alloy, and the influence of density gradients produced during electromigration.

Generally speaking, liquid solutions provide a simpler object for study than solid solutions. Since the activation energy of diffusion in liquid metals is smaller by about one order of magnitude than that in solid solutions and is close to the energy of the thermal movement of the atoms, the difference between the ground state and the transition state for a liquid is apparently of little significance. It is then possible, as a first approximation, to neglect the discontinuous nature of diffusion migrations and to take as a basis a model of electromigration according to which the impurity ion drifts at a constant velocity in a viscous liquid under the influence of an electric force. This treatment avoids the difficulties associated with a detailed examination of the immediate environment of the diffusing ion and facilitates the interpretation of experimental results.

Experimental work has revealed a fairly distinct boundary between e.m. in liquid and solid metals. This boundary apparently does not indicate any fundamental difference in their behaviour, but certain qualitative differences are evident. The main reasons for these differences may be assumed to be the absence of a rigid lattice in the crystals and, as already noted, the appreciable difference in the activation energies of diffusion. A position has thus arisen, in which studies in each of the two fields are carried out by different methods, and different results are obtained. The investigation of the reasons for the differences should lead to a better understanding of the mechanism of diffusion in both cases.

The present review deals with the results of the study of e.m. in liquid metallic solutions.

## II. PHENOMENOLOGICAL DESCRIPTION OF ELECTROMIGRATION IN LIQUID METALS

The first attempts to give a quantitative description of e.m. for the particular case of extremely dilute binary metallic solutions were made by Wagner[1] and Schwarz[2]. Wagner introduced the mobilities of the solvent and impurity $u_1$ and $u_2$, the coefficients of self-diffusion of the solvent $D_1$ and diffusion of the impurity $D_2$, the charges of the ions of the solvent $z_1 e$ and impurity $z_2 e$, where $e$ is the charge of the electron. The velocities of the ions in a field with intensity 1 V cm$^{-1}$ are

$$v_1 = \frac{z_1 e u_1}{300}; \quad v_2 = \frac{z_2 e u_2}{300}. \tag{1}$$

Wagner introduced the transport number of the impurity $t_2$ as the increase in the mole fraction of impurity at the cathode, related to a constant number of moles of the mixture at the cathode and divided by the number of equivalents of charge passed. Using Einstein's relationship

$$u_i = \frac{D_i}{kT}, \tag{2}$$

Wagner obtained[1,3]

$$\frac{t_2}{N_2} = \frac{96\,500}{300} \frac{z_2 D_2 - z_1 D_1}{\varkappa} \frac{Ned_1}{RTA_1}, \tag{3}$$

where $N_2$ is the mole fraction of the impurity, $\varkappa$ the conductivity of the solution in $\Omega^{-1}$ cm$^{-1}$, $N$ Avogadro's number, $d_1$ the density of the solvent, $A_1$ its atomic weight, $R$ the gas constant, and $T$ the absolute temperature. Wagner used formula (3) to calculate the values of $t$ for a number of amalgams, taking $z_1$ and $z_2$ equal to the chemical valencies.

Wagner's treatment of e.m. in liquid solutions cannot be regarded as satisfactory, for the following reasons.

1. If diffusion processes take place in a liquid, in most cases it is rational to select a system of taking readings which is related not to the liquid but to the vessel containing it. The total volume flow (the flow of particles multiplied by their volume) due to the diffusion of each component should then be equal to zero. In this case the kinetics of the process would be determined not by the two diffusion coefficients $D_1$ and $D_2$ but merely by a single hetero-diffusion coefficient $D = D_1 N_2 + D_2 N_1$ (see, for example, Belashchenko[5] and Wagner[6]).

2. The ions in the solution are influenced not only by the force of the field $Ff = eEz$, where $E$ is the field intensity, but also by other forces. In actual fact, in the presence of only field forces, all the ions of the solution or pure metal as a whole would be influenced by a force not equal to zero. Because of the electrical neutrality of the conductor, however, the passage of current through it should not lead to the production of a resultant force. It is therefore necessary to take account of other forces in addition to the field forces, and these should not be internal forces (of the type exemplified by Stokes' frictional forces), since the resultant of internal forces is equal to zero. These additional forces are produced by the interaction between the ion subsystems and the conductivity electrons. Moreover, it is necessary to take account of the interaction between different types of ion subsystem.

Schwarz[2] examined the problem of e.m. from a different viewpoint, making use of the analogy between the behaviour of charges in an electric field and that of particles of different mass in a gravitational field. A mass immersed in a liquid is acted upon by a displacing force. By analogy, when current is passed through a metallic solution, each impurity ion is acted upon by an "electrohydrostatic force" proportional to its volume and the solvent charge density. The charge densities of each component are

$$\alpha_1 = \frac{ez_1}{\bar{v}_1}; \quad \alpha_2 = \frac{ez_2}{\bar{v}_2}, \tag{4}$$

where $\bar{v}_1$ and $\bar{v}_2$ are the partial volumes of the solvent and impurity ions. Since the electrohydrostatic force opposes the field force (otherwise the components would not accumulate at the electrodes during e.m. but would be deposited on them), it should be directed towards the anode. Thus the impurity ion is acted upon by two forces: the field force $F_f = eEz_2$ and the electrohydrostatic force

$$F_{eh} = \bar{v}_2 \alpha_1 E, \tag{5}$$

which can be calculated from Archimides' law. The resultant force is

$$F_2 = F_f - F_{eh} = E\bar{v}_2(\alpha_2 - \alpha_1). \tag{6}$$

By using Einsten's relationship and taking the solvent as the fixed system of coordinates, Schwarz obtained

$$\frac{t_2}{N_2} = \frac{96\,500}{300} \frac{ND_2 d_1 e}{RTA_1 \varkappa} \left(\frac{z_2}{\bar{v}_2} - \frac{z_1}{\bar{v}_1}\right)\bar{v}_2. \tag{7}$$

The values of $z$ in Schwarz' treatment are arbitrary and are not equal to the ordinary chemical valencies.

Schwarz' treatment is also unsatisfactory, although it is better than Wagner's method. Schwarz does in fact take account of the existence of a force acting in a direction opposite to that of the field force, but he arbitrarily assumes that it is proportional to the volume of the ion. With this assumption, the total force acting on all the ions of the solution is again not equal to zero, and the condition of mechanical equilibrium between the current and the conductor is broken down.

Wagner[6] showed that Schwarz' introduction of the "electrohydrostatic force" is equivalent to the statement that in the solution the quantities of equal magnitude are not the transport numbers of each of the two components, as in Wagner's work[1], but the volume streams of the ions of each type, and this provides a more satisfactory description of the properties of the liquid. Wagner[6] also pointed out that no method has yet been found for determining the charges of the ions $z_1$ and $z_2$ (that is, for taking account of the interaction between the ions and the stream of electrons) and that formulae (3) and (7) are only approximate.

Drakin[7] calculated the stationary state in a concentrated binary solution on the basis of classical thermodynamics. In the virtual transfer of one mole of the first component from the origin of coordinates to the point $l$, the work of transfer is

$$A_1 = RT \ln \frac{a_0'}{a_l'}, \tag{8}$$

where $a_0'$ and $a_l'$ are the activities of the first component at the origin of coordinates and at the point $l$. At equilibrium, this work should be equal to the electrical work, so that

$$RT \ln \frac{a_0'}{a_l'} = \Delta U z_1 F, \tag{9}$$

where $\Delta U$ is the potential drop on the given section, and $F$ is the Faraday. Similarly, for the transfer of one mole of the second component in the opposite direction,

$$RT \ln \frac{a_l''}{a_0''} = -\Delta U z_2 F. \tag{10}$$

Combining (9) and (10), Drakin obtained the stationary-state equation

$$\ln \frac{a_0'}{a_0''} - \ln \frac{a_l'}{a_l''} = \frac{\Delta U F (z_1 - z_2)}{RT}. \tag{11}$$

The transport number $t_i$ in dilute solution is given by

$$\frac{t_i}{N_i} = \frac{D (z_1 - z_2) F^2}{\varkappa RT}. \tag{12}$$

The method used by Drakin to calculate the stationary state in e.m. was criticised by Baranowski[8], who pointed out that since the solution–current system is not an equilibrium system but merely a stationary system, it is necessary to apply to it the methods of not classical thermodynamics but the thermodynamics of irreversible processes. This criticism also applies to the theories of Schwarz and Wagner.

Baranowski[9,10] examined e.m. using Onsager's method. Let us use the symbols $I_k$ to denote the streams of the ions of the components, and $I_e$ to denote the stream of electrons. We then have

$$I_k = \sum_1^n L_{ki} X_i + L_{ke} X_e,$$
$$I_e = \sum_1^n L_{ei} X_i + L_{ee} X_e, \tag{13}$$

where $L_{ps}$ represents the kinetic coefficients ($L_{ps} = L_{sp}$), $n$ the number of components, and $X$ the thermodynamic forces

$$X_i = -\operatorname{grad} \mu_i - e_i \operatorname{grad} \varphi,$$
$$X_e = -\operatorname{grad} \mu_e + F \operatorname{grad} \varphi, \tag{14}$$

where $\mu_i$ is the molar chemical potential of the $i$th component, $e_i$ its molar charge, $\mu_e$ the molar chemical potential of the electron, and $\varphi$ the electric potential. Allowance is then made for the electrical-neutrality condition

$$\sum_1^n e_i c_i - F c_e = 0, \tag{15}$$

where $c$ is the concentration, and for the relationship between the flows of the components

$$\sum_1^n I_i \bar{v}_i = 0, \tag{16}$$

where $\bar{v}_i$ represents the partial volumes of the components, and the quantities $e_i'$ are introduced from the formulae

$$L_{ke} = \sum_{i=1}^{n-1} L_{ki} e_i'. \tag{17}$$

We then have[10]

$$I_k = \sum_{i=1}^{n-1} L_{ki} \left( X_i - \frac{\bar{v}_i}{\bar{v}_n} X_n + e_i' X_e \right),$$
$$I_e = \sum_{k=1}^{n-1} \sum_{i=1}^{n-1} L_{ki} e_i' \left( X_k - \frac{\bar{v}_k}{\bar{v}_n} X_n \right) + L_{ee} X_e. \tag{18}$$

The case of an extremely dilute binary solution is then taken. In this case

$$X_1 = -\operatorname{grad} \mu_1 - e_1 \operatorname{grad} \varphi,$$
$$X_2 = -e_2 \operatorname{grad} \varphi,$$
$$X_e = F \operatorname{grad} \varphi. \tag{19}$$

Introducing the symbol

$$e_1 - \frac{\bar{v}_1}{\bar{v}_2} e_2 - e_1' F = E^*, \tag{20}$$

Baranowski obtains for the stationary state ($I_1 = I_2 = 0$) the condition

$$\frac{\operatorname{grad} \mu_1}{\operatorname{grad} \varphi} = -E^*, \tag{21}$$

where the subscript "1" refers to the impurity.

In diffusion in a metallic solution, an electrodiffusion potential is produced

$$\frac{\operatorname{grad} \varphi}{\operatorname{grad} \mu_1} = \frac{t_1}{F}, \tag{22}$$

where $t_1$ is the transport number of the impurity, equal to $I_1/I_e$ when $\operatorname{grad} \mu_1 = 0$.

The relationship between the diffusion coefficient, $t_1$, and $E^*$ is given by

$$D = \frac{\varkappa t_1 RT [1 + \partial \ln f_1 / \partial \ln c_1]}{c_1 E^* F}, \tag{23}$$

where $f_1$ is the activity coefficient.

According to Baranowski[9,10], the quantity $E^*$ is the characteristic transport charge and has the significance of the "effective charge" of the impurity ions, calculated for 1 g-ion.

When $e_1' = 0$ and $\bar{v}_1 = \bar{v}_2$, Eqn. (21) becomes Drakin's formula (11). In the case of solid alloys, where the condition for the relationship between the streams of ions can

be neglected, the quantity $E^*$ becomes equal to $e_1 - e'_1F$ — see (20).

The quantities $\mu_i$ in (14) have the significance of the chemical potentials of the ions. The final result — Eqns. (21) and (22) — however, should contain the chemical potential of the "neutral" component, whose relation to the concentration of the solution is known from thermodynamic data. Let us denote the chemical potential of the first component (not the ion!) by the symbol $\mu_1^*$. We then have

$$\mu_1^* = \mu_1 + \frac{e_1}{F}\mu_e, \tag{24}$$

since in solution we have the equilibrium

$$i\text{th atom} \rightleftarrows i\text{th ion} + \frac{e_1}{F}(\text{electron}).$$

Thus

$$\operatorname{grad}\mu_1^* = \operatorname{grad}\mu_1 + \frac{e_1}{F}\operatorname{grad}\mu_e. \tag{25}$$

For a very dilute solution, however, $\operatorname{grad}\mu_e = 0$, so that $\operatorname{grad}\mu_1^* = \operatorname{grad}\mu_1$ and in Eqns. (21) and (22) it is possible to replace $\mu_1$ by $\mu_1^*$.

An examination of e.m. in a two-component metallic solution with any concentration at constant temperature was made by Belashchenko and Zhukhovitskii [11] for the particular case where $\bar{v}_1 = \bar{v}_2$, i.e. $I_1 + I_2 = 0$. Onsager's equations were written in the form

$$I_i = L_{ik}X_k (i, k = 1, 2, 3), \tag{26}$$

where $I_1$ and $I_2$ are the streams of ions of the first and second components, and $I_3$ the stream of electrons (summation with respect to $k$). The forces $X_i$ are

$$X_1 = -\frac{\partial\mu_1}{\partial x} - e_1\frac{\partial\varphi}{\partial x},$$
$$X_2 = -\frac{\partial\mu_2}{\partial x} - e_2\frac{\partial\varphi}{\partial x},$$
$$X_3 = -\frac{\partial\mu_3}{\partial x} - e_3\frac{\partial\varphi}{\partial x}, \tag{27}$$

where $\mu_1$, $\mu_2$, and $\mu_3$ are the chemical potentials of the individual ions (not the atoms of the components!) of the first and second types and of the electrons, $e_1$, $e_2$, and $e_3$ their charges (in cgs units), $x$ the coordinate of the length of the specimen, and $\varphi$ the electric potential. The electrical-neutrality condition is of the form

$$\sum_{i=1}^{3} e_i I_i = I, \tag{28}$$

where $I$ is the density of the external current passing through the system. From the condition $I_1 + I_2 = 0$, it follows [11] that

$$L_{11} = -L_{12} = L_{22},$$
$$L_{13} = -L_{23}. \tag{29}$$

The chemical potentials of the atoms $\mu^*$ (which can be measured in a thermodynamic experiment) were then introduced [11]:

$$\mu_1^* = \mu_1 - \frac{e_1}{e_3}\mu_3,$$
$$\mu_2^* = \mu_2 - \frac{e_2}{e_3}\mu_3. \tag{30}$$

Eqns. (30) are equivalent to Eqns. (24). Solution of systems (26)–(27) with allowance for (28)–(30) and the Gibbs–Duhem equation gives the result [11]

$$I_1 = c_1u_1E - D\frac{\partial c_1}{\partial x}, \tag{31}$$

where $\mu_1$ is the mobility of the first component, $E$ the field intensity due to the external current, and $E = I/\varkappa$, where $\varkappa$ is the conductivity. In e.m. the gradients of the chemical potentials of the ion and electron are combined in such a way that the diffusion (or electrodiffusion) stream depends, in the final analysis, only on the gradient of the chemical potential of the neutral atoms. This feature confirms the familiar view that the measurement of the potential jump at a phase boundary, not only by equilibrium measurements but also by kinetic measurements, is impossible.

Belashchenko and Zhukhovitskii [11] defined the "effective charge of the ion" $e_i^*$ by the relationship

$$u_i = \frac{D}{kT}e_i^*\frac{\partial\ln c_i}{\partial\ln a_i}, \tag{32}$$

where $a_i$ is the thermodynamic activity of the $i$th component. This charge has a simple physical significance: if a total moving force $F_i$ acts upon the $i$th ion in solution, we have

$$e_i^* = \frac{F_i}{E}, \tag{33}$$

where $E$ is the field intensity due to the external current. Thus the effective charge of the ion $e^*$ takes account of the ordinary field force, the interaction of the ion with the stream of electrons, the interaction of ion subsystems of different type, etc. The factor $d\ln c_i/d\ln a_i$ in (32) indicates, as usual, the deviations of the properties of the solution from ideal behaviour.

In the stationary state, $I_1 = 0$ and [11]

$$\frac{\partial\ln a_1}{\partial x} = \frac{e_1^*E}{kT}. \tag{34}$$

An analogous equation is applicable for the second component. The effective charges are related to one another by the condition that the total force acting on the whole of the solution is equal to zero (the condition of mechanical equilibrium)

$$c_1e_1^* + c_2e_2^* = 0. \tag{35}$$

It was shown [12] that Baranowski's formula (21) for the stationary state in the case of an infinitely dilute solution is equivalent to (34). In this case $E^*$ from (20) is equal to $Ne_1^*$, where $N$ is Avogadro's number.

In the case of diffusion in a non-uniform open specimen we should observe an effect which is the opposite of electromigration — the production of an electrodiffusion potential (e.d.p.). The suggestion that an e.d.p. exists in metals was first made by Lewis and coworkers [13]. For the value of the e.d.p. in the diffusion of an impurity from a very dilute solution into pure solvent, Schwarz [14] obtained the expression

$$t_1 = \frac{\Delta UF}{RT}, \tag{36}$$

where $t_1$ is the transport number of the impurity and $\Delta U$ the voltage between the solution and the solvent.

For the electric field in ordinary diffusion, the following expression was obtained [11]

$$\frac{\partial\varphi}{\partial x} = -\frac{1}{e_3}\frac{\partial\mu_3}{\partial x} - e_1^*\frac{D}{\varkappa}\frac{\partial c_1}{\partial x}\left(1 + \frac{c_1}{c_3}\right). \tag{37}$$

The first term on the right-hand side is the ordinary "internal" contact potential difference, that is, the contact potential difference when the jumps at the metal–vacuum interface are independent of composition; the second term

is the e.d.p. gradient. It can readily be shown that in the case considered by Schwarz, (36) and (37) are equivalent.

An interesting feature is that the e.d.p. gradient has a form which resembles Ohm's law. In actual fact, the factor $-D\frac{\partial c_1}{\partial x}$ in Eqn. (37) is equal to the flow of ions of the first component; the factor $-D\frac{\partial c_1}{\partial x}e_1^*\left(1+\frac{c_1}{c_2}\right)$ then describes a certain effective current density produced by the movement of the ions, and division of the current density by the conductivity $\varkappa$ gives the corresponding field intensity.

The heat of transport was also examined by Thompson's method [11]. It was shown that the heat of transport consists of two parts: a term related to the transport of the electronic charge $e_1 - e_2$ (compensating the transport of the ionic charges) from a point with one value for the chemical potential of the electron to a point with another value, and a term which describes the work of transport of ions with definite effective charges in the field of the external current $E$.

In this case the field and the electron stream perform work $(e_1^* - e_2^*)Edx$, where $dx$ is the path.

The results of this work [11] were generalised [15] for the case of an arbitrary $n$-component alloy. The calculations showed that the stationary distribution of each component in any case is determined only by the effective charge of the corresponding ion:

$$\frac{\partial \ln a_i}{\partial x} = \frac{e_i^* E}{kT}. \qquad (38)$$

The effective charges of the ions of different components are related to one another by the expression [see (35)]:

$$\sum_{i=1}^{n} c_i e_i^* = 0. \qquad (39)$$

Another approach to the problem of e.m. for the particular case of the separation of isotopes in an electric field was given by Klemm [16,17]. If $z_i$ is the valency, $\zeta_i$ the degree of ionisation, $N_i$ the mole fractions, $r_{ik}$ the "coefficients of friction" between particles of the $i$th and $k$th types and $v_{ik} = v_i - v_k$ the relative velocity of particles of the $i$th and $k$th types, the conditions for equality of the electric forces and the forces of friction for each type of particle can be written in the form:

$$\begin{aligned} -\zeta_1 z_1 F \operatorname{grad}\varphi &= r_{12}N_2 v_{12} + r_{1n}N_n v_{1n}, \\ -\zeta_2 z_2 F \operatorname{grad}\varphi &= r_{21}N_1 v_{21} + r_{2n}N_n v_{2n}, \\ \zeta_n z_n F \operatorname{grad}\varphi &= r_{n1}N_1 v_{n1} + r_{n2}N_2 v_{n2}, \end{aligned} \qquad (40)$$

where the subscript 1 refers to the light isotope, the subscript 2 to the heavy isotope, and the subscript $n$ to the electrons. It is assumed that $r_{ik} = r_{ki}$ and $z_1 = z_2 = z$. We also have

$$N_1 + N_2 = N_p,\ N_p + N_n = 1,\ N_n = zN_p,$$

$$\zeta_p = (N_1\zeta_1 + N_2\zeta_2)/N_p. \qquad (41)$$

The solution of system (40) has the form

$$\frac{v_{12}}{v_{pn}} = \left(\frac{\zeta_1 - \zeta_2}{\zeta_p} - \frac{r_{1n} - r_{2n}}{r_{pn}}\right) \Big/ \left(1 + \frac{r_{12}}{zr_{pn}}\right). \qquad (42)$$

The subscript $p$ is written where the difference between 1 and 2 is insignificant.

It was shown [16] that

$$z\zeta_p\left(1 + \frac{r_{12}}{zr_{pn}}\right) = \frac{RT\varkappa}{F^2 cD}, \qquad (43)$$

where $c$ is the concentration of the substance in g-equiv. $cm^{-3}$.

Klemm considers that this model cannot explain the experimentally observed movement of the light isotope towards the anode during electromigration and suggests that the ions of each type may exist in two states — mobile (activated) and immobile. It is then necessary, instead of the three equations (40), to write four equations: for the mobile ions of the light isotope, the mobile ions of the heavy isotope, the immobile ions, and the electrons. Using the subscript $b$ to denote the mobile ions and the subscript $u$ to denote the immobile ions, Klemm [17] obtained

$$\frac{v_{12}}{v_{pn}} = \frac{N_b}{N_p}\frac{v_{bn}}{v_{pn}}\frac{r_{2bu} - r_{1bu}}{r_{bn}} \Big/ \left(1 + \frac{N_b}{N_n}\frac{r_{1bab}}{r_{bn}}\right). \qquad (44)$$

The available experimental data on e.m. and diffusion in liquid metallic solutions do not, however, give sufficient grounds for accepting the hypothesis that the properties of ions in the ground state and transition state differ significantly. On the contrary, it has been shown [18,19] that diffusion in liquid metals is described satisfactorily by a theory which differs from the Frenkel'–Eyring theory and does not introduce the activation energy. Thus the question of the extent to which it is necessary to allow for the differences in the properties of the same ion at different moments of time (that is, at different points in its path) remains open. Nevertheless, the fact that the Stokes–Einstein relationship

$$D = \frac{kT}{4\pi\eta r}, \qquad (45)$$

applies satisfactorily to metallic solutions (see, for example, Ma and Swalin [19] and Sobol' [20]) indicates that the drift model is quite satisfactory. If this is the case, the differences in the properties of the ions at different points in its path can as a first approximation be assumed to be insignificant. It is possible that this is not the case for the effect of isotope separation by the e.m. method in liquid metals. Unique features may also be produced in liquid systems with strong interaction between the components (with the formation of intermetallic compounds), particularly at points close to the corresponding maxima on the liquidus curves. This question requires further study.

In the transfer of ions in electrolyte solutions it is necessary to take account of the relaxation and cataphoretic effects. Effects analogous to these may be produced in molten metals. In particular, the "electron wind" may be regarded as essentially an electronic cataphoretic effect. The relaxation effect, proportional to the rate of drift of the ions, is apparently negligibly small in metals, since in this case the fields which can be produced are weak. We may also, however, have an ionic cataphoretic effect, that is, entrainment of an ion during e.m. by the surrounding ions. This effect was examined [22] by the Debye–Fal'kenhagen method, with the assumption that each ion entrains its first coordination sphere, which moves as a single unit.

In a completely disordered solution there is no ionic cataphoretic effect, since the force acting on the first coordination sphere is equal to zero. When a statistical correlation exists, the second approximation of the theory of solutions [22] gives

$$e_i^{**} = e_i^*\left(1 + \frac{\Delta H}{2\pi\eta r_c N D}\right), \qquad (46)$$

where $e_i^{**}$ is the apparent effective charge, $e_i^*$ the effective charge taking account of only the "true charge" and the interaction with the conductivity electrons, $\Delta H$ the enthalpy of mixing of the given solution, $\eta$ its dynamic viscosity, $r_c$ the radius of the first coordination sphere, $N$ Avogadro's

number, and $D$ the diffusion coefficient. Formula (46) is applicable for $|\Delta H| \ll RT$, when the quasichemical method of the theory of solutions is applicable. Substituting $D$ from (45) and assuming that $r/r_c \simeq 1/3$, we obtain[22]

$$e_i^{**} \simeq e_i^{*}\left(1 + \frac{2}{3}\frac{\Delta H}{RT}\right). \quad (47)$$

Thus positive deviation from ideal behaviour should lead to the inequality $|e_i^{**}| > |e_i^{*}|$, and negative deviation should lead to the opposite inequality.

In the case where $|\Delta H| > RT$, it is fairly difficult to take account of the interaction of ions of different type during e.m. In this case, however, interesting effects are observed, particularly the inversion of the direction of e.m. at definite concentrations of the solution[23]. A solution of the problem of the influence of the strong interaction of ions in alloys on e.m. would be extremely useful.

## III. METHODS OF STUDYING ELECTROMIGRATION IN LIQUID METALS

The most common method involves the study of the stationary distribution of the components of the solution in a capillary. The liquid alloy is poured into the capillary and direct current is passed through it until a stationary state is established. The alloy is then cooled and analysed, graphs giving the distribution of the components along the capillary are constructed, and the electromigration characteristics are calculated.

Studies have shown[24,25] that the position and shape of the capillary have a very marked influence on the results of the experiment. In particular, the straight horizontal capillary used by Kremann and coworkers is unsuitable for the study of e.m. During e.m., a density gradient is produced along the capillary, leading to longitudinal convection; the heavier layers of metal flow under the lighter layers. Increase in the capillary diameter facilitates this process. Thus the results obtained in horizontal capillaries of appreciable diameter (1.5–3 mm) may be regarded as only qualitative.

Zigzag and spiral capillaries have been used[24,26-29] to reduce convection. This precaution is inadequate, since in the bends in the capillary, where the heavier component should migrate upwards, an unfavourable density gradient is created and convection is produced.

It is possible to estimate the part played by convection from the time required for the stationary state to become established. The order of magnitude of this time interval is

$$\tau \sim l^2/D, \quad (48)$$

where $l$ is half of the length of the capillary. For example, for a capillary with length 40–50 cm and $D \sim 10^{-5}$ cm$^2$ s$^{-1}$, the value of $\tau$ is ~ 300–400 d. The observed values, however, are $\tau_{obs} \simeq 20$ h,[23] $\tau_{obs} \simeq 300$–400 h,[27] and $\tau_{obs} \simeq 2000$ h,[24] that is, $\tau_{obs} \ll \tau$. Thus convection takes place in spiral and zigzag capillaries, so that the effective diffusion coefficient $D_{eff} \gg D$.

Straight vertical capillaries have also been used to study e.m.[25,30-34]. A vertical temperature gradient of ~ 0.5–1 deg cm$^{-1}$ was produced with a heater, and the direction of the current in the specimen was chosen in such a way that the lighter component migrated upwards. These precautions ensured a decrease in density from below upwards, and this favours suppression of convection. Under these conditions $\tau_{obs} \simeq \tau$.[35,36] For example, for a 40 mm column of metal, $\tau_{obs} \simeq 2$ d.

The influence of free convection and surface phenomena on diffusion was verified[25] in studies which showed that with change in the capillary diameter from 0.64 mm to 2.09 mm the diffusion coefficient of $^{113-123}$Sn in Pb at 350° changes insignificantly. Thus under these conditions (small) vertical temperature gradient, concentration of light component decreasing from above downwards) free convection can be suppressed. The same result was obtained in a study of the effect of the e.m. of $^{110m}$Ag in liquid Pb and Sn in capillaries with different diameters[25].

An extremely important factor in the capillary method is the current density. In work by Kremann and coworkers[23,37-47], a "saturation" effect was observed: at high current densities (10–20 A mm$^{-2}$ and above), the e.m. became independent of current density; this was attributed to the turbulent nature of the movement of the melt in the capillaries. At low current densities (~ 1 A mm$^{-2}$ and below) the e.m. effect is proportional to the current density[24,25].

It was established[48] that the scattering of electrons at the boundary between the molten metal and the walls of the capillary should produce electroconvection, in which the metal moves in the same direction as the electrons along the axis of the capillary, and in the opposite direction at the walls of the capillary. In this case the apparent effective charge will be less than the actual value. Let us introduce the symbol $z^*$ to denote the effective charge, expressed in units of the charge of the electron $e$, that is, $z^* = e^*/e$. It was shown[25] that

$$\frac{z^*}{z^*_{app}} = 1 + \frac{10^{-4}}{0.48 D_0 D}(1-\varepsilon)^2\left(\frac{end\lambda^2}{\eta}\right)^2 E^2, \quad (49)$$

where $D_0$ is the coefficient of self-diffusion of the solvent, $\epsilon$ a coefficient defining the proportion of electrons undergoing mirror reflection from the boundary, $d$ the diameter of the capillary, $n$ the concentration of free electrons, $\lambda$ the mean free path, $\eta$ the viscosity, and $E$ the field intensity.

It was found[22] that for the case of the e.m. of $^{60}$Co in liquid Sn at 350° the dependence of $z^*/z^*_{app}$ on $E^2$ is in fact linear up to a current density of 5.3 A mm$^{-2}$. The mean free path of the electrons, calculated from the slope of this straight line, is $2.2 \times 10^{-7}$ cm (with the assumption that $\epsilon = 0$), which is of the same order of magnitude as the value of $\lambda$ calculated from the electrical conductivity of tin ($0.92 \times 10^{-7}$ cm). The optimal current density in metals of the type Sn, Pb, and Bi, at which electroconvection can still be neglected, is 1–1.5 A mm$^{-2}$.

In this connection it should be noted that work on the separation of isotopes during e.m. in metals (the Haeffner effect)[49-52] is usually carried out at high current densities (10–20 A mm$^{-2}$ and above). This should lead to the development of electroconvection, so that the results obtained in this work can hardly be regarded as quantitative. The marked influence of electroconvection is indicated by the fact that the values of the effective diffusion coefficient in liquid Rb, K, and In [52] varied from $2.5 \times 10^{-4}$ cm$^2$ s$^{-1}$ to $10^{-3}$ cm$^2$ s$^{-1}$, that is, they are greater by 1–2 orders of magnitude than the real values. To obtain accurate results, it is necessary to carry out e.m. experiments at low current densities.

Another possible mechanism of the influence of current density on the e.m. effect was considered[35]: excitation of laminar convection as a result of the heating of the metal in a vertical capillary by the direct current. Since the temperature at the axis is slightly higher than that at the walls

of the capillary, the metal begins to rise along the axis and to descend at the walls, leading to convective agitation. It was found[35] that

$$\frac{z^*}{z^*_{app}} = 1 + 2.26 \times 10^{-7} \frac{R^{10}}{D^3} \left( \frac{g\beta\rho j^2}{\nu\gamma} \right)^3, \quad (50)$$

where $R$ is the capillary radius, $g$ the acceleration due to gravity, $\beta$ the coefficient of volume expansion, $\rho$ the resistivity, $j$ the current density, $\nu$ the kinematic viscosity, and $\gamma$ the thermal conductivity.

The convection effect is extremely sensitive to the radius of the capillary. It follows from formulae (49) and (50) that for a radius of 1 mm and current densities less than 10 A mm$^{-2}$, the effect of electroconvection should be more marked than that of thermal convection. At a radius of 2 mm and $j$ = 10 A mm$^{-2}$, however, the decisive role should be played by thermal convection (for common metals). In this case the ratio $z^*/z^*_{app}$ should be proportional to $j^4$ and not $j^2$. It is necessary, however, to take account of the fact that the presence of rough areas on the walls of the capillary or the existence of an immobile surface layer of liquid should suppress electroconvection.

Other reasons for the convective agitation of melts in capillaries during the passage of direct current have been discussed[53]: these include electroosmosis[54] and magnetic movement resulting from conicity of the capillaries. It was shown that convection and hence increased effective diffusion coefficients may be produced by a magnetohydrodynamic effect at conicities of the order of 0.01 cm$^{-1}$; the effect is proportional to the current density to the fourth power and the capillary radius to the tenth power. Unlike thermal convection — formula (50) — which develops in vertical capillaries, magnetohydrodynamic convection should be observed for any position of the specimen.

When the stationary state has been reached and fixed by cooling, the specimens are divided into sections and analysed, and a curve is constructed giving the dependence of the logarithm of the thermodynamic activity of a given component on the length along the axis of the specimen. The effective charge $z^* = e^*/e$ can be found from Eqn. (38)[31,32]. The authors of the works cited restricted themselves to the determination of the difference between the concentrations at the ends of the specimens or the calculation of various e.m. characteristics (for example, a constant[27-29] for which the name "electrodiffusion coefficient" was proposed), whose relationship to the effective charge can be established.

An interesting feature is that the e.m. effect depends little on temperature. Experimental work[24,25,27,47] has shown that change in temperature over a range of 100 deg has no influence on $z^*$ (there are grounds for expecting $z^*$ to show this behaviour, see below). The study of e.m. over a wide temperature range would be extremely valuable, however. Unique features in the behaviour of $z^*$ might possibly be observed at temperatures close to the melting point.

A direct determination of the rate of migration of an impurity in an electric field has been carried out[55,56]. Two identical capillaries, placed vertically and filled with mercury, were used. Contacts were sealed to the upper ends, and the lower ends were immersed in a dish containing mercury. If current is passed through the specimens in series, the two capillaries are heated to the same extent, and a differential thermocouple with junctions fixed at corresponding points in the capillaries will show no readings. If the mercury in one of the dishes is replaced by an amalgam, the impurity begins to migrate along the capillary and alters the resistance of the mercury. The temperature at different points in the capillary will then change as a result of the change in power. At the moment when the diffusion front reaches one of the thermocouple junctions, it will begin to give readings. From a knowledge of the time required for the diffusion front to move from the end of the capillary to the point where the junction was situated, Schwarz calculated the mobility of the impurities in mercury.

A feature of this method is that in the simultaneous e.m. of several impurities, the latter move at different rates and are separated in space, as in chromatography.

The mobilities of various impurities in mercury were studied[14] by measuring the electrodiffusion potential. To increase the effect, Schwarz connected ten cells in series, since the e.d.p. of a single cell amounted to $10^{-7}$–$10^{-8}$ V. The transport numbers of the impurities were determined from formula (36). The e.d.p. effect in liquid alloys of tin, lead, bismuth, tellurium, etc. has also been studied[57,58].

A method was recently proposed for studying e.m. in crossed electric and magnetic fields[59,60]. A gold amalgam was placed in a 10 cm × 1 cm × 0.025 mm vacuum-tight vessel. The electric current was passed in a direction parallel to the 1 cm edge and a magnetic field with induction 5500 G was applied in a direction perpendicular to the 10 cm × 1 cm face. After passage of a current of 15 A for 6 days, the amalgam at one end of the long edge showed threefold enrichment relative to that at the other end. The effect was assumed to be due to the fact that the velocities of the electrons directed at right angles to the electric and magnetic fields were not equal to zero (in a second approximation)[60]; the Hall field was assumed to be insignificant.

The force acting on the ion in crossed fields was calculated[61]. According to this calculation,

$$F_i = E_x e \bar{v}_i \left( \frac{z_i}{\bar{v}_i} - \frac{z_0}{\bar{v}_0} \right), \quad (51)$$

where $z_i$ and $z_0$ are the true charges of the impurity and solvent ions, $\bar{v}_i$ and $\bar{v}_0$ their volumes, and $E_x$ the intensity of the Hall field. Application of formula (51) to Knof's results[59] gives an absurd result for $z$ for gold (of the order of $10^4$ units of electronic charge[35]). Calculations made by Knof[60] also give a value for the effect which is smaller by two orders of magnitude than that observed in earlier work[59]. Further studies are required to find the reasons for this discrepancy. It is possible that in the earlier work[59] a characteristic multiplication effect operated, analogous to that in thermal-diffusion columns.

## IV. DETERMINATION OF THE EFFECTIVE CHARGES OF IONS IN METALLIC SOLUTIONS

As pointed out above, in order to establish the significance of the effective charge it is necessary to examine all the forces acting on the ion of a given type. According to Mangelsdorf[62], it is necessary to take account of the following forces: (1) the ordinary field force; (2) a force due to polarisation of the non-localised electrons by the field; (3) a force due to polarisation of the electrons by the current (the conductivity electrons are scattered on the ions and should "push" the charge cloud screening the ion in the direction of their movement; (4) a force due to polarisation of the surrounding ions by the field; and (5) a force related to the polarisation of the surrounding ions by the current.

Finally, if chemical forces operate between the impurity ion and the surrounding solvent, an important factor, according to Mangelsdorf[62], is the ratio of the radius of influence of these forces to the mean free path of the electrons, that is, the number of collisions with ions undergone by an electron scattered by the impurity in the sphere of action of the chemical forces. Mangelsdorf[62] did not give an analysis of the relative part played by these factors.

If the interaction between the ions of the components is not significant (energy of mixing $\Delta\epsilon = \epsilon_{12} - \frac{\epsilon_{11} + \epsilon_{22}}{2} \ll kT$, where $\epsilon_{ik}$ is the energy of interaction of pairs of ions which are nearest neighbours), the chief forces acting on an ion in a metal during e.m. are the field force and the "force of the electron wind" (forces 1 and 3 according to Mangelsdorf[62]). The first of these is determined by the so-called "true charge" of the ion and the second by the intensity of the interaction of the ion with the current. To describe the interaction it is more convenient to use not the coefficients of friction $r_{ik}$ introduced by Klemm[16,17] but the cross-section for the scattering of electrons on the ions[63].

Calculation of the interaction force of the electrons with the current, carried out by Fiks[64] for a free-electron model (degenerate gas), leads to the expression

$$F_e = -eEnl\sigma, \qquad (52)$$

where $e$ is the charge on the electron, $E$ the field intensity, $n$ the concentration of free electrons, $l$ the mean free path on the Fermi level, and $\sigma$ the cross-section of scattering of the electron on the impurity ion. In the case of a pure metal, $nl\sigma = z$, where $z$ is the valency of the ion, so that the force $F_e$ is equal to the field force $zeE$ with the opposite sign; this satisfies the condition for mechanical equilibrium of the specimen.

Fiks[64], like Klemm[17], assumed that it is necessary to take account of the differences in the properties of the ions in the ground state and transition state for e.m. in liquid metals, at least for the case of the separation of isotopes. For the total force acting on the $i$th ion in the transition state ("activated ion"), Fiks[64] obtained

$$F_i = eE\left(z_{ti} - \bar{z}\frac{\sigma_i^*}{\bar{\sigma}}\right), \qquad (53)$$

where $z_{ti}$ is the "true charge" of the $i$th ion in the transition state, $\sigma_i^*$ the corresponding cross-section of scattering, $\bar{z}$ and $\bar{\sigma}$ the mean values of $z$ and $\sigma$ for all the components of the solution. Thus for the effective charge the following expression is applicable

$$e_i^* = ez_i^* = \frac{F_i}{E} = e\left(z_{ti} - \bar{z}\frac{\sigma_i^*}{\bar{\sigma}}\right), \qquad (54)$$

that is,

$$z_i^* = z_{ti} - \bar{z}\frac{\sigma_i^*}{\bar{\sigma}}. \qquad (55)$$

It was shown[31] that relationship (55) can be obtained directly from the condition for mechanical equilibrium of the specimen (39). Here it was assumed that the difference in the electrical properties ($z$ and $\sigma$) of different ions of the same component is insignificant for e.m. in liquid metallic solutions. Thus for a two-component solution the following expressions are applicable[31]:

$$z_1^* = \frac{N_2(\sigma_2 z_1 - \sigma_1 z_2)}{\sigma_1 N_1 + \sigma_2 N_2},$$

$$z_2^* = \frac{N_1(\sigma_1 z_2 - \sigma_2 z_1)}{\sigma N_1 + \sigma_2 N_2}, \qquad (56)$$

where $z_i$, $\sigma_i$, and $N_i$ are the "true charge" of the $i$th ion, the cross-section of scattering of the conductivity electrons on the $i$th ion, and the mole fraction of the $i$th component respectively. For a very dilute solution ($N_2 \to 0$):

$$z_1^* \simeq 0, z_2^* = z_2 - z_1\frac{\sigma_2}{\sigma_1}. \qquad (57)$$

Determination of the values of the true charges on the ions of the components in different solutions would give information on the type of bond and the distribution of electrons close to the impurity atom, and would undoubtedly be extremely valuable for the theory of the metallic state. On the other hand, a knowledge of the cross-section of scattering is of interest for the theory of electrical conductivity, the thermal conductivity of metals, etc. It can be seen from (57)–(59) that it is impossible to calculate unambiguously all the values of $z$ and $\sigma$ for the ions of the components of the solution merely from e.m. data. It has been shown[30,31,33,34], however, that fairly reliable data on $z$ and $\sigma$ can be obtained by studying e.m. in a series of suitably selected solutions, for example, with a common solvent or a common impurity.

To estimate the cross-section for scattering of the electrons on the impurity ion $\sigma$ it is possible to use the relationship between $\sigma$ and the influence of the impurity on the electrical resistance of the solvent[65,66]

$$\Delta\rho_i = \frac{mv_0}{e^2} N_i\sigma_i, \qquad (58)$$

where $mv_0$ is the impulse of the electron on the Fermi level, $e$ its charge, $N_i$ the atomic fraction of the impurity, and $\Delta\rho_i$ the residual resistance due to the impurity. In the case of liquid alloys, however, Eqn. (58) appears to be unsuitable. According to (58), $\Delta\rho_i$ should always be positive. For solid solutions this is almost always the case. In the case of liquid alloys, however, positive values of $\Delta\rho$ are encountered no more frequently than negative values. This is due to the fact that in systems with low affinity of the components (for example, in simple eutectic systems) a tendency towards additivity of the resistivity of the alloys is observed. The applicability of Eqn. (58) to liquid alloys is thus doubtful.

Mott[65,66] examined a solution of a multivalent impurity in a univalent metal and used, to calculate $\sigma$, the ordinary theory of scattering of electrons by a force centre with spherically symmetrical field[63]. The form of the force field was obtained by the Thomas–Fermi method as a screened coulombic potential

$$\varphi = \frac{\Delta ze}{r}e^{-\beta r}, \qquad (59)$$

where $\Delta z$ is the difference in the valencies of the impurity and solvent, $\beta$ a screening constant, and $r$ the distance from the ion. Thus for the value of $\sigma$ we have[65]

$$\sigma = \frac{\pi}{2}\frac{e^4(\Delta z)^2}{\epsilon_0^2}\left\{\ln\left(1+\frac{1}{y}\right) - \frac{1}{1+y}\right\}, \qquad (60)$$

and

$$\frac{1}{y} = \frac{(2mv_0)^2}{\beta^2\hbar^2}. \qquad (61)$$

where $\epsilon_0$ is the Fermi energy and $\hbar$ Planck's constant divided by $2\pi$. Substitution of the value of $\beta$ gives for $1/y$ the expression

$$1/y = 5.1 \times 10^{-8} n^{1/3} z^{1/3}, \qquad (61a)$$

where $n$ is the concentration of free electrons and $z$ the charge of the ion.

It was also pointed out[65], however, that in metals the electron density is insufficiently high for the Thomas–Fermi method to be completely applicable. Kun[67] calculated the residual resistance for a solution of gold in silver; the electron density was found by the Thomas–Fermi method. and also by exact solution of the Schrödinger equation. The two methods gave similar values for $\Delta\rho$ (0.16 $\mu\Omega^{-1}$ per 1 at.% Au), which showed poor agreement with the experimental value (0.38 $\mu\Omega$ $cm^{-1}$ per 1 at.% Au). According to Kun[67], the discrepancy is due to the fact that the free-electron model is not completely applicable to the phenomenon of electrical conductivity. The results given by formula (60) are therefore only of the correct order of magnitude.

The cross-sections of scattering for impurities in multivalent-metal solvents have apparently not been calculated.

## V. RESULTS OF STUDIES OF ELECTROMIGRATION IN LIQUID METALLIC SOLUTIONS

### 1. Electromigration in Amalgams

A number of studies have been made of the phenomenon of e.m. in amalgams[13,14,23,24,43,46,55,56,68-72]. Some of these studies[13,14,24,55,56,72] produced more accurate results than the others, in which inadequate procedures made it impossible to obtain reliable results.

Lewis and coworkers[13] found that traces of sodium and potassium in dilute amalgams move towards the anode during e.m., that is, exhibit a negative effective charge. They therefore suggested[13] that the alkali metal atoms undergo chemical reaction with mercury, forming more or less stable complexes which are the actual diffusion units. These investigators noted[13] a relationship between the magnitude of the e.m. effect and the influence of the impurity on the electrical resistance of mercury. This correlation led them to the conclusion[13] that e.m. in amalgams is due to "friction" between the complexes and the stream of conductivity electrons.

The existence of "friction" between complexes and the stream of conductivity electrons was suggested even earlier by Skaupy[73,74], in whose opinion these complexes should also influence the viscosity, the conductivity being smaller, the greater the increase in viscosity of mercury when the impurity is added. If the impurity decreases the resistance of mercury, it should move to the cathode during e.m.

Results obtained[24] for amalgams of Na, Ba, Li, and Ca confirmed this viewpoint (see Table 1). The movement of complexes towards the cathode can be understood, however, only if account is taken of the action of the ordinary field force on the positive charge.

The results obtained by Schwarz by different methods are summarised in his monograph[14] and are given in Table 2. The second column gives the values of the transport numbers at 25°, divided by the atomic fraction of the impurity. The third column gives the values of the velocity of migration $V$ (cm $h^{-1}$) for a field intensity of 1 V $cm^{-1}$. The positive sign denotes that the impurity migrates towards the cathode. An interesting feature is that the values of the mobilities of the impurities in mercury, obtained by three different methods (establishment of the stationary state in a capillary, direct measurement of the velocity of migration, and measurement of the e.d.p.) show satisfactory agreement with one another[14], apparently indicating that in Schwarz's measurements convection played little part.

The fourth column of Table 2 gives the values of the diffusion coefficients $D$ for impurities in mercury at 25°, measured by Schwarz[76]. We used this data and the relationship

$$V(\text{cm h}^{-1}) = \frac{3600ez^*D}{300\,kT}, \qquad (62)$$

to calculate the effective charges $z^*$ of the impurities in mercury (fifth column in Table 2). The sixth column gives the values of the increments in the resistivity per 1 at.% of impurity[75].

It can be seen that for most impurities a relationship is observed between the signs of $z^*$ and $\Delta\rho$: a positive value of $z^*$ corresponds to a negative $\Delta\rho$, and vice versa. This correlation is not observed for Tl, Pb, and Bi; the first two undergo almost no migration in the field, and bismuth moves on the "wrong" direction. The suggestion that there exists friction between complexes and the stream of electrons evidently does not make it possible to explain all the phenomena of e.m. in amalgams.

The dependence of $z^*$ on $\Delta\rho/c$ (Fig. 1) constructed from the data in Table 2, shows that most impurities can be divided into groups, within which the relationship between $z^*$ and $\Delta\rho/c$ is approximately linear. However, if we construct the dependence of $\Delta\rho/c$ on the relative change in volume on the dissolution of impurities in mercury, we find that Zn, Cd, Tl, Sn. Pb, and Bi lie satisfactorily on the

TABLE 1. Electromigration of impurities in mercury[13] and their influence on the resistivity of mercury[75].

| Impurity | Composition, at.% | Current density $j$, A $mm^{-2}$ | Specific e.m. effect, $\Delta/j$ | Increment in resistance $\Delta\rho/c$, $\mu\Omega$ cm (at.%)$^{-1}$ | Direction of movement |
|---|---|---|---|---|---|
| Na | 2.89 | 0.43 | 1.24 | 0.7 | towards the anode |
| Ba | 0.509 | 0.36 | 0.10 | 1.6* | towards the anode |
| Li | 1.267 | 0.35 | —0.11 | —2.0 | towards the cathode |
| Ca | 1.245 | 0.40 | —0.14 | —3.51 | towards the cathode |

* Taken from Lewis and coworkers[13].

TABLE 2. Electromigration in amalgams[14] and the influence of impurities on the resistivity of mercury[75] at 20°.

| Impurity | $\frac{10^8 t}{c}$, g-atom (at. fraction)$^{-1}$ × × faraday$^{-1}$ | $V$, $cm^2 V^{-1} h^{-1}$ | $10^5 D$, $cm^2 s^{-1}$ | $z^*$ | $\Delta\rho/c$, $\mu\Omega$ cm (at.%)$^{-1}$ |
|---|---|---|---|---|---|
| Li | 7.5 | 0.41 | 0.92 | 0.31 | —2.0 |
| Na | — 7.8 | —0.43 | 0.86 | —0.43 | 0.7 |
| K | —23 | —1.3 | 0.71 | —1.31 | 2.9 |
| Cs | —79 | —4.3 | 0.63 | —4.87 | — |
| Ag | 40 | 2.2 | 1.11 | 1.43 | —3.7 |
| Au | 27 | 1.5 | 0.73 | 1.47 | — |
| Mg | 63 | 3.5 | — | ~1 | — |
| Ca | — | <0.2 | — | <0.1 | —3.51 |
| Zn | 77 | 4.2 | 2.4 | 1.25 | —4.4 |
| Cd | 64 | 3.5 | 2.0 | 1.25 | —3.7 |
| Tl | 1 | 0.0 | 1.18 | 0.0 | —2.1 |
| Pb | 1 | 0.0 | 2.08 | 0.0 | —5.8 |
| Bi | —52 | —2.9 | 1.5 | —1.38 | —3.7 |
| Sn | 35 | 1.9 | 2.09 | 0.65 | —6.5 |
| Ga | 52 | 2.9 | — | ~1 | — |

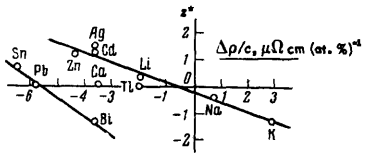



Fig. 1. Dependence of the effective charges of impurities in mercury on the increments in the electrical resistance.

same straight line[62]. The point corresponding to the changes in volume and resistivity during the crystallisation of mercury lies on the same straight line. This gave grounds for the suggestion[62] that the influence on the resistivity of mercury shown by those impurities which lower the resistance is that which would be expected if a certain volume of mercury "crystallised" around the impurity atom. This process leads to a decrease in resistance.

A noteworthy feature is that traces of Sn, Pb, and Bi in mercury form a separate group in Fig. 1. The displacement of the effective charges for these impurities towards more negative values compared with the other impurities may be due to the fact that, in addition to the above-mentioned complexes formed close to the impurity atoms, other factors also have an influence in this case, for example, the true charge $z$. It is significant that Sn, Pb, and Bi are multivalent, whereas the other metals given in Fig. 1 are univalent or bivalent (the properties of thallium resemble those of a univalent metal). The large excess of charge on the Sn, Pb, and Bi ions should lead to increased scattering of electrons on the impurity ions and should therefore displace $z^*$ towards more negative values.

The interesting phenomenon of inversion of e.m. was observed in amalgams of Na, K, and Ba.[23,43] The experiments were carried out in 20–80 cm capillaries with internal diameter 0.4–1.6 mm, at 240° and current density 3–7 A mm$^{-2}$. The duration of the experiment was 70 h. It was found that at impurity concentrations less than 15 at.% Na, 11 at.% K, and 3.9 at.% Ba, the impurities move towards the anode, whereas at higher concentrations they move towards the cathode.

In these systems the interionic interaction apparently has a significant influence on e.m. In the solid state a whole series of intermetallic compounds is formed ($BaHg_{11}$, $KHg_3$, $KHg_2$, KHg, $NaHg_4$, $NaHg_2$, etc.)[77], so that the short-range order in liquid amalgams should show corresponding characteristic features. There may be a change (even in the sign) of the "true charge" of each ion. Moreover, in systems with appreciable interionic interaction, the ionic cataphoretic effect discussed above may play an important part.

## 2. Electromigration of Impurities in Alkali Metals

From the viewpoint of the theory of the e.m. of impurities in alkali metals, an extremely interesting feature is that these metals are the simplest materials for study, and it is possible to carry out quantitative calculations for them; a number of studies have been made of e.m. in alkali metals[27–29,35,78–80]. Drakin and Mal'tsev[27] studied e.m. in the sodium–potassium system at 100° in bent capillaries and found that in this case inversion of the e.m. takes place; at concentrations less than 48 wt.%, sodium migrates towards the anode, and at higher concentrations it migrates towards the cathode. Study of the e.m. of traces of mercury (0.4 at.%) and lead (0.6 at.%) in liquid potassium at 100°[28] showed that in both cases the impurity migrates towards the anode, the e.m. effect being much greater than that in the liquid systems previously studied.

The e.m. of traces of thallium in potassium (0.19 at.%), mercury in sodium (0.6 at.% and 1.1 at.%), lead in sodium (0.45 at.%), and cadmium in sodium (0.21 at.%) was studied at 110° in a 15 cm capillary with internal diameter 2 mm.[29] The capillary was bent to form a spiral, and ten platinum leads were sealed into the walls of the capillary at equal intervals to measure the electrical resistance. It was possible to measure the e.m. effect with sufficient accuracy only for solutions of mercury in sodium and of thallium in potassium. More precise data for Pb and Cd in Na, and for Hg in K, were obtained later[78].

The effective charges $z^*$ of impurities in sodium and potassium, calculated from electrodiffusion coefficients[28,29,78] had the following values:

| Solvent | Na | Na | Na | K | K | K |
|---|---|---|---|---|---|---|
| Impurity | Hg | Pb | Cd | Tl | Hg | Pb |
| $z^*$ | −18 | −27.2 | −7.3 | −20 | −12.6 | −22 |

It was suggested[29] that the reason for such high negative values of $z^*$ for impurities in sodium and potassium is the entrainment of the particles of impurity by the stream of electrons ("electron wind").

The e.m. of $^{115m}$Cd and $^{204}$Tl in liquid sodium at 120° (impurity concentration 0.5 wt.%) was studied[35] in straight vertical capillaries with a 50 mm column of metal and internal diameter 1 mm. Electrodiffusion annealing was continued for 20 days with the passage of a current with strength 1.5 A through the specimens. The values found for the effective charges of Cd and Tl in sodium at 120° were -70 units and -55 units (accuracy ±15%). These charges were calculated for specimens with favourable direction of migration of the impurity (from above downwards).

The e.m. in a ternary K–Na–Hg system containing 46 wt.% Na, 50 wt.% K, and the rest Hg for different annealing times at 30° was studied[79] in a 77 mm vertical capillary with internal diameter 1.67 mm. Ten sealed-in platinum leads were used to follow the change in the concentration of the solution during e.m. It was assumed that in a melt with the above composition, potassium and sodium do not take part in e.m. (without allowance for the mercury, the composition coincides with that for which inversion of e.m. was observed[27]). The kinetic e.m. curves gave for the diffusion coefficient of mercury the value $1.16 \times 10^{-5}$ cm$^2$ s$^{-1}$ and for the "electrodiffusion constant" the value $1.82 \times 10^5$ deg V$^{-1}$. This value corresponds to an effective charge $z^* = -15$. This value is approximately equal to the mean of the values of $z^*$ for mercury in sodium and potassium.

The results of the measurement of the e.m. of impurities in alkali metals can be compared with their influence on the resistance of the solvent. Since the absolute value of $z^*$ for the impurities is high in all cases, it may be assumed that $|z| \ll |z^*|$. It then follows from (52) that

$$z_i^* \simeq -nl\sigma_i. \qquad (63)$$

From (63) and (58) we obtain

$$z_i^* \simeq -\frac{\Delta\rho_i}{N_i\rho_0}, \qquad (64)$$

where $\Delta\rho_i$ is the change in the electrical resistance of the solvent when the impurity is introduced, $N_i$ its mole fraction, and $\rho_0 = mv_0/(e^2nl)$ the electrical resistivity of the pure solvent.

Values were obtained for $\Delta\rho$ for a number of impurities in liquid sodium[81]. These can be used to calculate $z_i^*$(calc.). These values of $z^*$ are given in Table 3, together with published values[28,29,35].

The values of $z^*$ obtained experimentally in spiral capillaries[28,29] (Table 3) are much lower than the values obtained in vertical capillaries[35] and the values calculated from formula (64). On the other hand, the results obtained in vertical capillaries[35] show satisfactory agreement with the values of $z^*$ calculated from Eqn. (64). It may thus be assumed that Eqn. (58) is applicable to dilute solutions based on liquid sodium.

It is possible to verify the applicability of the Thomas–Fermi model for the case of solutions of impurities in sodium. The cross-section of scattering $\sigma$ for impurities with different ion charges in Na and K at 100° was calculated from Eqn. (60)[35] and the effective charges $z^*$ were calculated from the formula[61]:

$$z^* = z - nl\sigma \qquad (65)$$

(see Table 4). It can be seen from Table 4 that the calculated values of $z^*$ for impurities with an ion charge $z \leqslant 2$ have a reasonable order of magnitude, but that for $z = 3$ the calculation gives values of $z^*$ which are not observed experimentally.

The use of the Thomas–Fermi method in this case is hardly valid, since there is a fairly strong interaction between the atoms of the impurities Cd, Pb, Hg, etc. and the solvent. In the solid state, the alkali metals react with heavy metals to form intermetallic compounds of the type $NaCd_2$, $K_2Pb$, KTl, etc.[77] This interaction leads to ordering of the solvent close to the impurity atom: the bond becomes covalent or even partly heteropolar. The valency electrons of the impurity will therefore not become non-localised in the usual sense.

TABLE 3. Effective charges of impurities in liquid sodium.

| Impurity | $\Delta\rho_i/N_i$ (Ref. 81), $\mu\Omega$ cm (at. %)$^{-1}$ | $z^*$ calc. from Eqn. (64) | $z^*$ (Refs. 28, 29, and 78) | $z^*$ (Ref. 35) |
|---|---|---|---|---|
| Cd | 4.45 | —44 | —7.3 | —70±10 |
| Tl | 7.5* | —75 | — | —56± 8 |
| Hg | 6.0 | —60 | —18 | — |
| Sn | 9.5 | —95 | — | — |
| Pb | 10.8 | —108 | —27 | — |

* By interpolation.

TABLE 4. Effective charges of impurities in alkali metals at 100°, found by Thomas–Fermi method.

| $z$ for impurity | $\Delta z = z - 1$ | In potassium | | In sodium | |
|---|---|---|---|---|---|
| | | $10^{16}\sigma_i$, cm$^2$ | $z^*$ | $10^{16}\sigma_i$, cm$^2$ | $z^*$ |
| 1 | 0 | 0 | 1 | 0 | 1 |
| 2 | 1 | 2.27 | —42 | 1.34 | —49 |
| 3 | 2 | 10.7 | —207 | 6.16 | —235 |
| 4 | 3 | 25.8 | — | 15.3 | — |

TABLE 5. Effective charge of the spherical nonconducting complexes (radius = $r$) in potassium and sodium at 100°.[35]

| $10^8 r$, cm | Effective charge | |
|---|---|---|
| | in potassium | in sodium |
| 1 | —24 | —48 |
| 2 | —97 | —192 |
| 3 | —219 | —435 |

It was shown[22] that when the bonding is strong, it is possible to use a model according to which the impurity atom forms a stable complex with the solvent which behaves during e.m. as a non-conducting sphere of radius $r$. In this case[63]

$$\sigma = 4\pi r^2, \qquad (65a)$$

from which, in accordance with (63),

$$z^* = -4\pi nlr^2. \qquad (66)$$

The calculated values of $z^*$ for impurities in K and Na (Table 5) show that the non-conducting sphere model gives reasonable values of $z^*$ when the radii of the complexes have the values 1–2 Å. The real radius should be about twice this value. Thus the non-conducting sphere model gives values of $z^*$ which are too high by a factor of $\sim 2$–4. A possible reason is that the region inside the complex is not completely inaccessible to the conduction electrons, so that the non-conducting sphere model is not applicable in these cases.

The e.m. of oxygen in liquid sodium at 300° was studied[80] in U-shaped Pyrex capillaries with broadened sections at the ends. Extensive migration of oxygen towards the anode was observed, amounting to several tenths of a milligramme of oxygen for every 3600 C of electricity passed, at an average oxygen concentration of $\sim 5 \times 10^{-2}$ wt.%. Calculation using formula (62) shows that the value of $z^*$ for oxygen in liquid sodium has an order of magnitude of $-10^4$. If these results are reliable, they may be explained by means of the non-conducting sphere model. According to (66), the value of $z^*$ is $-10^4$ for $r \simeq 15$ Å, that is, the complex should contain 100–150 atoms of oxygen and sodium.

### 3. Electromigration in Various Solvents (Semiquantitative Data)

Here we shall deal chiefly with the results of Kremann and coworkers, but also some data obtained by others[26,82,83]. Kremann characterised the e.m. effect by the difference ($\Delta$) in the weight percentages of each component at the ends of the specimens. The results which he obtained can be regarded as only qualitative, because of the unsatisfactory features of the procedure used.

Drakin[26] made a special study of e.m. in eutectic tin–bismuth and cadmium–bismuth alloys close to the eutectic

point. If the initial state of the alloy is given by a point close to the eutectic on the equilibrium diagram, the portions of the alloy at the ends of the specimen during e.m. may fall in two-phase regions of the diagram, as a result of enrichment in one of the components. The corresponding solid solutions or pure metals begin to separate from the melt. It was shown[26] that the e.m. method makes possible the fairly satisfactory separation of the original eutectic alloy into almost pure components, particularly if the solid components have a higher resistivity than the liquid.

The results obtained by Kremann and coworkers and by other workers[26,82,83] are given in Table 6. The sixth column gives the components migrating towards the cathode, the fifth column gives the current density $j$, and the seventh column gives the e.m. effect $\Delta$.

Kremann[84] tried to explain his results on the basis of Skaupy's ideas[73] regarding dissociation in metallic solutions. According to Kremann, the more positive component in the solution should be the one with the lower ionisation energy; this component will also migrate to the cathode during e.m. Kremann[84] arranged the substances which he studied in the following order:

$$\text{Br Sb Hg Pb Sn Zn Cd Cu Ag Al Na K}. \qquad (67)$$

A solution component lying to the right in series (67) should migrate to the cathode during e.m.

Let us write in the same order the first ionisation potentials of the atoms of series (67) (in eV):

$$7.25 \quad 8.35 \quad 10.41 \quad 7.37 \quad 7.54 \quad 9.37 \quad 8.94 \quad 7.67 \quad 7.58 \quad 5.94 \quad 5.09 \quad 4.32. \qquad (68)$$

TABLE 6. Electromigration in liquid metallic alloys[26,82,83,14].

| System | Temperature, °C | Concentration, wt. % | Duration of annealing, h | Current density, A mm$^{-2}$ | Component moving to cathode | Effect $\Delta$, wt. % | Refs. |
|---|---|---|---|---|---|---|---|
| Ag—Al | 900 | 50—80 Al | | | Al | 15 | * |
| Ag—Bi | | 30 Ag | | | Ag | 3 | * |
| Ag—Cu—Sn | 1000 | 30 Cu, 1—11 Sn | 4 | 2.8 | Ag, Cu | 2.6 Cu | 45 |
| Ag—Pb | 1000 | 50 at. % | 4 | 13.2 | Ag | 4.2 | 38, 42 |
| Ag—Sb | | 10 Ag | | | Ag | 5 | * |
| Al—Sn | | 16 Ag | | | Ag | 2.5 | * |
| Al—Cu | 1050 | 50 | 4 | 13.2 | Cu | 4.5 | 37 |
| Al—Sn | 800—1600 | 58 at. % Sn | 4 | 4.3 | Al | 5.4 | 40 |
| Al—Au | 700 | 9 Au | | | Al | 0.4 | * |
| Al—Fe—Sn | 660 | | | | Fe | | * |
| Au—Bi | 680 | 50 | | | Au | 2 | * |
| Au—Pb | 450 | 50 | | | Au | 3 | * |
| Au—Sb | 400 | 50 | | | Au | 14 | * |
| Be—Cu—Fe | 1050 | 10 Be | | | Be (Fe) | | * |
| Bi—Cd | | 25—75 | | | Cd | 65 | * |
| Bi—Pb | 240—400 | 60 Bi | | 10 | Pb | 42 | 47 |
| Bi—Sb | 300 | 25—88 | | 8 | Sn | 40 | 47 |
| Bi—Cu—Sn | 1000 | 30 Cu, 2—20 Bi | 4 | | Cu | | 46 |
| Cd—Pb | 300 | 40 | | | Cd | 30 | * |
| Cd—Sn | 300 | 25—75 | | | Cd | 6 | * |
| Cu—Sn | 1000 | 50 at. % | | 6 | Cu | 6 | 47 |
| Cu—Pb—Sn | 1000 | 1 Pb | | | Cu | 10 | 44 |
| Cu—Pb—Zn | 1000 | | | | Cu | | * |
| Hg—Na—Sn | 240 | 1—5 Sn, 40 Na | 20 | 6 | Sn, Na | | 46 |
| Pb—Sn | 350 | 37 Pb | | 16 | Sn | 11 | 47 |
| Sb—Zn | 620 | 53—61 Sb | | 7.6 | Zn | 75 | 47 |
| Sn—Zn | 400 | 50 at. % | 4 | 12.3 | Zn | 12 | 39 |
| Fe—C | 1300 | 2.6 C | 0.25 | 0.1 | C | 0.11 | 83 |
| Pb—Sb | 470 | 13.5 Sb | | 1.1 | Pb | | 82 |
| Sn—Sb | | | | | Sn | | 82 |
| Cd—Pb | 360 | 3 Pb | 6.5 | 1.2—2.1 | Cd | 0.6—1.1 | 82 |
| Cd—Sn | 330 | 20—30 Cd | 5—6 | 1 | Cd | 1.3—2.6 | 82 |
| Bi—Pb | 225—300 | eutectic alloy | 4.5 | 0.5—0.8 | Pb | 3.9—6.6 | 82 |
| Bi—Sn | | | | | Sn | | 82 |
| Bi—Cd | | | | | Cd | | 82 |
| Ag—Pb | 360—390 | 2 Ag | 5—6.5 | 1 | Ag | 0.84—1.06 | 82 |
| Al—Cu | | | | | Cu | 2 | 82 |
| Cu—Sn | 370—420 | 3 Cu | 3—6.5 | 1—1.5 | Cu | 1—3.3 | 82 |

* Summarised results[14].

No appreciable tendency towards a monotonic change in ionisation potential is observed in series (68), so that the sequence (67) proposed by Kremann is purely empirical. Series (67) cannot explain all the observed e.m. data. For example, Na and K in amalgams migrate to the cathode only in sufficiently concentrated solutions. Sometimes series (67) predicts incorrectly the direction of migration, so that it may be assumed that the description of the direction of e.m. in different systems by a simple analogy with the potential series is hardly possible.

## 4. Electromigration in Dilute Solutions Based on Cd, In, Sn, Pb, Bi, Ag, Fe, Ni, etc.

The e.m. of traces of the radioactive isotopes $^{65}$Zn, $^{113-123}$Zn, $^{115m}$Cd, $^{72}$Ga, $^{210}$Bi, $^{75}$Se, $^{45}$Ca, and $^{110m}$Ag was studied in liquid lead, cadmium, bismuth, and tin[30,85], in 40 mm capillaries with internal diameter $\sim 1$ mm, at a current strength of 1.5 A, with duration of electrodiffusion annealing equal to 15 days. An interesting feature is that in most cases the value obtained for the effective charge was slightly higher when the light component migrated upwards. This means that the slight changes in density during e.m. in dilute solutions are still able to produce weak convection currents in the capillary. It can be seen from Table 7 that the direction of e.m. in the systems studied agrees with that found earlier by Kremann — see the "potential" series (67).

A semi-empirical relationship which makes it possible to explain the values of $z^*$ for the solutions studied was obtained[30]. An attempt was made to calculate the effective charges of the impurities in various solvents making the following assumptions: (1) the cross-section of scattering is proportional to the square of the "true charge" of the ion (of both impurity and solvent); and (2) the "true charge" of the ion is equal to the number of its group $\bar{z}$ in Mendeleev's Periodic System. Thus from (57) we have

$$z_2^* = z_2 - \bar{z}_1\left(\frac{\bar{z}_2}{\bar{z}_1}\right)^2 = \bar{z}_2 - \frac{\bar{z}_2^2}{\bar{z}_1}. \qquad (69)$$

The values of $z_2^*$ calculated from formula (69) are given in the sixth and last columns of Table 7. The good agreement between experiment and formula (69) is noteworthy. Deviations from the calculated values are observed only for silver and calcium. These results indicate that Belashchenko's suggestions[30] regarding $z$ and $\sigma$ for metallic solutions are apparently correct.

From this it follows, in particular, that the model assuming incoherent scattering of the conductivity electrons on the force centres is applicable to the case of liquid alloys

TABLE 7. Effective charges of impurities in various solvents[30,85].

| Solvent | Impurity: element | Impurity: wt. % | Temperature, °C | $z_2^*$ (mean) | $\bar{z}_2 - \frac{\bar{z}_2^2}{\bar{z}_1}$ | Solvent | Impurity: element | Impurity: wt. % | Temperature, °C | $z_2^*$ (mean) | $\bar{z}_2 - \frac{\bar{z}_2^2}{\bar{z}_1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Pb | Zn | 0.04 | 360 | 0.9 | 1.0 | Pb | Se | 0.05 | 360 | −2.9 | −3.0 |
| Cd | Sn | 0.41 | 360 | −5.4 | −4.0 | Bi | Ag | 0.001 | 300 | 0.14 | 0.8 |
| Bi | Cd | 2.53 | 300 | 1.36 | 1.2 | Pb | Ag | 0.001 | 360 | 0.4 | 0.75 |
| Cd | Bi | 4.75 | 350 | −16.4 | −7.5 | Sn | Ga | 0.1 | 300 | 0.7 | 0.75 |
| Sn | Bi | 4.8 | 350 | −0.8 | −1.25 | Bi | Ca* | ? | 300 | 0.4 | 1.2 |
| Bi | Se | 0.085 | 300 | −0.9 | −1.2 | Cd | Ca* | ? | 360 | −3.0 | 0 |

* Taken from Belashchenko[35].

not only for the impurities but also for the solvent. Thus the resistance of a pure liquid metal can be described not by the approximation assuming scattering of the electrons on phonons but by the approximation assuming incoherent scattering on individual atoms. This conclusion agrees with the almost linear behaviour of the electrical-resistance isotherms in a number of simple binary eutectic systems. When the electrical-resistance isotherm has a clearly--defined parabolic form, similar to that for solid solutions, this may mean either that the coherence of the scattering is largely preserved, or that the cross-section of scattering for the components depends on the composition, or that the scattering of the electrons by the ions is related not only to the charge on the ion but also to other properties of the ion. In the last case the cross-section may depend, for example, on the difference in the volumes of the atoms of solvent and impurity. In this case we would hardly expect that the cross-section of scattering would be related in simple fashion to the position of the components in Mendeleev's Periodic System.

The behaviour of the noble metals silver and gold in various solvents is of considerable interest, in view of their increased electron affinity. The results of a preliminary study of the e.m. of silver (Table 7) showed that $z^*$ for silver differs significantly from that calculated from formula (69). The effective charges of the isotopes $^{110m}$Ag and $^{198}$Au in liquid Cd, In, Tl, Sn, Pb, and Bi at 350° were determined[25] in vertical capillaries with diameter 1 mm and length of metal column 40 mm, at a current strength of 1.5 A. The results are given in Table 8 and Fig. 2 (the values of $z^*$ for gold and silver in mercury at 25° are taken from Table 2).

TABLE 8. Effective and "true" charges of noble metals in various solvents[25].

| Solvent | Period V | | | Period VI | | | |
|---|---|---|---|---|---|---|---|
| | Cd | In | Sn | Hg* | Tl | Pb | Bi |
| $z^*$ for silver | —1.25 | —0.74 | —1.07 | 1.43 | 0.64 | 0.48** | 0.14 |
| $z^*$ for gold | —2.2 | — | —2.0 | 1.47 | —0.28 | —0.10 | —0.18 |
| $z$ for silver | —0.87 | —0.6 | —0.9 | ? | 0.9 | 0.56 | 0.14 |
| $z$ for gold | —1.3 | — | —1.5 | ? | —0.26 | —0.10 | —0.18 |

* Data from Table 2.

** More accurate value than that given in Table 7.

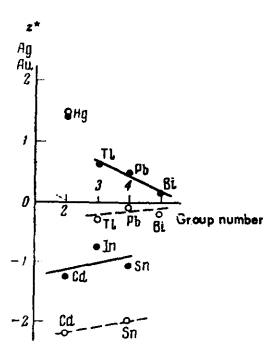



Fig. 2. Effective charges of traces of gold and silver in various solvents. ● — $z^*$ for silver, ○ — $z^*$ for gold.

To find the "true charge" of the Ag and Au ions in the solution[25], it was assumed, as in other work[30], that the cross-section of scattering is proportional to the square of the true charge. Eqn. (57) is then written in the form

$$z_3^* = z_3 - \frac{z_3^2}{\bar{z}_1}, \qquad (70)$$

where $\bar{z}_1$ is the Group number of the solvent.

It can be seen from Fig. 2 that the charges $z^*$ and $z$ for silver and gold change fairly regularly with change in the Group number of the solvent within a given period of Mendeleev's Periodic System. On going from solvents of the Fifth Period (Cd, In, and Sn) to solvents of the Sixth Period (Hg, Tl, Pb, and Bi), the charges of silver and gold change significantly, becoming more positive in the solvents of the Sixth Period. This change in $z^*$ is approximately the same for silver and gold and amounts to 1.5–2 electronic charges.

The simple zone model, which assumes that the valency electrons are free, does not explain this result. According to Friedel[86], a local bound-electron level may be produced in metals close to an impurity atom if the ionisation energy of the impurity atom is greater than the depth of the potential well for an electron in the solvent. The production of local levels should lead to the formation of neutral impurity atoms or even negative ions. Since Pb has a greater atomic volume, that is, a lower concentration of valency electrons, than Sn, the Fermi energy in Pb is smaller. If we assume that the work functions for Pb and Sn are about equal, we find that the bottom of the potential well in Pb is higher than that in Sn. Thus according to Friedel[86], the formation of local states is more probable in Pb than in Sn, that is, an impurity should be more negative in Pb than in Sn.

The data in Table 8 do not agree with this conclusion. Since the above discussion is applicable not only to Sn and Pb, the reasons for the deviation from Friedel's theory[86] should be general for all the solutions studied. Either this theory is inapplicable to multivalent solvents, or the interaction of the impurity ion with the surrounding ions of the solvent produces a significant displacement of local levels, not taken into account by this theory.

The marked influence of the nature of the interaction between the impurity and solvent is revealed by examining the equilibrium diagrams for the systems formed by silver and gold with the metals of Periods V and VI.[77] With metals of Period V (Cd, In, and Sn), silver and gold form exclusively diagrams with electron compounds and intermetallic compounds, but with metals of Period VI (Tl, Pb, and Bi) they form chiefly eutectic systems. Eutectic character in a system A–B is usually associated with a positive value for the energy of mixing

$$\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB}), \qquad (71)$$

where $\epsilon_{ik}$ is the potential energy of the pairing interaction. In systems with appreciable affinity of the components, the energy of mixing is usually negative. Thus the increase in the negative character of the charges of silver and gold on going from solvents of Period VI to solvents of Period V should be associated with a decrease in the energy of mixing (on going from positive values of $\epsilon$ to negative values) or should even be responsible for this decrease. The extremely incomplete data on heats of dissolution[87] suggest that these heats decrease on going from silver to gold and from solvents of Period VI to solvents of Period V; in the last case the sign of the heat of dissolution changes from negative to positive.

It can be seen from Table 8 that for the Ag–Sn, Au–Bi, and Au–Pb systems the direction of e.m. is opposite to those given in Table 4. This is apparently due to the inadequacy of Kremann's procedures.

The e.m. of traces of $^{204}Tl$ in liquid Cd, In, Sn, Pb, and Bi was studied at 350°.[32] The values of $z^*$ for thallium are given in Table 9. The dependence of $z^*$ for thallium on the position of the solvent in Mendeleev's Periodic System is the same as that for the noble metals silver and gold. Change in the Group number of the solvent again leads to a small change in $z^*$ for thallium, and change from solvents of Period VI to solvents of Period V is accompanied by a decrease in $z^*$ by 1.5–2 units. In the case of thallium, however, there is no sharp boundary between the types of equilibrium diagram which it forms with the metals of Periods V and VI.

The fact that for e.m. in dilute solutions thallium behaves like silver and gold is apparently related to the similarity between the structures of the electron clouds of the Ag, Au, and Tl atoms. The inner levels of these atoms have identical structures. The differences lie in the number of valency electrons ($5s^1$ for silver, $6s^1$ for gold, and $6s^26p^1$ for thallium). The similarity between Ag, Au, and Tl apparently indicates that the dissolution of thallium in a metal is accompanied by an appreciable displacement of the $6s^2$ level, so that the corresponding electrons remain bound.

The influence of incomplete filling of the 3*d* level on e.m. was studied[32,34] for the case of solutions of $^{60}Co$ and $^{63}Ni$ in Cd, In, Sn, Pb, and Bi at 350° in straight vertical capillaries with diameter ~ 1 mm at a current strength of ~ 2 A. The length of the metal columns was 40 mm. The results[32,34] (Table 10) show that $z^*$ for the transition-metal impurity depends to a marked extent on the Group number of the solvent. It was suggested[32] that the "true charge" of the transition metal is the same in all solvents and that, as before, the "true charge" of the solvent $z_1$ is equal to its Group number $\bar{z}_1$ in Mendeleev's Periodic Table, and $\sigma_1 \simeq k\bar{z}_1^2$. Eqn. (57) then acquires the form

$$z_2^* = z_2 - \frac{a}{z_1}. \qquad (72)$$

where $z_2$ and $a$ are constants which depend on the nature of the impurity but not on the nature of the solvent. The plot of $z^*$ for the impurity against $1/\bar{z}_1$ should be given by straight lines. Fig. 3 shows that this relationship is satisfied fairly well. The equations for the graphs in Fig. 3 are

$$z^*(\mathrm{Co}) = 10 - \frac{64}{\bar{z}_1}, \qquad (73)$$

$$z^*(\mathrm{Ni}) = 3 - \frac{22.8}{\bar{z}_1}. \qquad (74)$$

In all the solutions the predominant part in e.m. is played by the "electron wind".

Two explanations for the unique features of the e.m. of transition-metal impurities were put forward[32,34]. The first is based on Friedel's concept[88,89], according to which the 3*d* states of the impurity electrons are raised into the conductivity zone of the solvent and take part in resonance with the valency states, so that the 3*d* cloud of the transition-metal impurity is "smeared out". To explain the high value of the "true charge" of traces of Co and Ni — 10 and 3 according to formulae (73) and (74) — it was suggested[32] that the 3*d* electrons taking part in the resonance behave during e.m. in the same way as the valency electrons of non-transition elements. This is also responsible for the high values of the cross-sections of the scattering of electrons on transition-metal impurities.

Another reason for the high negative values of $z^*$ may be the scattering of the conductivity electrons on unfilled states of the 3*d* level[34]. In this case the e.m. effect should increase with increase in the number of unfilled 3*d* states[90]. It is suggested that an analogous mechanism is responsible, in particular, for the increased electrical resistance of pure transition metals[90].

It can be seen from Table 10 that the cross-section of scattering is approximately proportional to the square of the number of unfilled states in the free Co and Ni atoms. If we assume that the "true charges" of Co and Ni are small and positive, we find from Table 10 that $z^*_{Co}/z^*_{Ni} \simeq \sigma_{Co}/\sigma_{Ni} = 2.5$ (for solutions in Cd and In). The ratio of the numbers of unfilled 3*d* states in Co and Ni is 3:2, however. It is possible that the two mechanisms described are of equal importance in the e.m. of transition-metal impurities.

The electromigration of impurities in liquid transition metals (Fe and Ni) was studied[91] at 1500–1600° with wire specimens in quartz capillaries. A liquid zone of length 12–15 mm was produced by heating a section of the capillary with the wire in a molybdenum spiral. The results (Table 11) show that $z^*$ for impurities lying to the left of

TABLE 9. Electromigration of thallium in various solvents at 350°.[32]

| Solvent | Period V | | | Period VI | |
|---|---|---|---|---|---|
| | Cd | In | Sn | Pb | Bi |
| $z^*$ for thallium | −2.1 | −1.5 | −1.3 | 0.4 | 0.2 |

TABLE 10. Electromigration of traces of $^{60}Co$ and $^{63}Ni$ in various solvents at 350°.[32,34]

| Solvent | Cd | In | Sn | Pb | Bi |
|---|---|---|---|---|---|
| $z^*$ for cobalt | −22 | −12 | −6 | −11 | −1.2 |
| $z^*$ for nickel | −8.4 | −4.7 | −2.8 | − | −0.7 |

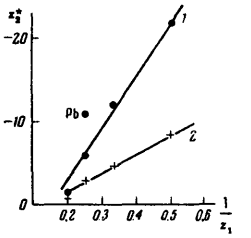



Fig. 3. Dependence of $z^*$ for traces of Co and Ni on the reciprocal of the Group number of the solvent.
1) $z^*$ for cobalt; 2) $z^*$ for nickel.

TABLE 11. Electromigration of impurities in liquid iron (~1600°) and nickel (~1500°).[91]

| Solvent | Impurity | At. fraction of impurity | $z^*$ |
|---|---|---|---|
| Fe | Mn | 0.005 | 5 |
| Fe | Ni | 0.08 | —4 |
| Ni | Mn | 0.10 | 56—76 |
| Ni | Fe | 0.02 | 15 |
| Fe | C | 0.016 | 11 |

the solvent in the Periodic System are positive, the values being greater, the further the impurity from the solvent. The high positive values of $z^*$ for the impurities were attributed[91] to the influence of the "hole wind", that is, to the scattering of holes in the 3*d* zone of the alloy on unfilled states of the 3*d* level of the impurity or on the ions of non-transition impurities (C in Fe).

The e.m. of traces of Cu, Ni, Mg, Zr, Pd, and U in liquid bismuth was studied[92] at 500°. The method involved the measurement of the quantity of impurity passing under the influence of current from a large volume of solution into a capillary with one end immersed in the solution (or in the opposite direction). The concentration of impurity amounted to 0.05–0.5 wt.%. The mobilities of the impurities (in the order given above) had the following values ($cm^2\ s^{-1}\ V^{-1}$): $-1.95 \times 10^{-4}$, $5.0 \times 10^{-4}$, $-5.97 \times 10^{-4}$, $2.61 \times 10^{-4}$, $3.05 \times 10^{-4}$, and $2.57 \times 10^{-4}$ (the results for nickel contradict those in Table 10). It was assumed[92] that the e.m. method can be used to separate the components of the solution.

Studies were made[93,94] of the e.m. of traces of sulphur in molten cast iron (1340°, duration of heating 11–29 h), length of specimens 35–40 mm, average composition 0.07–0.11 wt.% sulphur, cast iron saturated with carbon) and silver (1080°, duration of heating 12 h, length of specimens 35 mm, average composition 0.1% sulphur). The values found for the effective charges $z^*$ were 1.5–2.4 for sulphur in cast iron and -5.5–10.8 for sulphur in silver. These results indicate that the electron wind plays a significant part in e.m. in liquid silver, whereas in the case of cast iron the forces of the field, the electron wind, and the hole wind almost balance. The determination of the "true charge" of sulphur in cast iron and silver on the basis of the data obtained is difficult.

## 5. Electromigration in Binary Liquid Alloys

It was shown[30] that e.m. in the simplest cases is described satisfactorily by formula (69), that is, it agrees with the suggestion that the "true charge" $z$ is equal to the Group number of the element $\bar{z}$ and with the proportionality $\sigma \simeq k\bar{z}^2$. The applicability of these assumptions for concentrated solutions was verified[31,33] for the Cd–Sn, Cd–Bi, Cd–Pb, and Bi–Sn systems. Formula (56) can be written in the form

$$z_1^* = \frac{N_2\left(\frac{\sigma_2}{\sigma_1}Z_1 - Z_2\right)}{1-\left(1-\frac{\sigma_2}{\sigma_1}\right)N_2}. \qquad (75)$$

If $z_1$, $z_2$, and $\sigma_2/\sigma_1$ are constant within a given binary system, we have

$$z_1^* = \frac{aN_2}{1-bN_2}. \qquad (76)$$

It was found[31,33] that e.m. in the systems studied is described satisfactorily by equations of type (76):

in the cadmium–tin system

$$z_{Sn}^* = -\frac{1.01N_{Cd}}{1-0.813N_{Cd}}, \qquad (77)$$

in the bismuth–cadmium system

$$z_{Bi}^* = -\frac{1.87N_{Cd}}{1-0.886N_{Cd}}, \qquad (78)$$

in the bismuth–tin system

$$z_{Sn}^* = \frac{2.5N_{Bi}}{1+0.552N_{Bi}}, \qquad (79)$$

in the cadmium–lead system

$$z_{Pb}^* = -\frac{1.06N_{Cd}}{1-0.78N_{Cd}}. \qquad (80)$$

These equations were used to find the ratios $\sigma_i/\sigma_{Bi}$:

$$\frac{\sigma_{Cd}}{\sigma_{Bi}} = 0.114;\quad \frac{\sigma_{Sn}}{\sigma_{Bi}} = 0.644;\quad \frac{\sigma_{Pb}}{\sigma_{Bi}} = 0.519. \qquad (81)$$

It was shown[31] that

$$\sigma_i \sim (\bar{z}_i)^{2.36}, \qquad (82)$$

that is, the proportionality $\sigma \simeq k\bar{z}^2$ is satisfied approximately, but not rigorously.

The experimental values of $z^*$ for lead and tin in the cadmium–lead and cadmium–tin systems at 300°[31,33] are given in Fig. 4, together with a curve calculated from Eqn. (75) on the assumption that $z_1 = 4$, $z_2 = 2$, and $\sigma_2/\sigma_1 = \left(\frac{2}{4}\right)^{2.36}$ [in accordance with (82)]:

$$z_{Pb,Sn}^* = -\frac{1.222N_{Cd}}{1-0.805N_{Cd}}. \qquad (83)$$

It can be seen from Fig. 4 that as a first approximation, the agreement between calculation and experiment is satisfactory. The discrepancy amounts to ~10%. The discrepancy is slightly greater (40%) in the Cd–Bi and Bi–Sn systems[31]. Thus the assumptions that the true charge is

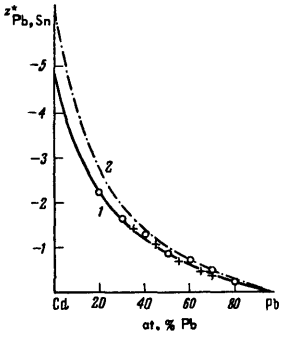



Fig. 4. Effective charges of tin and lead in the cadmium–tin and cadmium–lead systems. + — $z^*$ for tin, ○ — $z^*$ for lead. 1) Plot of $z^*_{Pb} = -\frac{1.06N_{Cd}}{1-0.78N_{Cd}}$, 2) plot of $z^*_{Pb,Sn} = -\frac{1.222N_{Cd}}{1-0.805N_{Cd}}$.

equal to the Group number and that $\sigma$ is approximately proportional to the square of the charge apply fairly satisfactorily to simple eutectic systems.

On going to more complex systems, however, the hyperbolic relationship (76) no longer applies. For example, in the Au–Sn system at 450°,[33] $z^*$ for gold shows a maximum in the range 20–30 at.% Au, but with further increase in the gold concentration, $z^*$ decreases. In the Cd–Tl system[35] the value of $\sigma$ for thallium is anomalously high (3 times the calculated value). It is as yet difficult to discuss the results of e.m. in these systems, because of the lack of experimental material.

## 6. Relationship Between Electrical Conductivity and Electromigration in Liquid Metals

The relationship between the scattering cross-sections responsible for e.m. and electrical resistance has been examined[33]. If it is assumed that these cross-sections are equal, it is possible to use the e.m. data and a knowledge of $\sigma_2/\sigma_1$ to calculate the ratio of the electrical resistivities of the corresponding pure liquid metals. The results[33] are given in Table 12. In the absence of e.m. data, the $\sigma_2/\sigma_1$ values were calculated from formula (82). Table 12 shows that the discrepancy between $\rho_{exp}$ and $\rho_{calc}$ is small for Pb, Bi, Sb, Ag, Cu, and Na. An appreciable difference is observed for Sn, Hg, and Al. The last two metals also show anomalous behaviour in the jump in the values of $\rho$ on fusion[95].

The results obtained indicate that the ratios of the cross-sections of scattering $\sigma_2/\sigma_1$ for the phenomena of e.m. and electrical conductivity are fairly close. The electrical resistivity of a liquid metal can evidently be regarded, as a first approximation, as due to incoherent scattering on ions.

It was shown[33], however, that constant values of $\sigma_2/\sigma_1$ within a given binary system should not be observed if the $\rho$ isotherms show a maximum. An example of this is the potassium–sodium system. It was observed[29] that the concentration dependence of the e.m. effect (with inversion) is similar to the function $\frac{\partial}{\partial N_2}(V_{mean}/\rho)$, where $N_2$ is the atom fraction of potassium, $V_{mean}$ the mean atomic volume of the alloy, and $\rho$ its electrical resistivity. The relationship between e.m. and $\rho$ for K–Na alloys was also examined by Belashchenko[33]. It was found that in systems with a maximum value of $\rho$ it is more convenient, as in the case of solid solutions, to consider the individual components of the electrical resistance: the additive component and the residual resistance, and also the corresponding components of the cross-section of scattering $\sigma$. Simultaneous examination of the data for e.m. and $\rho$ made it possible to determine the fraction $f$ of the residual resistance corresponding to all the sodium atoms in the solution[33]:

$$f \simeq 0.1 + 0.9 N_{Na}. \qquad (84)$$

TABLE 12. Calculation of the electrical resistivity $\rho$ of liquid metals from e.m. data[33].

| Metal | z | Temp., °C | $\rho_{exp}/\rho_{calc}$ | Metal | z | Temp., °C | $\rho_{exp}/\rho_{calc}$ |
|---|---|---|---|---|---|---|---|
| Cd | 2 | 321 | 1.00 | Hg | 2 | 0 | 2.81 |
| Sn | 4 | 232 | 0.45 | Al | 3 | 658 | 0.35 |
| Pb | 4 | 327 | 1.09 | Ag | 1 | 1000 | 1.52 |
| Bi | 5 | 269 | 0.77 | Cu | 1 | 1100 | 1.56 |
| Sb | 5 | 631 | 0.79 | Na | 1 | 100 | 1.11 |

The inversion of e.m. in the K–Na system is attributed[33] quantitatively to the fact that the potassium ion (diameter 4.76 Å) dissolved in sodium (diameter 3.82 Å) distorts the arrangement of the ions in several coordination spheres, whereas the sodium ion dissolved in potassium influences only its first coordination sphere.

## 7. Study of the Electrodiffusion Potential in Liquid Metallic Solutions

The first studies of electrodiffusion potential (e.d.p.) in amalgams were made by Schwarz[14]. The mobilities of the impurities, calculated from the results of e.d.p. measurements, showed good agreement with the e.m. data and are given in Table 2.

The e.d.p. effect was studied[35,57,58] in liquid alloys of the Pb–Sn, Bi–Sn, Bi–Cd, Bi–Te, and Na–Tl systems. In the last two systems, marked deviations from ideal behaviour were observed. In the solid state the components form intermetallic compounds $Na_2Tl$, NaTl, and $Bi_2Te_3$.

Since the magnitude of the e.d.p. is of the order of $10^{-6}$–$10^{-5}$ V, special precautions were necessary to eliminate the Seebeck effect. The experiments were carried out in glass capillaries of internal diameter 1 mm. The denser component was poured into the capillary first, followed by the second metal. The total length of the specimen was 20–40 mm. The heating was carried out in an oil thermostat at temperatures up to 350°, or in a vacuum furnace; the specimens were kept in a copper thermostat block. In the measurement of the e.d.p., molybdenum leads sealed to the ends of the capillary were connected to a galvanometer.

The initial values of the e.d.p. (after rapid heating to the required temperature) were $1.5 \times 10^{-6}$ V in the Bi–Sn system at 280°, $5 \times 10^{-6}$ V in the Pb–Sn system at 375°, $5 \times 10^{-5}$ V in the Bi–Cd system at 330°, $8 \times 10^{-5}$ V in the Na–Tl system at 310°, and $5 \times 10^{-5}$ V in the Bi–Te system at 590°. During the heating of the specimens, a sudden decrease in e.d.p. was observed at the melting points of the intermetallic compounds NaTl and $Bi_2Te_3$. During isothermal treatment the value of the e.d.p. decreased smoothly to zero as a result of the equalisation of the composition.

The results of e.d.p. measurements[57,58] were used to calculate the effective charges of the components. By integrating Eqn. (37) with allowance for (76), we obtain[35,58]

$$\epsilon \simeq -\frac{\bar{D}}{\bar{\varkappa}} e \left(\frac{\bar{N}}{\bar{V}}\right) z_{10}^{*} \frac{(1-b)\ln(1-b)}{b}, \qquad (85)$$

where the bar above the symbols denotes that the quantity is averaged with respect to composition within the binary system, $V$ is the volume of 1 g-atom of the alloy, and $z_{10}^*$ is the value of $z_1^*$ as $\bar{N}_1 \to 0$. If we assume that $\sigma_2/\sigma_1 = (\bar{z}_2/\bar{z}_1)^2$, where $\bar{z}$ is the Group number of the component, we can use the value of the e.d.p. $\epsilon$ to calculate $z_{10}^*$ and compare these results with the e.d.p. results. Since the averaging process is not sufficiently rigorous, the calculated values of $z_{10}^*$ are only approximate. Nevertheless, these values of $z^*$ show satisfactory agreement with those found from e.m., with respect to both sign and magnitude[96]. The calculation of $z^*$ for systems with intermetallic compounds was not carried out, since in these cases the values of $D$, $V$, and $\varkappa$ should depend to a marked extent on composition. The sign of the e.d.p. in these cases is given by the rule according to which $z^*$ for the component with the smaller Group number is positive — see Eqn. (69). The high values of the e.d.p. in these systems indicate, however,

that when there is a specific interaction between the ions of the components, formula (69) may give marked deviations from reality.

It was shown[57] that the temperature dependence of the e.d.p. is due chiefly to the change in the diffusion coefficient; this makes it possible to determine the activation energy of diffusion $Q$ in liquid alloys. For the Pb–Sn system, the mean value of $Q$ was found[57] to be 7 kcal mole$^{-1}$ with an accuracy of ~ 20%.

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The results of the study of e.m. in liquid alloys of metals of the type Cd, Sn, Pb, Bi, etc. make it possible to assume that the "true charge" $z$ is approximately equal to the Group number of the given element in the Periodic System. In other words, despite the small screening radii in metals (less than $10^{-8}$ cm), the valency electrons of these elements are almost completely delocalised for e.m. (and electrical conductivity). This is evidently related directly to the familiar Hume–Rothery rule. In the case of transition--metal impurities, the concept of "true charge" is more complicated. Data on the migration of traces of Co and Ni do not agree with the assumption that their 3$d$ levels are filled by the conductivity electrons of the solvent (so-called donor–acceptor interaction).

In the simplest cases, $\sigma$ depends on the Group number of the element and is approximately proportional to the square of the Group number. For systems with linear electrical-resistivity isotherms, the scattering on the ions of the components is found to be for the most part not a collective act but a separate act. The presence of unfilled $d$ levels leads to an increased scattering of electrons. From this it follows that the e.m. method is convenient for the study of interaction in systems containing transition metals. Filling of the sublevels should lead to a decrease in the contribution made to $z^*$ by the scattering of the charge carriers. Moreover, $z^*$ is extremely sensitive to specific interionic interaction. The limiting case of a strong bond is apparently exemplified by solutions of cadmium, etc. in alkali metals, where it is possible to use the spherical--complex model. In these systems inversion of e.m. may be expected.

In view of the similarity in the energetic properties of liquid and solid metallic alloys, it may be assumed that the "true charges" of the ions are similar in the two cases. However, the mechanisms of the scattering of conductivity electrons on the ions of the impurity and solvent are not the same. Moreover, the values of $\sigma$ for ions in the ground state and transition state also differ[16,17,64]. Thus other relationships are to be expected for e.m. in solid solutions.

## NOTE ADDED IN PROOF

It has been shown[97] that traces of Tl, In, and Ba in liquid Na move during e.m. to the positive electrode; however, traces of Sr and Ag, which do not form compounds with Na, take almost no part in e.m. These results provide evidence in support of the model according to which the complex is entrained by the electron wind. It has been proposed[98] that the characteristic features of interatomic bonding in solutions be studied by a "probe" method, in which the e.m. of an impurity with a known true charge in the solution being studied is determined. The method was applied to the Cd–Bi system; a trace of $^{113-123}$Sn was used as probe.


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# PYRAZOLONE DERIVATIVES AS ANALYTICAL REAGENTS

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## I. GENERAL REMARKS

Among the organic compounds which form cations and are used in analytical chemistry, the many derivatives of pyrazolone have recently found extensive application — antipyrine, pyramidone, and compounds obtained by condensing antipyrine with various aldehydes and ketones (we shall subsequently refer to these compounds, including pyramidone, as antipyrine derivatives)†. Of the latter, the following are used for the determination of many elements: diantipyrinylmethane, diantipyrinylmethylmethane, diantipyrinylpropylmethane, diantipyrinylphenylmethane, diantipyrinyl-*o*-hydroxyphenylmethane, diantipyrinyl-*p*-hydroxyphenylmethane, diantipyrinyl-*o*-nitrophenylmethane, diantipyrinyl-*p*-dimethylaminophenylmethane, diantipyrinyl-*p*-tolylmethane, diantipyrinylfurylmethane, diantipyrinyl-*p*-hydroxy-*m*-methoxyphenylmethane, antipyrinylbis-(*p*-methylaminophenyl)methane, and antipyrinylbis-(*p*-dimethylaminophenyl)methane. All these compounds in acid solutions are able to form complex organic cations

$$R + H^+ \rightleftarrows RH^+.$$

In the form of these cations they give compounds with many anions, particularly complex ions containing a metal

$$[M^{m+}X_n]^{(m-n)-} + (m-n)\,RH^+ \rightleftarrows (RH^+)_{(m-n)}\,[M^{m+}X_n]^{(m-n)-},$$

where M is a metal, X an electronegative ligand, and R the organic cation.

In neutral or almost neutral media, in which the equilibrium $R + H^+ \rightleftharpoons RH^+$ is displaced to the left, however, antipyrine and its derivatives are able to form compounds of the ammine type:

$$[M^{m+}X_n]^{(m-n)-} + pR \rightleftarrows [M^{m+}R_p]\,X_m + X^-_{(n-m)}.$$

Compounds of this type have been prepared for many metals with antipyrine, pyramidone, and diantipyrinylmethane[1-21]. In the case of the other antipyrine derivatives, the formation of such compounds is evidently hindered by the large size of the amine molecule; this is observed even for the case of complex formation with diantipyrinylmethane[19].

The formation of the various compounds in an R–M–X system depends on the acidity of the medium, the strength of the M–X, M–R, and R–H bonds, and the geometric dimensions of the molecule of the organic cation.

The resulting complexes of both types in a number of cases exhibit valuable properties — low solubility (which ensures a high sensitivity for the reaction), characteristic colour, extractability by organic solvents immiscible with water, etc. This has made it possible to develop gravimetric, titrimetric, photometric, and other methods of determination, and also methods for the separation of many elements.

† We shall not deal with picrolonic acid, 3-methyl-1-phenylpyrazol-5-one, etc., which are not strictly speaking antipyrine derivatives, nor with isopropylantipyrine, antipyrinylmethylenes, etc., which have not yet found extensive applications in analytical chemistry.

Several dyes with antipyrine nuclei have been proposed as analytical reagents: antipyrinylbis-(*p*-methylaminophenyl)methanol, antipyrinylbis-(*p*-dimethylaminophenyl)methanol, and antipyrinylbis-(*p*-benzylmethylaminophenyl)methanol.

In acid solutions they give large organic cations with an intense red colour. Many complex anions containing a metal react with them to form sparingly soluble precipitates. A characteristic feature of these reactions is the change in the colour of the solution during complex formation: the red characteristic of the reagent changes to bright blue, followed by the separation of a blue-violet precipitate and decolorisation of the solution. This colour effect has been used to develop titrimetric methods for the determination of elements forming sparingly soluble compounds with the dyes.

In a number of cases the compounds formed are readily extracted by benzene, ether, and toluene. The colour of the extracts is suitable for spectrophotometric determination. The method has a high sensitivity and in some cases a high selectivity.

Antipyrine and its derivatives listed above (including the dyes with antipyrine nuclei) have been used for the determination or separation of K, Cu, Ag, Au, Ca, Zn, Cd, Hg, Sn, Pb, Ga, In, Tl, the lanthanides, Si, Ti, P, V, As, Sb, Te, Bi, W, U, Re, F, Cl, Br, I, Fe, Co, Ni, Pd, Os, Ir, and Pt. In most cases the methods of determination and separation are based on the formation of onium compounds.

The essential features and possible applications of the proposed methods are examined briefly below.

## II. ELEMENTS OF GROUP I OF THE PERIODIC SYSTEM (K, Cu, Ag, Au)

### Potassium

Only an indirect method has been described for the determination of K using antipyrine, based on the formation of the green nitrosoantipyrine[22]. Potassium is first separated as $NaK_2[Co(NO_2)_6]$, the precipitate is dissolved, and antipyrine is added to the solution. The potassium content is found from the intensity of the resulting colour. The formation of nitrosoantipyrine is used for the determination of antipyrine and nitrites[23-34].

### Copper

In acid solutions in the presence of $Cl^-$, $Br^-$, $I^-$, $SCN^-$, and $CN^-$ ions, copper reacts with antipyrine and its derivatives to give compounds of the ammonium salt type, of which the compounds with antipyrine and pyramidone have been isolated and analysed[35]. A method has been proposed for the detection of Cu from the formation of the sparingly soluble yellow precipitate with antipyrine or pyramidone in the presence of KI.[36,37]

In acid medium, Cu reacts with antipyrine in the presence of $SCN^-$ ions to form a compound which can be extracted with chloroform to give a violet to brownish violet extract. The reaction is highly sensitive and selective and has been recommended for the detection of Cu.[38]

An analogous reaction is given by pyramidone[38]. Kolthoff and Hamer[39] found that pyramidone reacts with Cu salts in the presence of $SCN^-$ ions to give a grey-blue to violet precipitate. The detectable minimum corresponds to 1 $\mu g\ ml^{-1}\ Cu^{2+}$. At low Cu concentrations the solution is violet[40-43] (oxidation of pyramidone takes place).

It is possible to determine Cu by precipitation and weighing as $(C_{13}H_{17}ON_3.H)[Cu(SCN)_2]$.[35] Compounds of Cu with antipyrine and pyramidone, of the ammine type, have also been prepared[3,4,6,7,9,44], but they have not found analytical application.

### Silver

$AgNO_3$ oxidises pyramidone with the formation of the violet colour characteristic of the product of the oxidation of pyramidone and the separation of a grey-black precipitate of metallic silver[30-33]. The reaction can be used for the detection of Ag or pyramidone.

### Gold

A method has been described for the detection of small quantities (0.01 mg) of Au in the form of the sparingly soluble chloroaurate of antipyrine[45]. The chloroaurate of diantipyrinylmethane has been isolated from acid solutions in the form of red-brown crystals[46].

## III. ELEMENTS OF GROUP II OF THE PERIODIC SYSTEM (Ca, Zn, Cd, Hg)

Antipyrine and its derivatives have not been used for the determination of Mg, Sr, and Ba, although compounds of the ammine type formed by these elements with antipyrine and pyramidone are known[4,6-8].

### Calcium

An indirect method for the determination of calcium using antipyrine, based on the formation of nitrosoantipyrine, has been described[47]. Ca is first separated as $K_2CaNi(NO_2)_6$. The nitrite in the resulting precipitate is determined photometrically with antipyrine.

### Zinc

In acid solutions in the presence of $SCN^-$ ions, zinc reacts with antipyrine and its derivatives to form sparingly soluble compounds of the type $(RH)_2[Zn(SCN)_4]$. The compound with antipyrine has been proposed for the qualitative detection of Zn.[39,48,49] The precipitate can be detected at a concentration of 100 $\mu g\ ml^{-1}$ Zn. Precipitation with pyramidone makes it possible to detect 6-7 $\mu g\ ml^{-1}$ Zn in the presence of Ba, Ca, Mg, Sr, Al, Mn, As, and Cd, if the reaction is carried out in acetic acid[50-52].

Zhivopistsev[53] established that the compound of $Zn^{II}$ with pyramidone, $(C_{13}H_{17}ON_3.H)_2[Zn(SCN)_4]$, is isomorphous with the analogous cobalt compound $(C_{13}H_{17}ON_3.H)_2.[Co(SCN)_4]$. In the presence of Co, the Zn precipitate is coloured blue by the Co, which undergoes isomorphous coprecipitation. In this case it is possible to detect 0.2 $\mu g$ Zn.

The compound of Zn with pyramidone is readily obtained in the pure form, has a constant composition, and had been used to standardise solutions of Complexone III‡.[54]

The precipitation of Zn with pyramidone has also been used for the micro-crystalloscopic detection of pyramidone[55]. Diantipyrinylmethane has been used to purify Ni, Mn, Al, and Cr salts from Zn.[56]

The compound formed by Zn with diantipyrinylmethane is readily soluble in chloroform. This feature has been used for the determination of Zn in highly pure nickel, after preliminary extraction with chloroform (Ni remains in the aqueous phase)[57].

Gusev and Bitovt[58-61] found that the compound of Zn with diantipyrinylmethylmethane at pH 2-2.5 forms a stable white turbidity which makes possible the nephelometric determination of 0.12-2 $\mu g$ of Zn in the presence of the cations of analytical groups I and II, and also Al, Mn, $Fe^{III}$, Cu, Ni, and Co respectively. The method has been used to determine Zn in industrial atmospheres, alloys, foodstuffs, blood, and other materials.

Zhivopistsev[62] proposed that the precipitation of $Zn(SCN)_4^{2-}$ ions with antipyrinylbis-(*p*-dimethylaminophenyl)methane be used for the detection of small quantities (0.1-0.28 $\mu g \times \times ml^{-1}$) of Zn.

Sparingly soluble bright blue precipitates $(RH)_2[Zn(SCN)_4]$ are formed by Zn in acid solutions with antipyrinylbis-(*p*-methylaminophenyl)methanol and antipyrinylbis-(*p*-dimethylaminophenyl)methanol (the detectable minimum corresponds to 0.2-0.3 $\mu g$ and 2-3 $\mu g$ of Zn respectively)[63,64]. It has been shown possible to determine Zn gravimetrically as $(C_{29}H_{32}O_2N_4)_2[Zn(SCN)_4]$. The error in the determination of 5-20 mg of Zn does not exceed 3-4%.[65] The determination of Zn can be completed photometrically after dissolving the precipitate in 1 *N* HCl. The error in the determination is 2-4%.[66] A titrimetric method has been developed for the determination of Zn using antipyrinylbis-(*p*-dimethylaminophenyl)methanol[67]. The error in the determination of 0.001-0.03 g of Zn amounts to 2-3%. In neutral or almost neutral solutions Zn forms a compound of the ammine type, $Zn(R)_2(SCN)_2$.

Zhivopistsev[68] has developed a titrimetric method for the determination of Zn using pyramidone. The method has been used to determine Zn in alloys of the "Elektron" type [Mg-base alloys (Ed. of Translation)].

### Cadmium

In acid solutions, cadmium gives sparingly soluble compounds $(RH)_2[CdX_4]$ with antipyrine§ and its derivatives, not only in the presence of $SCN^-$ ions as in the case of Zn, but also in the presence of $Br^-$ and $I^-$ ions.

Precipitation by antipyrine in the presence of $Br^-$ and $I^-$ ions has been proposed for the detection of Cd and antipyrine[36,37,69,70]. When the reaction is carried out in the presence of bromides, it is possible to detect 50 $\mu g\ ml^{-1}$ Cd. Gusev[70] developed a gravimetric method for the determination of Cd as $(C_{11}H_{12}ON_2.H)_2[CdBr_4].2C_{11}H_{12}ON_2$. Korenman and coworkers[71,72] studied the completeness of

‡ Sodium salt of EDTA (Ed. of Translation).

§ In the case of antipyrine, the compound $(C_{11}H_{12}ON_2H)_2.[CdBr_4].2C_{11}H_{12}ON_2$ is formed.

precipitation of Cd as antipyrine tetrabromocadmate¶ and the possible coprecipitation of $Fe^{3+}$, $Zn^{2+}$, and $Hg^{2+}$ ions with the Cd precipitate, and established that the precipitation of Cd is not quantitative and that $Fe^{3+}$, $Zn^{2+}$, and $Hg^{2+}$ are coprecipitated.

The determination of Cd can be completed not only by weighing the precipitate but also iodometrically or by titration with alkali and Methyl Orange after dissolving the antipyrine tetrabromocadmate precipitate[73]. The iodometric method is based on the formation of iodopyrine. The excess of iodine is titrated with thiosulphate.

The compound of Cd with pyramidone $(C_{13}H_{17}ON_3 \cdot H)_2 \cdot [CdI_4]$ has been recommended for the detection of Cd ($> 3.64$ μg ml$^{-1}$) and pyramidone (the detectable minimum corresponds to 5 μg of pyramidone in one drop of solution)[51,55]. The precipitate is also suitable for the gravimetric determination of Cd in the presence of small quantities of Zn.[35] Diantipyrinylmethane precipitates Cd quantitatively from 0.5–2.0 $N$ $H_2SO_4$ solutions as $(C_{23}H_{24}O_2N_4 \cdot H)_2 \cdot [CdBr_4]$. The formation of diantipyrinylmethane tetrabromocadmate has been made the basis of gravimetric[74-77], potentiometric[78], and amperometric[79] methods for the determination of Cd.

In the presence of iodides, an even less soluble compound of Cd with diantipyrinylmethane is formed; this has been used for the determination of small quantities (0.002–0.0001%) of Cd in highly pure nickel[80].

Diantipyrinyl-*o*-hydroxyphenylmethane also precipitates Cd quantitatively as $(C_{29}H_{26}O_3N_4 \cdot H)_2[CdBr_4]$. The precipitate has a definite composition and is suitable for the gravimetric determination of Cd[81].

The dyestuffs antipyrinylbis-(*p*-methylaminophenyl)-methanol and antipyrinylbis-(*p*-dimethylaminophenyl)-methanol react with Cd in acid medium in the presence of $SCN^-$ or $I^-$ ions to form sparingly soluble compounds which, as in the case of Zn, are suitable for the qualitative and quantitative determination of Cd.[64,67].

A method has been developed for the detection of Cd in the presence of Cu and also Al, Mn, Cr, Ni, Co, Fe, As, and the alkali and alkaline earth metals, using antipyrinylbis-(*p*-benzylmethylaminophenyl)methanol, which reacts with Cd in acid medium to give a precipitate of $(C_{40}H_{39}ON_4)_2 \cdot [CdBr_4]$.[82] The drop method makes it possible to detect 0.01 μg of Cd.

Compounds of the ammine type have also been used for the determination of Cd. A method has been developed for the gravimetric determination of Cd by precipitation and weighing as $[Cd(C_{13}H_{17}ON_3)_2](SCN)_2$.[83]

Popel'[79] obtained good results in the amperometric titration of Cd with $(NH_4)_2[Hg(SCN)_4]$ solution in the presence of antipyrine or pyramidone.

A method has been proposed for the amperometric determination of Cd, based on the formation of a sparingly soluble precipitate of $(C_{13}H_{17}ON_3)_2[CdI_2]$† at pH 2–5 in the presence of an excess of pyramidone. The titration is carried out with KI solution from the cathodic Cd current.

The successive determination of Bi (titration in 4.5–6 $N$ $H_2SO_4$) and Cd (titration at pH 2–5) has been shown to be possible. The method was tested on alloys containing Cd and Bi, together with Zn, Al, and Mn.[84]

### Mercury

Antipyrine, pyramidone, antipyrinylbis-(*p*-methylaminophenyl)methanol, antipyrinylbis-(*p*-dimethylaminophenyl)methanol have been used for the qualitative and quantitative determination of Hg.

Antipyrine and pyramidone form compounds with $Hg^I$ and $Hg^{II}$ in the presence of $Cl^-$, $Br^-$, $I^-$, $CN^-$, $NO_3^-$, and $SCN^-$ ions[85-92]. Mercury is precipitated by antipyrine from acidic solutions in the presence of KI as $(C_{11}H_{12}ON_2 \cdot H)_2[HgI_4]$ (sensitivity 4 μg ml$^{-1}$ Hg,[93] limiting dilution 1 : 200 000 [36,37]).

In dilute solutions, a stable turbidity suitable for the nephelometric determination of Hg is formed[93].

Antipyrine tetraiodomercurate is readily extracted by chloroform from 0.3–1.3 $N$ $H_2SO_4$, HCl, or $HNO_3$ solutions. The colour of the extracts can be used for the spectrophotometric determination of 1–80 μg of Hg in 5 ml of solution at $\lambda = 330$ mμm.[94]

In the presence of bromides, the compound $(C_{11}H_{12}ON_2 \cdot H)_2[HgBr_4] \cdot 2C_{11}H_{12}ON_2$ is formed. Cd, Zn, and $Fe^{III}$ are coprecipitated, but in a number of cases the coprecipitation is slight and cannot influence the accuracy of the gravimetric determination of Hg as antipyrine tetrabromomercurate[72,95].

The coprecipitation of Cd with the Hg precipitate can be used for the separation of small quantities (20–70 μg) of Cd from solutions of Zn and Cu salts[96].

Sudo[97] showed that the antipyrine–thiocyanato-complex of Hg is extracted quantitatively from weakly acidic (pH 1.8–2.3) solutions by a 3 : 1 mixture of pentanol and ethyl acetate. The optical density of the extracts ($\lambda = 325$ mμm) is proportional to the Hg concentration in the range 5–40 μg ml$^{-1}$.

Zhivopistsev[98] developed a titrimetric method for the determination of Hg using antipyrinylbis-(*p*-dimethylaminodiphenyl)methanol, based on the precipitation of $[HgI_4]^{2-}$ by the dyestuff from 0.7–1.5 $N$ HCl solutions. The method can be used to determine 0.0003–0.06 g of Hg with an error of 3–4%.

Hg can also be determined with antipyrinylbis-(*p*-methylaminophenyl)methanol, which forms an even less soluble compound with $[HgI_4]^{2-}$ (the detectable minimum corresponds to 0.6 μg Hg).[64]

A method for the detection of Hg using pyramidone is based on the oxidation of pyramidone by mercury(II) (the blue-violet product of the oxidation of pyramidone is formed). The detectable minimum corresponds to 20 μg Hg.[99] The reaction can be used to distinguish the $Hg_2^{2+}$ cation from the $Hg^{2+}$ cation.

## IV. ELEMENTS OF GROUP III OF THE PERIODIC SYSTEM (Ga, In, Tl, lanthanides)

### Gallium

Gallium is precipitated from acidic solutions in the presence of $Cl^-$, $Br^-$, and $I^-$ ions by diantipyrinylmethane,

¶ We shall use this terminology, since it is widespread in the literature, although it would be more correct to refer to these as "antipyrinium" salts.

† This is presumably a compound of the ammine type (Ed. of Translation).

diantipyrinylpropylmethane, and diantipyrinylphenylmethane. A gravimetric method has been developed for the determination of Ga as $(C_{26}H_{30}O_2N_4.H)[GaCl_4]$.[100]

The compound of Ga with diantipyrinylphenylmethane is extracted quantitatively by chloroform and this has been used for the separation of Ga from Al, Zn, Cd, Pb, Bi, As, Fe, Cu, In, and Ge by extraction[101].

Ga reacts with the dyestuffs to form the compounds $RHGaCl_4$, which are readily extracted by toluene and chloroform[102]. The use of antipyrinylbis-(*p*-benzylmethylaminophenyl)methanol has been proposed for the spectrophotometric determination of Ga. Ga is extracted from 6 *N* HCl to the extent of 90%. The sensitivity corresponds to 0.2 $\mu g\ ml^{-1}$ Ga. The method is applicable to the determination of Ga in bauxites, alumina, and copper–zinc ores.

### Indium

In sulphuric acid solutions (~0.5 *N*) in the presence of $SCN^-$ ions, indium reacts with antipyrine, pyramidone, and diantipyrinylmethane to form sparingly soluble compounds $[In_2(R)_3](SCN)_6$.[103] The compound with antipyrine has the composition $[In(C_{11}H_{12}ON_2)_3](SCN)_3$. The least soluble compound is that formed with diantipyrinylmethane. It has been shown possible to determine In gravimetrically as $[In_2(C_{23}H_{24}O_2N_4)_3](SCN)_6$.

A nephelometric method has been developed for the determination of microgramme quantities (0.5–1.0 $\mu g\ ml^{-1}$) of In.

### Thallium

Tervalent thallium in acid medium in the presence of $Cl^-$, $Br^-$, and $I^-$ ions reacts with antipyrine and its derivatives to form sparingly soluble compounds $(RH)[TlX_4]$. The compound of $TlBr_4^-$ with antipyrine has the composition $(C_{11}H_{12}ON_2.H)[TlBr_4].C_{11}H_{12}ON_2$.

The compound with antipyrinylmethane $(C_{23}H_{24}O_2N_4.H).[TlBr_4]$ has been used for the gravimetric determination of $Tl^{III}$ in the presence of Cu, Zn, $PO_4^{3-}$, $AsO_4^{3-}$, and also Fe, Bi (after their conversion into the complexonates) and Sb (converted beforehand into the tartrato-complex)[104]. The method has been used to determine $Tl^{III}$ in its alloys with Sb, As, or P.[105]

The determination of $Tl^{III}$ as $(C_{23}H_{24}O_2N_4.H)[TlBr_4]$ can be finished titrimetrically[105]. Diantipyrinylpropylmethane has been recommended for the precipitation of $Tl^{III}$ from hydrochloric acid (1–6 *N*) solutions[106]. The precipitate has a definite composition corresponding to the formula $(C_{26}H_{30}O_2N_4.H)[TlCl_4]$, is sparingly soluble ($5.6 \times 10^{-5}$ M), and is suitable for the gravimetric determination of $Tl^{III}$. The method has been used to determine $Tl^{III}$ in cadmium.

Diantipyrinyl- and diantipyrinylpropyl-methane tetraiodothallates are readily extracted by benzene with the formation of yellow extracts ($\lambda$ = 400–405 m$\mu$m, $\epsilon$ = 12 000)[107]. The extraction-photometric determination of $Tl^{III}$ is possible in the presence of Fe, Bi, Cu, Zn, Cd, Pb, Ga, and In. The minimum detectable quantity corresponds to 0.3 $\mu g \times \times ml^{-1}$ Tl.

An extraction-photometric method for the determination of $Tl^{III}$ using antipyrinylbis-(*p*-dimethylaminophenyl)methanol has also been proposed[108]. The method is based on the formation of a compound by $TlCl_4^-$ and the dyestuff, readily extracted by a 2 : 3 mixture of benzene and $CCl_4$.

In weakly acidic solutions $Tl^{III}$ oxidises pyramidone with the formation of a blue-violet compound. After 30 min the solution (pH 3.5–4.5) becomes red ($\lambda$ = 510 m$\mu$m) and this colour is preserved for 50–100 min. Kamemoto[109] has used this for the colorimetric determination of $Tl^{III}$. The method makes it possible to determine 0.5–4.5 mg Tl in 50 ml solution.

### The Lanthanides

These react with antipyrine and pyramidone to form compounds of the ammine type[5,10,11]. The solubilities and rates of formation of the compounds differ. Marsh[110,111] has used this feature to separate the lanthanides by fractional crystallisation; he showed that in the form of the compounds $[M(C_{11}H_{12}ON_2)_6]I_3$, Lu and Tu, Lu and Er, Lu and Yb, and Y and Ho are readily separated; Ho, Dy, and Tb are less readily separated; and Pr and Nd are not separated.

## V. ELEMENTS OF GROUP IV OF THE PERIODIC SYSTEM (Ti, Si, Ge, Sn, Pb)

### Titanium

In hydrochloric acid (0.5–6 *N*) or sulphuric acid solutions, titanium reacts with diantipyrinylmethane to form a yellow compound ($\lambda$ = 385 m$\mu$m, $\epsilon$ = 15 000). The molar ratio of Ti to diantipyrinylmethane in the complex is 1 : 3.[112] The compound is an ammine‡. Thus in 0.01–2 *N* HCl solutions the complex $[Ti(C_{23}H_{24}O_2N_4)_3]^{4+}$ exists[114].

The solutions obey Beer's law in the range 1–3 $\mu g\ ml^{-1}$ Ti. Ti can be determined spectrophotometrically in the presence of $Fe^{II}$, Al, Cd, Hg, Zn, and the alkali and alkaline earth metals; fluorides and phosphates do not interfere[115]. The method is 20 times more sensitive than the peroxide method and has the advantage over the chromotropic acid method that it does not require strict observation of the reaction conditions (pH, etc.). The method has been used to determine small quantities of Ti (0.0001–0.00005%) in aluminium and magnesium[116], and also to determine Ti in the presence of V in heat-resistant nickel- and iron-base alloys[117].

In the presence of thiocyanates, Ti reacts with diantipyrinylmethane to give a complex which is readily extracted from hydrochloric acid solutions by chloroform. On this basis a method has been developed for separating Ti from Al and Fe with subsequent determination as $TiO_2$.[118]

The composition of the complex formed in an excess of $SCN^-$ ions corresponds to the formula $[Ti(C_{23}H_{24}O_2N_4).(SCN)_4]$.[114,119] The chloroform extracts ($\lambda$ = 420 m$\mu$m, $\epsilon$ = 60 000) are suitable for the spectrophotometric determination of 2–20 $\mu g$ Ti in 25 ml extract[120].

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‡ Compounds of the ammonium salt type have been isolated from chloroform solutions and analysed: $(C_{23}H_{24}O_2N_4.H)_2[TiCl_6]$ and $(RH)_2[Ti(SCN)_6]$. The compounds $(RH)[TiO(SCN)_3]$, where R = diantipyrinylpropyl-, diantipyrinylisobutyl-, and diantipyrinylphenyl-methane[113], have been isolated from aqueous alcohol solutions.

In hydrochloric acid or sulphuric acid solutions, $Ti^{III}$ and $Ti^{IV}$ react with diantipyrinyl-*o*-hydroxyphenylmethane to give readily soluble inner-complex compounds. The $Ti^{III}$ compound has an intense yellow colour. The solutions are suitable for the qualitative and quantitative determination of Ti.[121] The minimum detectable quantity corresponds to 0.35 $\mu$g ml$^{-1}$ Ti. The spectrophotometric method can be used to determine 2–30 $\mu$g ml$^{-1}$ Ti.

The salts of the diantipyrinyl-*o*-hydroxyphenylmethane complex of $Ti^{IV}$ with $NO_3^-$, $ClO_3^-$, $SCN^-$, and $ClO_4^-$ ions are sparingly soluble and separate as characteristic crystalline precipitates suitable for the qualitative detection of Ti.[122-124]

Antipyrine has also been used to precipitate the tannin complex of Ti. The antipyrine-tannin method has been used to determine small quantities (0.1–0.01 g) of Ti in the presence of Fe, Al, and Cr.[125] The reaction has been proposed for the detection of Ti by the spot method[126].

## Silicon

Silicon in the form of molybdosilicic and tungstosilicic acids is precipitated from acid solutions by antipyrine and pyramidone in the form of the sparingly soluble compounds $(C_{13}H_{17}ON_3)_3H_8Si(Mo_2O_7)_6.6H_2O$,[127,128] $4C_{11}H_{12}ON.SiO_2.12WO_3$, and $3C_{13}H_{17}ON_3.SiO_2.12WO_3$.[129] A method has been developed for the gravimetric determination of Si as pyramidone molybdosilicate[128]. The other compounds have been used for the amperometric[129-132] and titrimetric[133] determination of antipyrine and pyramidone. The methods developed can probably be used no less successfully for the determination of Si or W.

## Germanium

Germanium is precipitated from acid solutions as the sparingly soluble antipyrine or pyramidone molybdogermanates[134]. It has been shown possible to determine Ge gravimetrically as the antipyrine compound. Pyramidone molybdogermanate can be used to develop a vanadometric method for the determination of Ge by titration of the excess of pyramidone after separation of the precipitate. The vanadometric method for the determination of pyramidone makes it possible to determine 0.004–0.02 g of pyramidone with an error of ±3%.[135]

## Tin and Lead

Tin and lead react with antipyrine and its derivatives to give sparingly soluble compounds[36,37,52,56,57,62,136-140]. The compound formed by Sn with antipyrine in the presence of KI has been used to detect Sn after separation from interfering elements as the sulphide[141].

# VI. ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM (P, V, As, Sb, Bi)

## Phosphorus

Molybdophosphoric or tungstophosphoric acids are precipitated by antipyrine and pyramidone from acid solutions. The compounds have been used for the spectrophotometric[142-144] and amperometric[130,131] determination of antipyrine and pyramidone and also for the detection of phosphoric acid[145].

Gusev[146] proposed a nephelometric method for the determination of phosphates, based on the formation of a stable turbidity when ammonium molybdate and antipyrine are added to a nitric acid (~ 2 *N*) solution of the phosphates. The method can be used to determine 0.05 $\mu$g ml$^{-1}$ P with an error of ±10%.

## Vanadium

Vanadium has been determined using diantipyrinylphenylmethane by precipitation and weighing as $(C_{28}H_{28}O_2N_4)_2H_4V_6O_{17}$ (or as $V_2O_5$ after ignition of the precipitate)[147].

Sokolova[148] has proposed a spectrophotometric method for the determination of V using pyramidone. The method is based on the formation of a blue solution by the reaction of pyramidone with V and tungstophosphoric acid in $Na_2CO_3$ solution. The detectable minimum corresponds to 0.3 $\mu$g ml$^{-1}$ V. Beer's law is observed in the range 0.6–30 $\mu$g ml$^{-1}$.

## Arsenic

Arsenic(V) in nitric acid solutions in the presence of ammonium molybdate reacts with antipyrine to form a stable turbidity, which is suitable for the nephelometric determination of As.[149] The method makes it possible to determine 0.1–2 $\mu$g ml$^{-1}$ As with an error of ±10%.

## Antimony

Antimony(III) reacts with antipyrine in acid solution in the presence of KI to give a yellow precipitate[141,150-153]. The sensitivity corresponds to 25 $\mu$g ml$^{-1}$ Sb and the limiting dilution is 1 : 20 000 (according to Korenman 1 : 40 000[36,37]). In dilute solutions (0.2 *N* with respect to HCl) a stable turbidity is formed, shown by Gusev[154] to be suitable for the nephelometric determination of 2.5 $\mu$g ml$^{-1}$ Sb in the presence of 75 $\mu$g ml$^{-1}$ $Sn^{2+}$. The error in the determination does not exceed ±5–6%.

The complex of Sb with antipyrine is readily extracted by chloroform. The coloured extracts ($\lambda$ = 345 m$\mu$m) can be used for the spectrophotometric determination of 1–100 $\mu$g Sb.[155]

Diantipyrinylmethane precipitates Sb quantitatively even at low concentrations of KI in the solution (0.1 M); from very dilute solutions antimony is coprecipitated quantitatively with the sparingly soluble diantipyrinylmethane iodide. This has been used for the separation and subsequent polarographic determination of microgramme quantities ($5 \times 10^{-9}$ g litre$^{-1}$) of Sb.[156]

## Bismuth

In acid solutions in the presence of $Cl^-$, $Br^-$, $I^-$, and $SCN^-$ ions, bismuth(III) reacts with antipyrine and its derivatives to form the compounds $(RH)[BiX_4]$, sparingly soluble in water. The reaction is highly sensitive. Thus precipitation of $BiI_4^-$ makes it possible to detect Bi at a dilution of 1 : 2 000 000 using antipyrine, or 1 : 48 000 using pyramidone[36,37,157,158].

The formation of pyramidone tetraiodobismuthate has been made the basis of nephelometric [159], amperometric [160], and heterometric (by Bobtelsky and Cohen) [161,162] methods for the determination of Bi and also for the titrimetric determination of pyramidone [163].

The nephelometric method based on the formation of a stable turbidity in dilute nitric acid solutions makes it possible to determine 0.5 μg $ml^{-1}$ Bi in the presence of 0.1 mg $ml^{-1}$ Sb, 0.015 mg $ml^{-1}$ Pb, and 10 mg $ml^{-1}$ Sn with an error of ±3–7%.

The amperometric determination is carried out by titrating sulphuric acid (2.5 M $H_2SO_4$) solutions of the Bi salt with potassium iodide in the presence of pyramidone, from the cathodic Bi current at a dropping mercury electrode.

The heterometric titration of nitric acid (~ 0.5 $N$) solutions of $Bi(NO_3)_3$ with pyramidone solution (in the presence of KI) or with KI solution (in the presence of pyramidone) can be used to determine ~ 1 mg Bi.

The titrimetric determination of pyramidone using potassium iodobismuthate involves the precipitation of pyramidone with standard $KBiI_4$ solution with subsequent titration of the excess of Bi with Complexone III until the disappearance of the yellow of the potassium iodobismuthate solution. The formation of the sparingly soluble compound with diantipyrinylmethane $(C_{23}H_{24}O_2N_4.H)[BiI_4]$ was used by Zhivopistsev and Parkacheva [164] to develop a titrimetric method for the determination of Bi. The method can be used to determine 80–50 mg Bi with an error of 2–3%.

A gravimetric method for the determination of Bi using diantipyrinylmethane by precipitation and weighing as $(C_{23}H_{24}O_2N_4.H)[BiCl_4]$ has been proposed [165]. The precipitation is carried out from hydrochloric acid (0.5–2.0 $N$) solutions; the error in the determination is 2–3%.

The compounds of Bi with antipyrine and diantipyrinylmethane are readily extracted by various organic solvents with the formation of coloured extracts suitable for the spectrophotometric determination of Bi.

Sudo [94,155] developed an extraction-photometric method for the determination of Bi using antipyrine in the presence of $SCN^-$ or $I^-$ ions. In the first case, Bi is extracted from weakly acidic solution (pH 1.8–2.3) by a 1 : 4 mixture of pentanol and ethyl acetate. The optical density of the extracts is measured at 325 mμm. The method makes it possible to determine 1–100 μg Bi in 5 ml solution.

In the second case (in the presence of KI) the extraction is carried out with chloroform. Measurement of the optical density of the extracts at 500 mμm makes it possible to determine 1–50 μg Bi in 5 ml solution.

In the presence of diantipyrinylmethane, $BiI_4^-$ ions are readily extracted by chloroform over a wide range of acidity (up to 3 $N$ with respect to HCl or $H_2SO_4$) of the original solution [166]. The colour of the extracts can be used for the photometric determination of 20–30 μg Bi in 25 ml.

## VII. ELEMENTS OF GROUP VI OF THE PERIODIC SYSTEM (Te, W, U)

Antipyrine and its derivatives have not yet been used for the determination of Cr and Mo. Compounds of $Cr^{III}$ with antipyrine [6,7] and of $Cr^{VI}$ (as $Cr_2O_7^{2-}$) with diantipyrinylphenylmethane [167] have been prepared. The addition of pyramidone solution to potassium dichromate solution produces a dark green which changes to wine red [168,169].

### Tellurium

In acid solutions tellurium(IV) reacts with the antipyrine derivatives diantipyrinylmethane, diantipyrinylpropylmethane, and diantipyrinylphenylmethane to give compounds of the type $(RH)_2[TeCl_6]$ and $(RH)_2[TeBr_6]$, which are readily extracted by dichloroethane to give coloured extracts [170]. On this basis, a method has been developed for the extraction-photometric determination of tellurium. The method makes it possible to determine 10–100 μg $ml^{-1}$ Te.

$Se^{IV}$, unlike $Te^{IV}$, is not extracted from hydrochloric acid solutions by dichloroethane in the presence of diantipyrinylpropylmethane. This has been used for the separation of Se and Te by extraction. A single extraction gives almost complete separation of 0.05–2 mg of Se and Te. [171]

### Tungsten

In acid solutions, tungsten forms sparingly soluble compounds with antipyrine [172–176], pyramidone [177–180], diantipyrinylphenylmethane [181], diantipyrinyl-*o*-hydroxyphenylmethane [182], and various other antipyrine derivatives. These reagents have been used for the gravimetric determination of W. In all cases the determination is finished by igniting the precipitates and weighing the resulting $WO_3$. The accuracy of the proposed methods is no less than the classical cinchonine method, but is more rapid and uses more readily available reagents.

### Uranium

In sulphuric acid solutions in the presence of $SCN^-$ ions, uranium in the form of uranyl nitrate reacts with antipyrine and some of its derivatives to form sparingly soluble compounds with variable composition [183]. At low U concentrations the compound with diantipyrinyl-*p*-dimethylphenylmethane gives a stable turbidity which is suitable for the nephelometric determination of U. The method makes it possible to determine 0.5–5 μg $UO_2^{2+}$ in the presence of 2.5 mg $La^{3+}$.

In the presence of bromides, uranyl nitrate reacts with diantipyrinyl-*p*-hydroxy-*m*-methoxyphenylmethane with the formation of yellow compound. Maximum development of the colour is observed at pH 2–3. The extraction-photometric method makes it possible to determine 5–60 μg × × $ml^{-1}$ $UO_2^{2+}$ in the presence of appreciable quantities of $Th^{4+}$, $Ni^{2+}$, $Mn^{2+}$, $Mg^{2+}$, and $Cu^{2+}$. The error in the determination amounts to ±3.5%. The method is suitable for the determination of uranium in various minerals (samarskite, aeschynite, sooty uranite, etc.).

## VIII. ELEMENTS OF GROUP VII OF THE PERIODIC SYSTEM (Mn, Re, F, Cl, Br, I)

### Manganese

Compounds of $Mn^{II}$ with antipyrine, of the ammine type, have been prepared [6] but these have not been used for the determination of Mn.

Rhenium

Re in the form of perrhenate and chlororhenate forms sparingly soluble compounds with antipyrine [184].

Fluorine

Čelechovsky and Holer [185] developed a photometric method for the determination of fluorides, based on the decolorisation of the red solution of the $Fe^{III}$–antipyrine complex in the presence of fluorides. The method makes it possible to determine 35–300 μg F in 25 ml solution. The error in the determination is 3.1–4%.

Chlorine, Bromine, and Iodine

These oxidise pyramidone with the formation of a blue-violet colour [186]. The reaction with I has been recommended for the detection of pyramidone [186].

In the presence of $I^-$ ions and also $Br^-$, $SCN^-$, and $S_2O_3^{2-}$ ions, the copper–pyramidone complex is decomposed with the formation of the salt of Cu with the corresponding anion; the solution is coloured violet by the product of the oxidation of pyramidone [43]. The reaction has been recommended for the detection of iodides. The sensitivity corresponds to 3.2 μg $ml^{-1}$ $I^-$ (limiting dilution 1 : 12 500).

Antipyrine has also been used to combine with the iodine liberated in the determination of iodides using iodate [187].

IX. ELEMENTS OF GROUP VIII OF THE PERIODIC SYSTEM (Fe, Co, Ni, Pd, Os, Ir, Pt)

Iron

In hydrochloric acid, sulphuric acid, acetic acid, and neutral solutions, iron(III) reacts with antipyrine to form a red compound readily soluble in water. This was observed at an early date by Knorr [23], who was the first to prepare antipyrine. The reaction is fairly sensitive (according to Knorr the limiting dilution is 1 : 100 000) and suitable for the qualitative and quantitative determination of Fe and antipyrine [24,26,28,30–33,188,189]. The complex formed is of the ammine type. The compound $(C_{11}H_{12}ON_2)_3.FeCl_3$ has been prepared in the crystalline state [190]. The addition of $K_4[Fe(CN)_6]$ solution to a solution containing $Fe^{3+}$ and antipyrine gives an immediate dark red precipitate of $[Fe(C_{11}H_{12}ON_2)_3][Fe(CN)_6].3H_2O$. Analogous compounds have been obtained with other complex anions: $[Fe(CN)_5.(NH_3)]^{2-}$, $[Co(CN)_6]^{3-}$, and $[Fe(CN)_5(NO_2)]^{2-}$. [191,192]. This indicates that in solution $Fe^{III}$ reacts with antipyrine to form the complex cation $[Fe(C_{11}H_{12}ON_2)_3]^{3+}$.

Other authors [189] report the formation of the cation $[Fe_2(C_{11}H_{12}ON_2)_3]^{6+}$. Compounds confirming the possible formation of this cation have been prepared in the crystalline state: $[Fe_2(C_{11}H_{12}ON_2)_3][Fe(CN)_5(NO_2)]_3$ [191] and $(C_{11}H_{12}.ON_2)_3.2FeCl_3$. [32,33,193,194]

In the presence of $SCN^-$ ions the red sparingly-soluble compound $[Fe(C_{11}H_{12}ON_2)_3](SCN)_3$ is formed [191,194,195].

Sudo [196] established that the complex of $Fe^{III}$ with antipyrine is readily extracted from weakly acidic solutions (pH 2.5) in the presence of $SCN^-$ ions by certain organic solvents. The best of these is a 4 : 1 mixture of ethyl acetate and isobutanol. The red extracts are suitable for the spectrophotometric determination of Fe. The method has been used to determine small quantities (0.0002%) of Fe in the metals aluminium, magnesium, zinc, and lead. The error in the determination is < 5%. [197]

Dick [198] found that from acetic acid solutions containing an excess of thiocyanate ions, $Fe^{III}$ is precipitated quantitatively as $[Fe(C_{11}H_{12}ON_2)_3](SCN)_3$. The sensitivity of the reaction corresponds to 0.2 μg Fe.

In acid medium, antipyrine forms with $K_4[Fe(CN)_6]$ the sparingly soluble compound $(C_{11}H_{12}ON_2)_2H_4[Fe(CN)_6]$. [190,199,200] Hexacyanoferrate(III) does not form a compound of this type and this has been used to identify $[Fe(CN)_6]^{4-}$ in the presence of $[Fe(CN)_6]^{3-}$. [201]

The reaction of $K_4[Fe(CN)_6]$ with antipyrine was used by Gusev [51] for the titrimetric determination of antipyrine involving titration of the excess of $K_4[Fe(CN)_6]$ with $KMnO_4$ solution after separation of the precipitate.

Diantipyrinylmethane, like antipyrine, reacts with $Fe^{III}$ in hydrochloric acid solutions to form a red complex. The number of diantipyrinylmethane molecules entering the resulting compound depends on the acidity of the medium [202]. Thus at pH 1–2 the complex $Fe(C_{23}H_{24}O_2N_4)_2^{3+}$ is formed. In 1 *N* HCl solutions the cation $Fe(C_{23}H_{24}O_2N_4)^{3+}$ predominates. The solutions of the complex (λ = 440–460 mμm), formed at pH 2.2–2.5, are suitable for the spectrophotometric determination of Fe. [203] The sensitivity of the reaction corresponds to 0.08 μg $ml^{-1}$ Fe.

Zhivopistsev and Chelnokova [204] found that $Fe^{III}$ is extracted quantitatively from strongly acidic (5–7 *N* HCl) solutions by chloroform in the presence of diantipyrinylmethane. In this case a compound of $Fe^{III}$ with diantipyrinylmethane, of the ammonium salt type, is probably formed. A method was developed [204] for the quantitative separation and subsequent determination (from the colour of the extracts in the case of small quantities, or as $Fe_2O_3$ after re-extraction with water in the case of large quantities) of Fe from Ti, Cr, Ni, Al, Mn, and Mg, using diantipyrinylmethane and chloroform.

In the presence of $SCN^-$ ions, coloured compounds $Fe(C_{23}H_{24}O_2N_4)_3(SCN)_3$ ( pH 2, λ = 455 mμm, ε = 10 000) and $(C_{23}H_{24}O_2N_4.H)_3[Fe(SCN)_6]$ (1 *N* HCl, λ = 475 mμm, ε = 35 000), readily extracted by chloroform, are formed [202]. This forms the basis of a method proposed by Zhivopistsev [205] for the extraction-photometric determination of Fe. The detectable minimum corresponds to 0.04–0.05 μg Fe. In the presence of Co the determination of Fe can be finished using *o*-phenanthroline after re-extraction with acetate buffer solution (pH 5.37). [206]

Iron is coprecipitated quantitatively in the form of the diantipyrinylmethane–thiocyanato-complex with diantipyrinylmethane thiocyanate. This has been used to purify Ni, Mn, Al, and Cr salts from Fe. [56] Thus after the precipitation, nickel contains < 0.0002% Fe.

Diantipyrinylphenylmethane, unlike antipyrine, precipitates $[Fe(CN)_6]^{3-}$ ions from sulphuric acid solution and gives no precipitate with $[Fe(CN)_6]^{4-}$. The precipitate has a definite composition corresponding to the formula $(C_{29}H_{28}O_2N_4.H)_3[Fe(CN)_6]$ and is suitable for the gravimetric determination of cyanoferrate(III) in the presence of cyanoferrate(II), and also for the determination of cyanoferrate(II) after oxidation to $[Fe(CN)_6]^{3-}$. [167]

In acid medium in the presence of $SCN^-$ ions, antipyrinylbis-(*p*-dimethylaminodiphenyl)methane reacts with

$Fe^{III}$ to form a sparingly soluble compound[62]. The reaction is extremely sensitive (0.02–0.03 μg $ml^{-1}$ Fe).

Diantipyrinylfurylmethane in acid medium reacts with $Fe(SCN)_3$ to give a red compound which is sparingly soluble in water and readily soluble in acetone. The acetone solutions are suitable for the spectrophotometric determination of 0.3–1 μg $ml^{-1}$ Fe.[207]

It is also possible to determine Fe using pyramidone. The proposed methods are based on the oxidation of pyramidone by $Fe^{III}$ with the formation of an intense blue-violet colour. The detectable minimum corresponds to 0.1 μg $ml^{-1}$ Fe.[188,208] In the acidity range 0.1–0.2 *N* HCl the colour of the solution depends little on the acidity, and the spectrophotometric determination of 0.5–3.0 μg $ml^{-1}$ Fe is possible[209].

The reaction has also been used to identify $[Fe(CN)_6]^{3-}$ in the presence of $[Fe(CN)_6]^{4-}$ [210,211] and for the determination of pyramidone[30-33,47,212].

## Cobalt

In acid solutions in the presence of $SCN^-$ ions, cobalt(II) reacts with antipyrine§ and its derivatives to form blue compounds $(RH)_2[Co(SCN)_4]$ which are sparingly soluble in water but readily soluble in certain organic solvents. The compound with antipyrine has the composition $(C_{11}H_{12}ON_2.H)_2[Co(SCN)_4].2C_{11}H_{12}ON_2$.[215]

The formation of antipyrine tetrathiocyanatocobaltate has been recommended as a sensitive and selective reaction for the detection of Co.[38,48,215,216]

Antipyrine tetrathiocyanatocobaltate is readily extracted from weakly acidic solutions (pH 1.8–2.2) by a 5:1 mixture of ethyl acetate and benzene[217]. The coloured extracts ($\lambda$ = 630 mμm, $\epsilon$ = 3156) can be used for the spectrophotometric determination of 1–100 μg of Co in 5 ml.

The formation of pyramidone tetrathiocyanatocobaltate is highly sensitive (the detectable minimum corresponds to 1 μg Co) and has been used for the detection of Co in nickel[218,219] and for the identification of pyramidone[55]. Zhivopistsev[220] has suggested that the reaction be carried out in the presence of $Zn^{2+}$ ions, which react with pyramidone to give the compound $(C_{13}H_{17}ON_3.H)_2[Zn(SCN)_4]$, isomorphous with the compound $(C_{13}H_{17}ON_3.H)_2[Co(SCN)_4]$. In this case the Co compound does not form supersaturated solutions (which is the case at low $Co^{2+}$ contents) and the sensitivity of detection increases: the white Zn precipitate is coloured blue in the presence of as little as 0.4 μg Co.[2]

The compound of Co with diantipyrinylmethane $(C_{23}H_{24}O_2N_4.H)_2[Co(SCN)_4]$ has been recommended by Zhivopistsev for the detection[74] and quantitative determination[221] of Co. The spot test method has been used to detect 0.06 μg Co in the presence of Cr, Ni, $Fe^{II}$, Mn, Al, Zn, and the alkali and alkaline earth metals. The complex is readily extracted by chloroform with the formation of a blue extract. The colour of the extracts can be used for the spectrophotometric determination of Co in the presence of the elements indicated above. The error in the determination is 1 μg at a Co content less than 10 μg $ml^{-1}$, and 2 μg at a Co content of 10–50 μg $ml^{-1}$. The method has been used to determine small quantities (0.1–1.25%) of Co in steels containing up to 20% Ni.[222]

In the presence of Fe or Cd, which are also readily extracted in the form of compounds with diantipyrinylmethane, the determination of Co can be finished using nitroso-R-salt after re-extraction with acetate buffer solution. This method has been used to determine 0.0007% Co in pure nickel[206]. Ikramov[223] has made a comparative study of the diantipyrinylmethane and nitroso-R-salt methods for the determination of Co.

Diantipyrinylmethane has also been used for the detection of $SCN^-$ ions (the detectable minimum corresponds to 0.13 mg $ml^{-1}$).[224]

Equally sensitive reactions with Co in the presence of $SCN^-$ ions are given by diantipyrinylmethylmethane, diantipyrinylpropylmethane, diantipyrinyl-*o*-hydroxyphenylmethane, and diantipyrinyl-*p*-hydroxyphenylmethane (sensitivity 7.5 μg Co in 2 ml); less sensitive reactions are given by diantipyrinyl-*p*-tolylmethane (10 μg Co), diantipyrinyl-*o*-nitrophenylmethane (15.0 μg Co), and diantipyrinyl-*p*-dimethylaminophenylmethane (20.0 μg Co)[225]. All these reagents, like diantipyrinylmethane, are suitable for the photometric determination of cobalt from the blue colour of the benzene extract. The optimum acidity corresponds to 0.02 *N* $H_2SO_4$. The error in the determination of 0.06–0.1 mg Co in 2–5 ml of extract does not exceed ±10%. The method has been used for the determination of Co in bronze and cast iron.

A titrimetric method has been proposed for the determination of Co using pyramidone, based on the formation, at pH 5–6, of the complex $Co(C_{13}H_{14}ON_3)_2(SCN)_2$, which is sparingly soluble in water[226].

## Nickel

From acetic acid solutions in the presence of pyramidone and $NH_4SCN$, nickel is precipitated as $[Ni(C_{13}H_{17}ON_3)_2].(SCN)_2$. The precipitate is almost insoluble in solution containing an excess[227] of the reagents and is suitable for the gravimetric determination of Ni and pyramidone[228,229]. The sensitivity corresponds to 10 μg $ml^{-1}$ Ni.

## Palladium

In acid solutions, palladium(II) reacts with antipyrine and diantipyrinylmethane to form complexes which are readily extracted by chloroform with the formation of coloured extracts. On this basis, Sudo[94] developed a spectrophotometric method for the determination of Pd using antipyrine. The optimum acidity of the solution corresponds to 0.3–1.5 *N* HCl or $H_2SO_4$, or 0.3–1.0 *N* $HNO_3$. The method can be used to determine 1–20 μg Pd in 5 ml of extract.

Kreimer and coworkers[230] proposed the use of antipyrinylmethane instead of antipyrine. The optical density of the extracts was measured at 450 mμm. The sensitivity corresponds to 0.43 μg $ml^{-1}$ Pd. The method was used for the determination of 0.01–0.05% Pd in the products of nickel manufacture, containing up to 40% Ni, 20% Cu, and 5% Fe.

§ A spot test for the detection of $Co^{2+}$ using antipyrine has been described, based on the formation of a blue-green or pale green (depending on the Co content) colour, developed by drying a strip of filter paper moistened first with $Co^{2+}$ solution and then with 20–30% antipyrine solution[213,214].

Palladium is readily extracted from hydrochloric acid (0.5–5 *N* HCl) solutions with dichloroethane in the presence of diantipyrinylpropylmethane (with a sixfold excess of the reagent the degree of extraction of Pd is >99%). This has been used to remove traces of Pd from Rh.[231,232]

Compounds of Pd with antipyrine and pyramidone have also been prepared: $(C_{11}H_{12}ON_2.H)_2[Pd(CN)_4]$, $(C_{13}H_{17}ON_3.H_2)_2[Pd(SCN)_4]$, and $(C_{11}H_{12}ON_2.H)_2[PdCl_4].2H_2O$.[233–235] No practical use has been made of these compounds, however,

## Osmium

In acid solutions, osmium in the form of $OsCl_6^{2-}$ or $OsBr_6^{2-}$ reacts with antipyrine, diantipyrinylmethane, diantipyrinylpropylmethane, and diantipyrinylphenylmethane to form the compounds $(RH)_2[OsCl_6]$ and $(RH)_2[OsBr_6]$.[236] A method has been proposed for the gravimetric determination of osmium by precipitation and weighing as $(C_{23}H_{24}O_2N_4.H)_2.[OsBr_6]$ and $(C_{26}H_{30}O_2N_4.H)_2[OsCl_6]$.[237] The method can be used to determine 5–13 mg Os with an error of ±3%.

$Os^{IV}$ is readily extracted by dichloroethane, with the formation of coloured extracts, from hydrochloric and hydrobromic acid solutions (0.5–5 *N*) containing diantipyrinylmethane, diantipyrinylpropylmethane, and diantipyrinylphenylmethane. On this basis a method has been developed for the extraction-photometric determination of Os using diantipyrinylpropylmethane[238,239].

$Os^{IV}$ is extracted from hydrochloric acid (0.5–5 *N*) solutions with a 0.1% solution of the reagent in dichloroethane. The optical density of the extracts ($\lambda$ = 346 mμ, $\epsilon$ = 10 500; $\lambda$ = 378 mμ, $\epsilon$ = 8000) is measured relative to a solution of the reagent saturated with 1 *N* HCl. The method can be used to determine 2–20 μg ml$^{-1}$ Os in the presence of 40 mg Ru with an error of ±10%.

## Iridium

In acid solutions, iridium in the form of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ reacts with antipyrine, diantipyrinylmethane, diantipyrinylpropylmethane, and diantipyrinylphenylmethane to give the compounds $(RH)_2[IrCl_6]$ and $(RH)_2[IrBr_6]$.[240]

The compound formed by iridium with diantipyrinylpropylmethane is sparingly soluble in water (the solubility in 0.5 *N* HCl amounts to $3.8 \times 10^{-5}$ M) and has been used for the gravimetric determination of iridium by precipitation and weighing as $(C_{26}H_{30}O_2N_4.H)_2[IrCl_6]$. The error in the determination of 5–13 mg Ir amounts to ±3%.

The complex of $Ir^{IV}$ with diantipyrinylpropylmethane is readily extracted by dichloroethane with the formation of a coloured extract (the degree of extraction for a tenfold excess of the reagent amounts to 98.5%). On this basis a method has been developed for the extraction-photometric determination of 4–40 μg ml$^{-1}$ Ir using diantipyrinylpropylmethane[231,232].

## Platinum

Platinum(IV) is readily extracted by dichloroethane from hydrochloric acid (0.5–6 *N*) solutions in the presence of diantipyrinylpropylmethane (the degree of extraction with a sixfold excess of the reagent is greater than 99%).[231,232] This has been used for the separation of traces of Pt from Rh by extraction.

Compounds of Pt with antipyrine, pyramidone, and diantipyrinylmethane have also been prepared: $(C_{11}H_{12}ON_2.H)_2[PtCl_6]$,[199] $(C_{11}H_{12}ON_2.H)_2[PtCl_4]$, $(C_{11}H_{12}ON_2.H)_2[Pt(CN)_4]$,[234,235] $(C_{13}H_{17}ON_3.H)_2[PtCl_6]$,[239] and $(C_{23}H_{24}O_2N_4)H_2[PtCl_6]$.[46] These compounds have not, however, found application in analysis.


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# COVALENT ORGANOMETALLIC COMPOUNDS OF THE TRANSITION METALS

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## INTRODUCTION

The ability to form organometallic compounds has for long been regarded as a characteristic property of metals. D. I. Mendeleev, describing the then undiscovered elements eka-boron and eka-silicon, stated that they should form organometallic compounds. The many attempts to prepare organic derivatives of metals of the transition periods were until recently always unsuccessful. The only exceptions were the polyphenyl derivatives of chromium discovered in the 1920's by Hein. Later, however, it was established that these have the peculiar sandwich structure characteristic of a variety of transition elements.

The lack of experimental success was attributed to the impossibility of existence of this type of compound. In the most complete monograph published at that time, Krause and von Grosse [1] provided theoretical justification for the assumption that the covalent bond between a transition metal and an organic radical is unstable. As an example, they examined the possibility of the existence of organometallic compounds of titanium. In their opinion, the bivalent titanium derivatives, formed by means of the valency *s* electrons, should be more stable than the quadrivalent titanium derivatives, whose formation should involve the valency *s* and *d* electrons of the transition metal.

Nesmeyanov [2] divided all the elements of the Periodic System into two classes, depending on the possibility of formation of stable alkyls and aryls. For transition metals, which have incomplete lower *d* levels in addition to valency *s* and *p* electrons, sandwich or diarene derivatives are more characteristic. Several excellent reviews and monographs dealing with the latter have recently been published.

In the last 10–12 years, increasing experimental evidence has appeared for the formation of $\sigma$ bonds between transition metals and carbon. A number of truly covalent compounds of transition metals have been prepared, and these have attracted greater attention from research workers.

Alkyl and aryl derivatives of transition elements have been the subject of a review by Cotton [3], covering material up to 1955, and a section of a monograph by Zeiss [4], including some material up to 1960. This field of chemistry is making rapid progress, and it seemed to us useful to review briefly recent work on the organometallic compounds of the transition metals. The review deals with compounds containing a metal–carbon $\sigma$ bond. The only $\pi$-cyclopentadienyl derivatives dealt with are those which, in addition to the $\pi$-cyclopentadienyl group, contain an organic radical covalently bound to the element.

In this review the alkyls and aryls of the transition metals are examined according to the groups of the Periodic System, starting with Group IV (titanium, zirconium, and hafnium). The compounds of vanadium, niobium, and

tantalum in Group V, chromium, molybdenum, and tungsten in Group VI, and manganese and rhenium in Group VII are characterised. In the case of Group VIII, only the compounds of iron, cobalt, and nickel are included. The review does not deal with the peculiar organometallic derivatives of the first "b" subgroup — copper, silver, and gold — or with the platinum subgroup.

## GROUP IV

### Titanium

Of the organometallic compounds of the transition metals of Group IV, the titanium derivatives have been most extensively studied. This has been due largely to the industrial use of catalysts of the Ziegler–Natta type for the polymerisation of alk-1-enes. The complex polymerisation catalysts of this type contain alkyl compounds of zinc, aluminium, and sodium together with halides of transition metals, chiefly titanium. Reaction between the components leads to halogen–alkyl exchange on the titanium atom and is accompanied by the reduction of quadrivalent titanium to lower-valency compounds.

The large number of papers on the study of various catalytic systems of this type served as the starting point for the development of the chemistry of organotitanium compounds, whose existence, up to 1952, had been regarded as impossible. Since the catalytic systems contained alkyl components, chiefly of aluminium, preparative work in the chemistry of organometallic compounds of titanium had a distinct bias towards aliphatic derivatives.

At the present time, the known alkyl compounds of titanium include products of the type $R_nTiX_{4-n}$ (where $n$ = 1, 2, 3, or 4, R = methyl, ethyl, or butyl, and X = Cl, Br, or I) obtained by alkylation of a quadrivalent titanium halide with the corresponding derivatives of lithium, zinc, aluminium, lead, and other metals.

The mono- and di-alkyl compounds have been most extensively studied. The exchange reaction between a titanium halide and an organoaluminium derivative of general formula $R_nAlX_{3-n}$ is carried out in an inert atmosphere in solution in organic solvents (hexane, benzene, methylene chloride, etc.) at temperatures from -80° to 0°. To obtain the monoalkyl product, the reaction is carried out in an excess of $TiX_4$. Dialkyltitanium dihalides are obtained at a ratio of $TiX_4 : R_nAlX_{3-n}$ = 1 : 2. When the reaction is complete, the resulting organoaluminium compound $R_{n-1}AlX_{3-(n+1)}$ is converted into the insoluble or non-volatile state by the action of alkali or alkaline earth metal halides, and also higher ethers, phosphines, etc.[5,6]. The titanium mono- and di-alkyls are isolated by vacuum distillation of the reaction mixture. Thus methyltitanium trichloride is obtained by the exchange reaction of trimethylaluminium or of dimethylaluminium chloride with titanium tetrachloride in hexane solution[7]. The aluminium compound is added slowly to an excess of $TiX_4$ at room temperature

$$(CH_3)_2AlCl + TiCl_4 \rightleftarrows CH_3AlCl_2 + CH_3TiCl_3.$$

Sodium chloride is added to the reaction mixture to bind the organoaluminium compound in the complex $Na[AlCl_3(CH_3)]$, and the mixture is vacuum-distilled to give methyltitanium chloride in the form of dark violet crystals with m.p. 28.5° and b.p. 37° at 1 mmHg. Methyltitanium trichloride melts to form a yellow liquid, and is soluble in many organic solvents — hexane, benzene, and halogeno--derivatives — to give yellow solutions. Methyltitanium trichloride is monomolecular in benzene solution[5]. Dimethylzinc can be used instead of dimethylaluminium chloride and in this case the yield of product is 75% of the theoretical[7].

The monoethyl derivative was prepared in analogous fashion by the alkylation of an excess of $TiCl_4$ with tetraethyllead at -80°; the product has a lower thermal stability than the methyl derivative[8]. At 20° the ethyl derivative is a reddish liquid which decomposes in 24 h; iso-$C_4H_9TiCl_3$ is obtained by a method analogous to that for the methyl derivative but at a lower temperature[5].

Dimethyltitanium dichloride can be obtained from the monomethyl derivative by further methylation. Thus the action of trimethylaluminium on a hexane solution of $CH_3TiCl_3$ cooled to -80° gave almost black crystalline $(CH_3)_2TiCl_2$:

$$CH_3TiCl_3 + Al(CH_3)_3 \rightarrow (CH_3)_2TiCl_2 + (CH_3)_2AlCl.$$

Solutions of the latter in hexane are also pale yellow. Dimethyltitanium dichloride can be obtained by the disproportionation of methyltitanium trichloride with dicyclopentadienyldimethyltitanium at temperatures from -80° to 0° and a molar ratio of 1 : 2, and also by the reaction of dicyclopentadienyldimethyltitanium with titanium tetrachloride in hydrocarbon solutions[9]:

$$2(C_5H_5)_2Ti(CH_3)_2 + TiCl_4 \rightarrow 2(C_5H_5)_2Ti(CH_3)Cl + (CH_3)_2TiCl_2.$$

At a component ratio of 1 : 1 the reaction is

$$(C_5H_5)_2Ti(CH_3)_2 + TiCl_4 \rightarrow (C_5H_5)_2TiCl_2 + (CH_3)_2TiCl_2.$$

The dialkyl derivatives are less stable than the monoalkyl derivatives[10-13].

Tri- and tetra-methyltitanium can be obtained by the successive replacement of all the halogen atoms in a titanium halide by alkyl groups. Tetramethyltitanium is obtained in 50–70% yield from the ether addition compound in ethereal solution by the action of methyllithium or methylmagnesium chloride at temperatures from -50° to -80°.[14,15] It is obtained as glistening yellow crystals which distil with ether *in vacuo* at a temperature not exceeding 0°, and are stable at -78°.

$$TiCl_4 + 4CH_3Li \rightarrow (CH_3)_4Ti + 4LiCl.$$

Tetramethyltitanium was isolated in crystalline form from hexane solutions. After removal of ether, the hexane solution at temperatures between -30° and -50° gave glistening yellow needles of tetramethyltitanium, which forms methane on hydrolysis. Analysis of the product[16] gave the ratio $Ti : CH_4$ = 1 : 4.

Trimethyltitanium iodide $(CH_3)_3TiI$ is obtained by the exchange reaction of tetramethyltitanium in 2 : 1 ether — hexane solution with gaseous $CF_3I$ at reduced temperature (-78°).[17] Methyl iodide is a side-product of the exchange reaction. When the temperature is raised to -50°, the solution becomes brown and does not give a positive Gilman reaction. Trimethyltitanium iodide is obtained as yellow needles by removal of the solvent. The compound is stable in the absence of oxygen at low temperatures. On hydrolysis of the product, the ratio of liberated methane to hydrogen iodide is 2.95 : 1.

In ether, titanium trichloride does not react appreciably with methyllithium, but the pale blue suspension of $TiCl_3$ in tetrahydrofuran or its pale brown suspension in dimethoxyethane react rapidly at temperatures between -50°

and -80° with an ethereal solution of methyllithium, to form lithium chloride and a dark green solution, evidently containing trimethyltitanium [14]. The possibility of formation of the bivalent and tervalent titanium compounds RTiX and $RTiX_2$ has also been reported briefly [13,18].

The interesting observation that organomagnesium compounds undergo isomerisation in the presence of small quantities of $TiCl_4$ is attributed to the intermediate formation of organotitanium compounds according to the scheme

$$(CH_3)_2CHMgBr + TiCl_4 \rightarrow (CH_3)_2CHTiCl_3 + MgClBr,$$
$$(CH_3)_2CHTiCl_3 \rightarrow CH_3CH{=}CH_2 + TiCl_3H,$$
$$CH_3CH{=}CH_2 + TiCl_3H \rightleftarrows CH_3CH_2CH_2TiCl_3,$$
$$CH_3CH_2CH_2TiCl_3 + RMgBr \rightleftarrows CH_3CH_2CH_2MgBr + RTiCl_3.$$

This is confirmed by the displacement of propene by the addition of other alkenes [19]

$$RCH{=}CH_2 + CH_3CH_2CH_2MgBr \xrightarrow{TiCl_4} RCH_2CH_2MgBr + CH_3CH{=}CH_2.$$

Repeated attempts to prepare aryl derivatives of titanium were unsuccessful for almost a century. The reactions of titanium tetrachloride with diphenylmercury, phenylsodium, and an aryl Grignard reagent, with heating of the components to 200°, always led to the formation of biphenyl and titanium trichloride [20]. The reaction of titanium tetrachloride with diphenylmercury took place according to the equation

$$TiCl_4 + (C_6H_5)_2Hg \rightarrow C_6H_5HgCl + TiCl_3 + {}^1/_2(C_6H_5)_2.$$

The formation of titanium trichloride and biphenyl might indicate decomposition of an unstable organotitanium compound formed initially.

The first aryl organotitanium compound isolated in pure form was phenyltitanium triisopropoxide, obtained by the reaction of titanium tetraisopropoxide with phenyllithium [21]

$$Ti(OC_3^iH_7)_4 + C_6H_5Li \rightarrow C_6H_5Ti(OC_3^iH_7)_3 + LiOC_3^iH_7.$$

This was the first compound to be prepared containing a carbon–titanium σ bond. The complex $C_6H_5Ti(OC_3^iH_7)_3 \cdot LiOC_3^iH_7 \cdot LiBr \cdot (C_2H_5)_2O$ is first formed, and this is decomposed by a slight excess of titanium tetrachloride:

$$C_6H_5Ti(OC_3^iH_7)_3 \cdot LiOC_3^iH_7 \cdot LiBr \cdot (C_2H_5)_2O + {}^1/_4TiCl_4 \rightarrow$$
$$\rightarrow C_6H_5Ti(OC_3^iH_7)_3 + LiCl + LiBr + (C_2H_5)_2O + {}^1/_4Ti(OC_3^iH_7)_4.$$

Unlike the alkyl derivatives, phenyltitanium triisopropoxide is an almost colourless compound with m.p.88–90°, stable in an inert atmosphere in the absence of moisture. It can be obtained in almost quantitative yield by the reaction of phenyllithium with $TiCl(OC_3^iH_7)_3$ in ether solution [22].

With change in the ratio of titanium tetraisopropoxide and phenyllithium from 1 : 1 to 1 : 2 and 1 : 4, the thermal stability of the resulting organotitanium compounds decreases considerably. It was concluded that, in compounds of general formula $RnTiX_{4-n}$, the stability is determined chiefly by the value of $n$, but also depends on the electronegativity of R and X. It was found that stable compounds are formed only when $n \leqslant 2$ and X is sufficiently electronegative [23]. It was suggested that tetraphenyltitanium is extremely unstable, but yellow-orange crystals of this compound, fairly stable at low temperature, have recently been obtained by reaction of the ether addition compound of titanium tetrachloride with phenyllithium

$$TiCl_4 + 4C_6H_5Li \rightarrow (C_6H_5)_4Ti + 4LiCl.$$

The formation of phenyltitanium chlorides $(C_6H_5)_nTiX_{4-n}$ (where $n$ = 1–2) as intermediate products was observed in the reaction of diphenylmercury with $TiCl_4$ in solutions of various organic solvents at ~ 90°. [24] The presence of the phenyl–titanium bond was proved by the reaction with mercuric chloride, leading to the formation of phenylmercury chloride, and also by oxidation to phenol and biphenyl. The possible disproportionation of the monophenyl derivative to the disubstituted product, and also its decomposition to biphenyl and titanium dichloride, were noted

$$2C_6H_5TiCl_3 \rightarrow (C_6H_5)_2TiCl_2 + TiCl_4,$$
$$(C_6H_5)_2TiCl_2 \rightarrow (C_6H_5)_2 + TiCl_2.$$

The replacement of all the chlorine atoms in $TiCl_4$ by phenyl groups, on reaction with phenyllithium in ether solution at -80°, gives glistening orange-yellow leaflets of tetraphenyltitanium. The formation of tetraphenyltitanium is proved by the reaction with mercuric chloride, leading to the quantitative separation of phenylmercury chloride. The reaction with cyclopentadiene leads to the replacement of two phenyl groups by cyclopentadienyl groups, with the formation of dicyclopentadienyldiphenyltitanium [25]

$$(C_6H_5)_4Ti + 2C_5H_6 \rightarrow (C_6H_5)_2Ti(C_6H_5)_2 + 2C_6H_6.$$

Tetraphenyltitanium, as predicted [23], is thermally unstable; with increase in temperature to -30° it decomposes with the formation of biphenyl and diphenyltitanium

$$(C_6H_5)_4Ti \rightarrow (C_6H_5)_2 + (C_6H_5)_2Ti.$$

The latter is a black pyrophoric substance, soluble in tetrahydrofuran and benzene. Its thermal stability is greater than that of its quadrivalent analogue.

A covalent titanium–radical bond is found in dicyclopentadienyl derivatives of the type $\pi\text{-}(C_5H_5)_2TiR_2$, where $\pi\text{-}C_5H_5$ is the cyclopentadienyl group or a monosubstituted cyclopentadienyl group joined to titanium in a $\pi\text{-}(C_5H_5)_2Ti$ sandwich, and R = $CH_3$, $C_2H_5$, or $C_6H_4X$. In these mixed organometallic compounds the electronic energy levels of the transition metal are filled by the π electrons of the sandwich group, leading to an increase in the stability of the compound as a whole and of the metal–carbon σ bonds in particular. The alkyl and aryl compounds were prepared by the action of the alkyls of Li, Mg, Zn, and Al on dicyclopentadienyltitanium dichloride. The dibromo-, diiodo-, dicyano-, dithiocyanato-, or dialkoxy-derivatives can be used instead of the dichloride.

$$\pi\text{-}(C_5H_5)_2TiCl_2 + RLi \rightarrow \pi\text{-}(C_5H_5)_2Ti(R)Cl + LiCl,$$
$$\pi\text{-}(C_5H_5)_2TiCl_2 + 2RLi \rightarrow \pi\text{-}(C_5H_5)_2TiR_2 + 2LiCl.$$

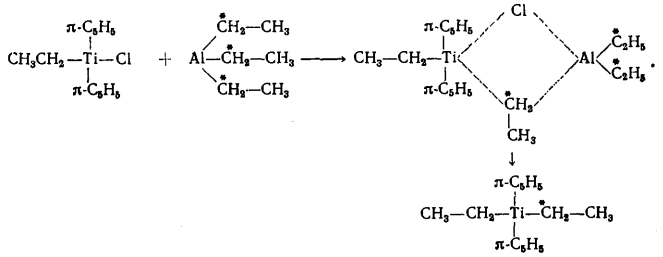
Products of complete and partial substitution $(C_5H_5)_2TiR_2$ and $(C_5H_5)_2Ti(R)X$ were obtained in this way [11,26–28]. Brief mention may be made of individual representatives of this type. The monomethyl derivative $\pi\text{-}(C_5H_5)_2Ti(CH_3)Cl$ forms red-orange crystals with m.p. 168–169°, soluble in water in the cold without decomposition. The first value given for the yield of this product was 1%; [26] the compound was later prepared in 90% yield [11,27]. The action of direct sunlight produces a rapid irreversible change in the compound. The monopropyl compound $(C_5H_5)_2Ti(C_3H_7)Cl$ begins to decompose at 160°; it is prepared from dicyclopentadienyltitanium dichloride and propyllithium.

Dicyclopentadienyldimethyltitanium $(C_5H_5)_2Ti(CH_3)_2$ forms orange needles with a characteristic odour and is prepared in analogous fashion in 95% yield [27]. It is stable to the action of water and oxygen, but darkens and decomposes rapidly on exposure to light.

The compound $(CH_3C_5H_4)_2Ti(CH_3)_2$ is obtained in 65% yield in the form of yellow crystals which are stable in air and in water but decompose on strong illumination or heating.

All these compounds can be used as catalysts for the polymerisation of alkenes, particularly in conjunction with organoaluminium compounds.

The reaction of ethyldicyclopentadienyltitanium chloride with $^{14}C$-labelled triethylaluminium leads to further exchange of ethyl groups by the titanium and aluminium atoms



The resulting diethyl derivative decomposes at 40°, as indicated by the isolation of the labelled decomposition products — ethane and ethylene[20].

Diaryl derivatives of dicyclopentadienyltitanium $\pi$-$(C_5H_5)_2TiR_2$ were prepared with R = $C_6H_5$, $m$-$CH_3C_6H_4$, $p$-$CH_3C_6H_4$, and $p$-$(CH_3)_2NC_6H_4$. These compounds form yellow-orange crystals which melt with decomposition[29,30]. The most stable is $\pi$-$(C_5H_5)_2Ti(C_6H_5)_2$, which melts at 146–148° and is monomolecular in benzene solutions. All these compounds are readily soluble in organic solvents. Their thermal stability depends to a marked extent on the nature of the aryl group. Thus dicyclopentadienyldiphenyltitanium can be kept for several days at room temperature, whereas the $p$-dimethylaminophenyl derivative could not be isolated in pure form. With an excess of phenyllithium, the formation of dark-coloured complexes $Li[Ti(C_5H_5)_2(C_6H_5)_3]$ and $Li_2[Ti(C_5H_5)_2(C_6H_5)_4]$ is observed; hydrolysis of ethereal solutions of these compounds leads to regeneration of the original product.

$$(C_5H_5)_2Ti(C_6H_5)_2 + C_6H_5Li \rightarrow Li[Ti(C_5H_5)_2(C_6H_5)_3] \xrightarrow{H_2O} \xrightarrow{H_2O} (C_5H_5)_2Ti(C_6H_5)_2 + C_6H_6 + LiOH.$$

In addition to the dicyclopentadienyl compounds, monocyclopentadienyl derivatives of quadrivalent titanium, of the type $\pi$-$C_5H_5TiR_3$, with a titanium–radical bond, are known. These compounds are obtained by an exchange reaction, analogous to that described above, between monocyclopentadienyltitanium trichloride and alkali-metal alkyls or aryls. Thus the reaction of $C_5H_5TiCl_3$ with methyllithium gave the trimethyl compound $C_5H_5Ti(CH_3)_3$, which is stable at -70° and can be distilled at -20° and 0.5 mmHg.[31] At -80° the compound can be isolated from pentane solution in the form of lemon yellow crystals which are pyrophoric in air at room temperature[27].

The phenyl analogue $C_5H_5Ti(C_6H_5)_3$ is obtained in solution in analogous fashion by the use of phenyllithium. It is a yellow compound, stable in solution at -70°. With increase in temperature to room temperature it decomposes with formation of the bivalent titanium compound $C_5H_5TiC_6H_5$; the products of the decomposition carried out in ethereal solution contain also biphenyl and benzene[32]. The presence of phenyl–titanium bonds in these compounds was proved by the reaction with mercuric chloride. In the case of $C_5H_5Ti(C_6H_5)_3$, the quantity of phenylmercury chloride formed corresponds to three phenyl–titanium bonds, and in the case of the monophenyl compound, the yield of phenylmercury chloride amounts to 1 mole per mole of $C_5H_5TiC_6H_5$ taken. In both cases the cyclopentadienyl–titanium bond is unaffected, as indicated by the formation of cyclopentadienyltitanium trichloride in the products of the reaction with mercuric chloride. $C_5H_5TiC_6H_5$ is a black compound which is oxidised extremely readily in air and is soluble in benzene and tetrahydrofuran. It reacts at low temperatures with halogen-containing organic solvents ($CHCl_3$ and $CCl_4$).

Thermal stability. A distinctive feature of organotitanium compounds is their extremely low thermal stability. In the series of alkyl or aryl derivatives of the type $RnTiX_{4-n}$, compounds with a smaller number of organic groups and with more strongly electronegative groups X are the more stable[23]. Thus methyltitanium trichloride is stable at 20° for several days in the absence of air and moisture. The yellow dioxan addition compounds of $R_2TiX_2$ are stable at 20° for 24 h. Tetramethyltitanium is stable at -70°. The decomposition of methyltitanium trichloride has been studied in more detail. At about 100° the compound decomposes with the formation of $TiCl_3$, methane, and polymethylene. The $TiCl_3$ produced catalyses the decomposition, which takes place more readily in ether and hydrocarbons. The rate of decomposition of methyltitanium trichloride increases on irradiation or treatment with $BF_3$.[5] In a mixture of $CCl_4$ and ether, considerable quantities of methyl chloride are formed, as a result of the disproportionation of methyltitanium trichloride[7]. In a recent paper[33], the reactions of $CH_3TiCl_3$ with carbon tetrachloride in the presence of metallic mercury are interpreted as free-radical reactions. Evidence for this is provided by the formation of methylmercury chloride, hexachloroethane, and other products of the free-radical reaction.

With increase in temperature to room temperature, tetramethyltitanium decomposes spontaneously with the formation of a black precipitate and a metallic mirror[16]. The decomposition products are pyrophoric and possibly contain derivatives of bivalent titanium.

The same is observed in the case of the phenyl derivatives. The thermal decomposition of tetraphenyltitanium gives diphenyltitanium and biphenyl[24]. The thermal stability of diphenyltitanium is much greater than that of tetraphenyltitanium. The former decomposes at 200–250° *in vacuo* with the formation of biphenyl and metallic titanium.

The thermal stability of organotitanium compounds of the above types decreases sharply when one or two cyclopentadienyl groups, joined to the metal in a sandwich, are introduced into the molecule:

$$R_4Ti > R_3TiC_5H_5 > R_2Ti(C_5H_5)_2.$$

The monocyclopentadienyl derivatives of quadrivalent titanium $C_5H_5Ti(CH_3)_3$ and $C_5H_5Ti(C_6H_5)_3$ darken and decompose when warmed to room temperature in the light. Cyclopentadienyltriphenyltitanium decomposes in ethereal solution with the loss of two phenyl groups in the form of benzene and biphenyl:

$$C_5H_5Ti(C_6H_5)_3 \xrightarrow{ether} C_5H_5TiC_6H_5 + C_6H_6 + (C_6H_5)_2.$$

A bivalent titanium derivative is formed. The presence of the cyclopentadienyl and phenyl groups in this compound was proved by the reaction with mercuric chloride

$$C_6H_5TiC_6H_5 + HgCl_2 \rightarrow [C_6H_5TiCl] + C_6H_5HgCl,$$
$$[C_6H_5TiCl] + HgCl_2 \rightarrow C_6H_5TiCl_3 + Hg,$$
$$[C_6H_5TiCl] + 2HgCl_2 \rightarrow C_6H_5TiCl_3 + 2HgCl.$$

In the thermal decomposition of mixed dicyclopentadienyl derivatives of titanium under mild conditions, the titanium–radical σ bond is broken first[34]. When dicyclopentadienyldiphenyltitanium is heated in solution at ~90°, the two phenyl groups are removed successively in the form of free radicals:

$$(C_5H_5)_2Ti^{4+}(C_6H_5)_2 \rightarrow (C_5H_5)_2Ti^{3+}C_6H_5 + C_6H_5^{\cdot},$$
$$(C_5H_5)_2Ti^{3+}C_6H_5 \rightarrow (C_5H_5)_2Ti^{2+} + C_6H_5^{\cdot}.$$

A derivative of tervalent titanium is produced in the first stage of the process. The two cyclopentadienyl–titanium bonds are unaffected, as indicated by the conversion of the dark-coloured product of the thermal decomposition to the stable dichloride $(C_5H_5)_2TiCl_2$ by the action of halogen-containing compounds ($CCl_4$, $HgCl_2$, benzyl chloride, etc.)[35,36].

The low thermal stability of organotitanium compounds results from the electron-unsaturation of the structure of the central titanium atom. Stabilisation results when the *d* electron level is filled by donor atoms and the electronic structure shows maximum approach to that of the nearest inert gas (krypton). The least stable tetramethyltitanium has a deficit of ten electrons, whereas the more stable $(C_5H_5)_2TiR_2$ has a deficit of only four electrons. Filling of the *d* level of titanium may also be brought about by electron donors such as amines, phosphines, and ethers. Complexes obtained with the above ligands are more stable, Thus methyltitanium trichloride forms a tetrahydrofuran derivative which is soluble in organic solvents and very sensitive to oxygen and moisture, but which has a higher thermal stability (m.p.107–108°). It reacts with metallic mercury in $CCl_4$ medium by a free-radical mechanism to give methylmercury chloride[37]. Insoluble complexes of methyltitanium trichloride with triphenylphosphine and dioxan are known[5]. Dimethyltitanium dichloride also forms a dioxan derivative. An ammine of diphenyltitanium which is readily oxidised in air and is hydrolysed with the liberation of ammonia has been described[25]. Diphenyltitanium reacts with tetrahydrofuran to give a tetrahydrofuran derivative. The latter is a black substance which is readily oxidised with the formation of biphenyl and phenol. Its reaction with mercury derivatives is similar to that of diphenyltitanium.

Action of water, acids, and alcohols. The Ti–R σ bond is generally broken by the action of water, alcohols, and other hydroxyl-containing compounds. In the case of the simplest alkyl derivatives $CH_3TiCl_3$, $(CH_3)_2TiCl_2$, $(CH_3)_4Ti$, etc., the reaction takes place with the quantitative liberation of methane. The compounds $(C_5H_5)_2Ti(CH_3)X$, $(C_5H_5)_2Ti(CH_3)_2$, and $C_5H_5Ti(CH_3)_3$ are stable towards water but are decomposed quantitatively by dilute acids[27]. The phenyl derivatives react with water, aqueous acids, or alcohols, with the formation of benzene. The products of the hydrolysis of $C_6H_5Ti(OC_3^iH_7)_3$ contain isopropanol and benzene[23]. Diphenyltitanium reacts with dilute hydrochloric acid with the formation of hydrogen, benzene, and $TiCl_3$:

$$(C_6H_5)_2Ti + 2HCl \rightarrow 2C_6H_6 + TiCl_2,$$
$$TiCl_2 + HCl \rightarrow {}^1/_2H_2 + TiCl_3.$$

The reaction of $(C_6H_5)_2Ti$ with isopropanol gives benzene as the main product[24]. Cyclopentadienyltriphenyltitanium reacts with isopropanol to give benzene in quantities corresponding to three phenyl groups, the cyclopentadienyl–titanium bond being unaffected. Small quantities of acetone are also detected[32].

Dicyclopentadienyldiphenyltitanium is stable to water. Dilute inorganic acids at room temperature lead to quantitative rupture of the $Ti–C_6H_5$ bonds but do not affect the $(C_5H_5)_2Ti$ group. The action of hydrochloric acid gives benzene and dicyclopentadienyltitanium dichloride:

$$(C_5H_5)_2Ti(C_6H_5)_2 + 2HCl \rightarrow 2C_6H_6 + (C_5H_5)_2TiCl_2.$$

The reaction with alcohols takes place at elevated temperatures with the formation of benzene, acetone, and, apparently, a dicyclopentadienyltitanium dialkoxide[35].

Action of halogens and halogeno-derivatives. The reaction with halogen provides an analytical test for an alkyl–titanium σ bond. Quantitative formation of alkyl iodides has been observed with $CH_3TiCl_3$, $(CH_3)_4Ti$, and $(CH_3)_2Ti(C_5H_5)_2$:

$$(CH_3)_4Ti + 4I_2 \rightarrow 4CH_3I + TiI_4,$$
$$(C_6H_5)_2Ti(CH_3)_2 + 2I_2 \rightarrow (C_6H_5)_2TiI_2 + 2CH_3I.$$

In the case of the phenyl derivatives this reaction is incomplete. Thus the reaction of a benzene solution of diphenyltitanium with iodine at room temperature leads to the formation of 20% of iodobenzene and $TiI_4$.

The phenyl–titanium bonds in diphenyltitanium are readily broken by the action of chloroform or carbon tetrachloride. The reaction with chloroform takes place at room temperature, as indicated by a change in colour from black to yellowish brown. The reaction products are benzene, biphenyl, and titanium tetrachloride; derivatives of bivalent or tervalent titanium were not observed[25].

Cyclopentadienyltriphenyltitanium is decomposed by chloroform between -70° and -50° with the formation of almost the theoretical quantity of benzene and dicyclopentadienyltitanium dichloride[32].

The thermochemical and photochemical reactions of dicyclopentadienyldiphenyltitanium in chloroform solution give benzene and dicyclopentadienyltitanium dichloride in analogous fashion. With carbon tetrachloride, chlorobenzene is formed[35,36].

It was noted above that the reactions of methyltitanium trichloride with carbon tetrachloride gave appreciable quantities of methyl chloride[7,33,37].

The reaction of tetramethyltitanium with $CF_3I$ gives methyl iodide in addition to trimethyltitanium iodide, but the mechanism of the reaction is not clear[17].

Action of metal halides. Metal halides react with the R–Ti bond. The action of the halides of tin, titanium, mercury, and other metals on a variety of organotitanium compounds has been noted. The action of $SnCl_4$

on methyltitanium trichloride leads to the formation of titanium tetrachloride and the methyl derivative of tin:

$$4CH_3TiCl_3 + SnCl_4 \rightarrow 4TiCl_4 + Sn(CH_3)_4.$$

The catalytic action of $TiCl_3$ on the decomposition of methyl derivatives of titanium was noted above. An analogous influence is shown by titanium dichloride. Titanium tetrachloride decomposes methyltitanium trichloride [7] and tetramethyltitanium [14]:

$$CH_3TiCl_3 + TiCl_4 \rightarrow 2TiCl_3 + CH_3Cl,$$
$$(CH_3)_4Ti + 3TiCl_4 \rightarrow [4CH_3TiCl_3] \rightarrow 4TiCl_3 + 4\dot{C}H_3.$$

Phenyltitanium triisopropoxide reacts with mercuric chloride to give heterolytic exchange of phenyl for halogen with the formation of phenylmercury chloride. Addition of titanium tetrachloride to the isopropoxide gave a catalyst for the intensive polymerisation of propene [38]. The reaction with $TiCl_4$ was studied in more detail in hexane or benzene medium at room temperature. Biphenyl, isopropoxytitanium trichloride, and a tervalent titanium compound were isolated from the reaction mixture:

$$C_6H_5Ti(OC_3H_7)_3 + 2TiCl_4 \longrightarrow \begin{matrix} C_6H_5TiCl_2(OC_3H_7) \\ \swarrow \qquad \searrow \\ 1/2(C_6H_5)_2 \quad + \quad C_3H_7OTiCl_2 \end{matrix} + 2C_3H_7OTiCl_3.$$

The biphenyl isolated from the products of the reaction carried out in labelled benzene was almost inactive.

To prove the presence of a C–Ti $\sigma$ bond, extensive use is made of the reaction with mercuric chloride, leading to formation of an unsymmetrical organomercury compound and titanium halides. Thus methyltitanium trichloride gives the methyl derivative of mercury [33]; phenylmercury chloride is the chief product of the reaction of phenyl compounds of titanium [24,32,34,35].

Oxidation. Oxidation is a characteristic reaction for the Ti–R bond. The oxidation of lower-valency titanium derivatives takes place very vigorously, often with spontaneous ignition. Thus diphenyltitanium, particularly in the finely divided state, ignites in air [24]. The oxidation of diphenyltitanium in benzene solution is complete in 1–2 h at room temperature; phenol and biphenyl are found among the reaction products. Special experiments on oxidation in labelled benzene medium showed that the products contained no tracer atoms from the solvent [25]. The products of the decomposition of tetramethyltitanium are pyrophoric [16], and cyclopentadienylphenyltitanium is vigorously oxidised [32].

In a series of quadrivalent derivatives, the stability to the action of oxygen increases with the introduction of cyclopentadienyl groups into the molecule. Methyltitanium trichloride reacts rapidly with the absorption of $\frac{1}{2}O_2$ per mole, the solution giving a precipitate which is coloured pale brown by impurities:

$$CH_3TiCl_3 + 1/2O_2 \rightarrow CH_3OTiCl_3.$$

This is followed by disproportionation of the alkoxytitanium trichloride:

$$3CH_3OTiCl_3 \rightarrow CH_3OTiCl_3 \cdot (CH_3O)_2TiCl_2 + TiCl_4.$$

Other alkyls and aryls of quadrivalent titanium — dialkyltitanium dihalides, tetramethyltitanium, the monophenyl derivatives $C_6H_5TiX_3$, and tetraphenyltitanium — are readily oxidised.

Alkyl or aryl derivatives of monocyclopentadienyltitanium are also oxidised vigorously; cyclopentadienyltrimethyltitanium is pyrophoric [31].

The dicyclopentadienyl compounds $(C_5H_5)_2TiR_2$ are more stable towards oxygen. In the solid state they are stable in air at low temperatures. In solution, oxidation is more rapid. Dicyclopentadienyldiphenyltitanium is readily oxidised by atmospheric oxygen in solutions in benzene, chloroform, and carbon tetrachloride at 50–60°.

Oxidation in isopropanol is accompanied by the formation of phenol, cyclopentadiene, acetone, and the oxidised organometallic compound. In $CCl_4$ medium, dicyclopentadienyltitanium dichloride is formed in addition to biphenyl, chlorobenzene, and carbonyl chloride; this indicates that reaction with the solvent, initiated by oxygen, takes place.

The sandwich group $(C_5H_5)_2Ti$ is unaffected under these conditions. Oxidation with aqueous hydrogen peroxide at 40–50° leads to complete decomposition of the original compound to CO and $CO_2$. Considerable quantities of acetophenone are found among the reaction products in addition to phenol [39].

Reduction. The discovery and study of polymerisation catalysts of the Ziegler–Natta type led to the development of work on the reduction of organotitanium compounds. The alkylation of titanium halides taking place in the systems formed by these catalysts leads to reduction of the quadrivalent titanium to the tervalent and bivalent states. The second component of the catalyst is an organometallic compound of lithium, magnesium, or, most frequently, aluminium. We shall not deal with the widely studied processes of formation and mechanism of action of "bridged" catalysts for the polymerisation of alk-1-enes, but merely point out that reduction of $Ti^{4+}$ to $Ti^{3+}$ often takes place in the synthesis of organotitanium compounds if the reaction is carried out at higher temperatures. The monosubstituted product $RTiCl_3$ forms $TiCl_3$ on decomposition:

$$RTiCl_3 \rightarrow R' + TiCl_3.$$

The reduction of the mono- and di-alkyl compounds is accompanied by the liberation of methane and ethane in the case of the methyl derivatives, and of ethane, ethylene, and butane in the case of the ethyl derivatives. This is due to disproportionation or dimerisation of the radicals.

The reactions of alkyl derivatives of titanium with hydrogen have been studied recently [27]. $CH_3TiCl_3$ and its mixtures with $(CH_3)_nAlCl_{3-n}$ do not react at all with $H_2$, whereas $(C_5H_5)_2Ti(CH_3)_2$ is reduced immediately in aliphatic and alicyclic hydrocarbons at room temperature, with the formation of two moles of methane and the sparingly soluble dark green dicyclopentadienyltitanium:

$$(C_5H_5)_2Ti(CH_3)_2 + H_2 \rightarrow (C_5H_5)_2Ti + 2CH_4.$$

No reaction with hydrogen takes place in halogen-containing solvents. Methyldicyclopentadienyltitanium chloride does not react with hydrogen at 20°. Dicyclopentadienyldiphenyltitanium in toluene is reduced appreciably only at 60°.

There is an interesting analogy between reduction under the influence of hydrogen or another organometallic compound and the thermal decomposition of titanium compounds with the formation of lower-valency derivatives.

Qualitative test for the C–Ti bond. The reaction with Michler's ketone provides a qualitative test

for a bond between a radical and a metal in the first three groups of the Periodic System. Alkyl derivatives of titanium also give a positive Gilman test. The final reaction products in the case of titanium compounds, however, differ from the analogous products for organoaluminium derivatives.

A slow positive reaction with Michler's ketone was observed for $C_6H_5Ti(OC_3^iH_7)_3$ and also for the products of the reaction of titanium tetraisopropoxide with phenyllithium in the proportions 1 : 2 and 1 : 4; the rate of the colour reaction increases with increase in the number of phenyl groups[23]. Phenyltitanium triisopropoxide reacts with benzophenone with the formation of triphenylmethanol. Diphenyltitanium gives a colour reaction with Michler's ketone.

### Zirconium and Hafnium

There are isolated data on organometallic compounds of zirconium and hafnium. In Cotton's review[3] it is stated that zirconium tetrachloride does not react with diethylzinc and that metallic zirconium does not react with ethyl iodide or diethylmercury. According to recent data, however, exchange of radicals is observed in the systems formed by $ZrCl_4$ with $R_2Hg$ or RMgX. $ZrCl_4$ reacts with diethylmercury and diphenylmercury[40] and with organolithium and organomagnesium compounds[41]. The reaction of phenylmagnesium chloride with $ZrCl_4$ gives biphenyl in 56% yield; $ZrCl_4$ or $Zr(OC_6H_5)_4$ reacts with methyllithium to give up to 70% of methane[42]. Hydrolysis of the reaction mixture gives hydrogen in addition to hydrocarbons. The reaction of a phenyl Grignard reagent with zirconium tetrachloride to give a compound of the type $RZrCl_3$ has recently been reported[43]. Hafnium and zirconium chlorides have been used as additives to aluminium triisobutoxide in order to study the resulting propene-polymerisation catalysts. The relative reactivity of the catalyst increases in the order

$$HfCl_4<ZrCl_4<TiCl_4<VOCl_3<VCl_4.$$

The formation of organometallic compounds of hafnium and zirconium by halogen–radical exchange reactions is probable in these cases. A brief report of the preparation of $Zr(C_5H_{11})_2$ from hydrides and diazohydrocarbons at low temperatures appeared in the patent literature[44].

## GROUP V

### Vanadium

The early papers cited in Cotton's review[3] contained no convincing proof of the formation of alkyl or aryl compounds of vanadium. The reaction of $VOCl_3$ with a Grignard reagent gives a dark green crystalline product which burns in air with a smoky flame and contains vanadium[45]. This substance was not studied more closely.

Recent papers contain reliable evidence of the formation of a phenyl–vanadium bond. Thus the reaction of ten moles of phenyllithium with one mole of the tetrahydrofuran addition compound of vanadium(II) chloride in ether in the cold, in the absence of moisture and air, gave the paramagnetic complex $4C_6H_5Li.V(C_6H_5)_2.3.5(C_2H_5)_2O$. The complex is very sensitive towards air and moisture. It loses ether *in vacuo* at 50°, and decomposes above 80° with the formation of biphenyl. Chemical reactions confirm the presence of a phenyl–vanadium σ bond. Decomposition by acids, water, or alcohols leads to the formation of benzene. The reaction with iodine gives iodobenzene and the reaction with mercuric chloride gives phenylmercury chloride. The tetrahydrofuran addition compound of vanadium chloride reacts with phenylmagnesium chloride to form a complex containing vanadium and magnesium[46]. Vanadium halides react with organometallic compounds of aluminium, mercury, and titanium with exchange of halogen atoms for phenyl groups. It was shown that triisobutylaluminium containing added halides of the transition metals of Groups IV–VI (Ti, V, Cr) form catalysts for the polymerisation of alk-1-enes, the greatest activity being shown by vanadium halides[47,48]. In the process, reduction of quadrivalent and quinquevalent vanadium to the bivalent and tervalent states is observed, together with the formation of a black precipitate which fumes in air and contains aluminium, vanadium, halogen, and a hydrocarbon radical. It was shown convincingly for the analogous systems formed by organometallic compounds of aluminium with titanium halides that the complexes with a "bridged" structure are intermediate products in the formation of true organotitanium compounds. The formation of individual derivatives in the case of vanadium halides might also be expected.

It was shown that diphenylmercury reacts in cyclohexane solution under ordinary conditions with vanadium halides and oxide halides, with the quantitative formation of phenylmercury chloride and a red solution of phenyl derivatives of vanadium:

$$(C_6H_5)_2Hg + VOCl_3 \rightleftarrows C_6H_5VOCl_2 + C_6H_5HgCl,$$
$$(C_6H_5)_2Hg + VCl_4 \rightleftarrows C_6H_5VCl_3 + C_6H_5HgCl.$$

Their formation is confirmed by spectroscopic data and also by hydrolysis, which leads to the formation of benzene. Benzene is also formed by the action of hydrogen bromide:

$$C_6H_5VOCl_2 + HBr \rightarrow C_6H_6 + VOCl_2Br.$$

The phenyl derivatives of vanadium were not isolated in pure form, since they are thermally unstable. Decomposition gives biphenyl, evidently as a result of disproportionation:

$$2C_6H_5VOCl_2 \rightleftarrows (C_6H_5)_2VOCl + VOCl_3,$$
$$(C_6H_5)_2VOCl \rightleftarrows (C_6H_5)_2 + VOCl.$$

It was proved that free phenyl radicals are not formed at this stage[49].

In the $(C_6H_5)_4Sn + VCl_4$ ($VOCl_3$) system, exchange of phenyl radicals is observed under more severe conditions (100°).[50] Rapid reduction of vanadium and formation of biphenyl was observed on the addition of $AlCl_3$, $AlBr_3$, or $Al(OC_4^iH_9)_3$. Diphenylzinc and $CH_3TiCl_3$ bring about partial reduction of vanadium from the quadrivalent to the bivalent state and give catalysts for the polymerisation of ethylene[47].

Phenyl derivatives of vanadium can be obtained by replacing the cyclopentadienyl group of $C_5H_5V(CO)_4$ by a phenyl group. If a current of hydrogen chloride, a mixture of HCl and $O_2$, and, finally, pure oxygen are passed in turn through a benzene solution of $C_5H_5V(CO)_4$, the colour changes from violet to pale blue. Removal of the solvent and distillation in a high vacuum gives $C_6H_5VOCl_2$, which is soluble in benzene, chloroform, ether, methylene chloride, and other organic solvents[51].

Replacement of the halogen in $\pi$-$(C_5H_5)_2VCl$ by a phenyl group by the action of an equimolar quantity of phenyllithium gave $(C_5H_5)_2VC_6H_5$ in pure form[52]. The same compound was obtained by the action of phenyllithium on $\pi$-$(C_5H_5)_2VCl_2$ in the molar ratio 2 : 1 in 1,2-dimethoxyethane solution at -50°. The solvent was removed *in vacuo* and the residue was extracted with petroleum ether. Black crystals of $(C_5H_5)_2VC_6H_5$ with m.p. 92° were isolated in 50% yield by freezing to -80°. Phenyldicyclopentadienylvanadium solution is stable in the absence of oxygen at room temperature for one week. The presence of phenyl–vanadium $\sigma$ bond was proved by the formation of benzene on decomposition with HCl; the initial green colour of the solution changed to blue and then to green again, and crystals of $(C_5H_5)_2VCl$ separated from the reaction mixture:

$$(C_5H_5)_2\,V\,C_6H_5 + HCl \rightarrow C_6H_6 + (C_5H_5)_2VCl\,.$$

The vanadium derivatives are very sensitive towards oxygen.

### Niobium and Tantalum

Data on the reactions of niobium and tantalum halides with aromatic hydrocarbons are contradictory[3]. The reactions of $NbCl_5$ and $TaCl_5$ with benzene, naphthalene, anthracene, and tetralin in a boiling solvent (benzene, $CCl_4$, or $CS_2$) led to the formation of compounds containing metal, halogen, and an organic residue[53]. The formulae $RMX_4$ or $R_2MX_3$ were ascribed to the products, but the latter were not isolated in pure form, with the exception of the complex $C_6H_6.NbCl_5$. Attempts to repeat these reactions with specially purified benzene were unsuccessful[54].

Reaction of a Grignard reagent with tantalum compounds gives red solutions, which are unstable towards water and oxygen and contain tantalum compounds in the dissolved state. Complete hydrolysis gives the oxide $Ta_2O_5$.[55]

The preparation of a complex of tetraphenylniobium with phenyllithium by the reaction of $NbBr_5$ with phenyllithium in ethereal solution has recently been reported[56]:

$$NbBr_5 + 8C_6H_5Li + 3(C_2H_5)_2O \xrightarrow[N_2]{} \underset{(I)}{Li_3Nb(C_6H_5)_7.3(C_2H_5)_2O} + 5LiBr + \frac{1}{2}(C_6H_5)_2.$$

The complex (I) crystallises as a black-violet compound which is pyrophoric in the dry state. The ether is removed in a high vacuum at room temperature. The substance is non-volatile, stable up to 40–50°, and is readily oxidised and hydrolysed. The magnetic moment is 1.66 $\beta$, which is characteristic of $Nb^{4+}$. The infrared spectra confirmed the presence of a phenyl–niobium $\sigma$ bond; the formula $Nb(C_6H_5)_4.3C_6H_5Li.3(C_2H_5)_2O$ was ascribed to the substance.

## GROUP VI

### Chromium

Phenylchromium compounds became known as early as the 1920's, as a result of Hein's work. The compounds were prepared by the reaction of phenylmagnesium bromide with sublimed anhydrous chromium(III) chloride at -10°. Three series of compounds were isolated from the reaction mixture and these were named as derivatives of "triphenylchromium", "tetraphenylchromium", and "pentaphenylchromium". It appeared strange that all these compounds had the same orange colour, apparently indicating the same oxidation state. Reduction with lithium tetrahydroaluminate in all cases gave more biphenyl than benzene, and phenol was also obtained from the "penta"-derivative[57]. Reduction with $LiAlD_4$ showed that the biphenyl is formed at this stage and not by hydrolysis. It was thus established that each of these three products contains biphenyl, not phenyl, groups. The structure of Hein's polyphenylchromium compounds began to be explained in the light of a diarene $\pi$ structure analogous to that of dibenzenechromium.

Measurement of the magnetic properties, the X-ray and infrared spectra, and analytical data proved that dibiphenylchromium iodide obtained by the Grignard reaction[58] was identical to that obtained from biphenyl and chromium(III) chloride in the presence of Friedel–Crafts catalysts[59].

Further work showed the possibility of the existence of true organometallic compounds of chromium. The formation of phenylchromium compounds of the type $C_6H_5CrCl_2$ or $(C_6H_5CrCl_2)_2CrCl$ as intermediate products was postulated in 1956.[60] In a description of the reaction of triphenylaluminium with $CrCl_3$, mention was made of the formation of the tetrahydrofuran addition compound of phenylchromium dichloride $C_6H_5CrCl_2.3THF$†.[61] Anhydrous chromium(III) chloride reacts with phenyllithium in ethereal solution to form a red solid (A)[62]:

$$CrCl_3 + 6C_6H_5Li \xrightarrow{\text{ether}} (C_6H_5)_3Cr\cdot 3C_6H_5Li\cdot 2.5\,(C_2H_5)_2O\ (A)\,.$$

The compound (A) is extremely sensitive to oxygen and moisture. Hydrolysis leads to the formation of benzene, and biphenyl is formed in the absence of oxygen. With iodine, biphenyl and iodobenzene are formed:

$$Li_3Cr\,(C_6H_5)_6 + {}^9/_2I_2 \longrightarrow 3\,LiI + CrI_3 + 3C_6H_5I + {}^3/_2\,(C_6H_5)_2\,.$$

The product (A) is paramagnetic (3.87 $\beta$ and 3.61 $\beta$), which corresponds to tervalent chromium and confirms the presence of three phenyl–chromium $\sigma$ bonds. The triphenylchromium complex can be obtained free from ether by dissolving compound (A) in benzene with subsequent crystallisation. Under normal conditions, the solutions absorb hydrogen and form the hydro-pentaphenyl derivative $Li_3[CrH(C_6H_5)_5].3(C_2H_5)_2O$ as shiny red crystals. Further treatment with hydrogen leads to the formation of complex products[63]. The reaction of $3C_6H_5Li.(C_6H_5)_3Cr\,.\,2.5(C_2H_5)_2O$ with lithium tetrahydroaluminate in ether in a current of pure dry argon gave a pyrophoric substance decomposing above 75°, and having the composition $Li_6CrAl_3H_{16}.\frac{1}{3}(C_2H_5)_2O$ (apparently a complex hydride of univalent chromium). The compound is insoluble in the usual solvents, readily deposits chromium, reduces azobenzene to aniline, and reacts with phenyllithium under ordinary conditions to give a hydride of composition $Li[AlH(C_6H_5)_3]$.[64]

Reaction of phenylmagnesium bromide with chromium(III) chloride in tetrahydrofuran solution at -20° gave the tetrahydrofuran addition compound $(C_6H_5)_3Cr.3THF$, which is readily hydrolysed to green $[Cr(H_2O)_6]^{3+}$ and reacts with mercuric chloride to give a quantitative yield of phenylmercury chloride[65,66]:

$$(C_6H_5)_3Cr\cdot 3THF + 3HgCl_2 \xrightarrow{THF} 3C_6H_5HgCl + CrCl_3\,.$$

† THF represents tetrahydrofuran.

On being heated *in vacuo*, and also as a result of the addition of diethyl ether, the precipitate loses all its tetrahydrofuran with formation of a black substance, which on hydrolysis in the absence of oxygen gives the $\pi$ complexes dibenzenechromium and benzenebiphenylchromium[67]:

$$(C_6H_5)_3Cr\cdot 3THF \xrightarrow[H_2O]{heat} \pi\text{-}(C_6H_6)_2Cr + \pi\text{-}C_6H_6Cr(C_6H_5 - C_6H_5).$$

The double compound $(C_6H_5)_3Cr.3THF.3(MgBrCl.THF)$ (B) has also been isolated[68]. The action of ether on (B) gives the tetrahydrofuran addition compound of triphenylchromium. Drying *in vacuo* at 20–40° yields an extremely pyrophoric product, which on careful hydrolysis also gives a mixture of the $\pi$ complexes dibenzenechromium and benzenebiphenylchromium. The $\pi$ complexes can also be prepared by appropriate treatment of (B). The action of $D_2O$ on the black intermediate product in an atmosphere of nitrogen gives a mixture of bismonodeuterobenzenechromium and biphenylmonodeuterobenzenechromium[69].

Carboxylation of the black intermediate product leads to the formation of carboxy-derivatives. Thus chromium(II) chloride in ethereal solution reacts with a phenyl Grignard reagent at -10°; after 4 h, saturation of the reaction mixture with carbon dioxide and hydrolysis with an aqueous solution of sodium tetraphenylborate give a red-orange precipitate having the composition[70]

$$(C_6H_5COOH)[(C_6H_5)_2Cr]^+(C_6H_5)_4B^- \text{ (yield 12\%, m.p. 144–147°).}$$

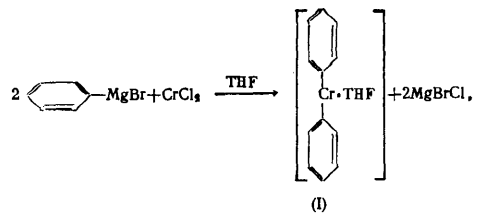
Substituted phenyl derivatives of chromium have recently been described. The action of *o*-methoxyphenyllithium on a chromium halide gives fine yellow crystals of bis-*o*-methoxyphenylchromium, which is pyrophoric in air, is slowly decomposed by alcohol, and has a low magnetic moment (0.55 $\beta$). Attempts to prepare this compound from the lithium derivative and the tetrahydrofuran addition compound of chromium(II) bromide led to formation of the red-brown crystalline complex $LiCr(o\text{-}CH_3OC_6H_4)_4.L$, where L is the solvent. This complex was also obtained by the disproportionation of bismethoxyphenylchromium with an ethereal solution of methoxyphenyllithium[71].

Tris-($\omega$-*NN*-diethylaminotolyl)chromium has been prepared by the reaction of chromium(III) chloride in ether with $\omega$-*NN*-diethylaminotolyllithium. The compound forms glistening garnet red crystals which are comparatively stable in air and even more stable in alcoholic solution; it was assumed to have an inner-complex structure[72]. The analogous reaction with $p\text{-}N(CH_3)_2C_6H_4Li$ gave a yellow substance of composition

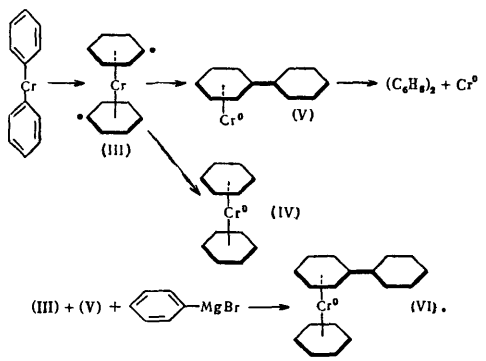
$$[p\text{-}N(CH_3)_2C_6H_4]_3Cr.3p\text{-}N(CH_3)_2C_6H_4Li.3THF \text{ (Ref. 71),}$$

which is sensitive to air and sparingly soluble in ether.

Tsutsui regards the formation of true phenylchromium compounds as an intermediate stage in the formation of the more stable arene $\pi$ complexes. In his opinion[73] the reaction of chromium(II) chloride with a phenyl or mesityl Grignard reagent involves initially the formation of diphenyl- or dimesityl-chromium. Diphenylchromium was not isolated from the reaction products: it undergoes rapid rearrangement to dibenzenechromium and benzenebiphenylchromium. The true organochromium compounds formed initially undergo further rearrangement to the transition state — a $\pi$-radical hybrid — which may be stabilised in the form of the diradical sandwich $\pi$ complex (III) or the half-sandwich $\pi$ complex (V). In the process, the bivalent chromium is reduced to the zerovalent state.




(I)




The $\pi$ complexes (III) and (V) undergo rearrangement to sandwich compounds (IV) or (VI), with the stable electronic configuration of an inert gas, or else decompose with the formation of biphenyl, depending on the reaction conditions. Rearrangement to dibenzenechromium and benzenebiphenylchromium takes place as a result of hydrolysis or subsequent reaction with the Grignard reagent under the conditions of Hein's reaction. Decomposition to biphenyl takes place under more severe conditions.

Tsutsui suggests that the $\pi$-radical–electron hybridised complex (VII), in which the two phenyl groups are tilted relative to the chromium atom, is formed in an intermediate state between diphenylchromium and the $\pi$ complex (III) or (V).



(VII).

In the case of dimesitylchromium, there is an increase in the strength of the mesityl–chromium $\sigma$ bond. Dimesitylchromium is a stable compound, which can be isolated in the pure state and which does not undergo rearrangement to the $\pi$ complex under any conditions[74]. This is due to steric hindrance to free rotation of the mesityl groups about the central chromium atom. Formation of $\pi$ complex sandwich compounds cannot take place in this case, since it would require the two mesityl groups to be coplanar. For dimesitylchromium, only one reaction remains possible — formation of the biaryl under more severe experimental conditions — and bimesityl is in fact obtained in quantitative yield on boiling a tetrahydrofuran solution of dimesitylchromium.

The tetrahydrofuran addition compound of triphenylchromium, obtained by the reaction of phenylmagnesium bromide with chromium(III) chloride, can also be converted into a sandwich compound by rearrangement with the inter-

mediate formation of a $\pi$-radical hybrid complex, similar to diphenylchromium. At the instant of decomposition, which takes place by a free-radical mechanism, formation of a highly active "radical metal", which may attack the arene with formation of a stable $\pi$ complex (IV) or (VI), is possible. The suggestion that a "radical metal" is formed in the reduction of a halide of a transition metal has been confirmed by new syntheses of diarene complexes[75]. Triethylaluminium has been used successfully as reducing agent for this purpose. The dimesitylene $\pi$ complex of chromium has been obtained from mesitylene, chromium(III) chloride, and triethylaluminium in n-heptane solution at room temperature. The same method has been used to prepare the bridged dibenzenechromium 1,1'-($\beta\gamma$-diphenyltetramethylene)dibenzenechromium iodide[76].

Alkyl derivatives of chromium have not yet been isolated in the pure state. Mention of these compounds is made in a description of the reaction of methyllithium with chromium(II) chloride, which leads to the formation of a black solution, apparently of dimethylchromium. The reaction with chromium(III) chloride gives a brown-red solution, evidently of trimethylchromium[14].

$\sigma$-Trialkyl derivatives of chromium are of particular interest in connection with their use for the catalytic cyclisation of disubstituted acetylenes[77]. Triethylchromium cyclises diphenylacetylene to hexaphenylbenzene with the simultaneous formation of tetraphenylbenzene. In the presence of trimethylchromium, tetraphenylcyclopentadiene is obtained from diphenylacetylene. Condensation of disubstituted acetylenes also takes place with aryl derivatives of chromium. The tetrahydrofuran addition compound of triphenylchromium gives hexamethylbenzene and 1,2,3,4-tetramethylnaphthalene from but-2-yne, depending on the experimental conditions[78]. The intermediate formation of a complex of triphenylchromium with three molecules of the alkyne $R_3Cr.(H_3CC{:}CCCH_3)_3$ was postulated. The condensation of acetylene with triphenylchromium or triethylchromium in tetrahydrofuran solution gives only hexamethylbenzene. Trimethylchromium reacts exothermally with but-2-yne to give 2-mesitylbut-2-ene in addition to hexamethylbenzene[79]. The exothermic reaction of triphenylchromium with dimethyl acetylenedicarboxylate in tetrahydrofuran solution at room temperature leads to the attachment of two phenyl groups with the formation of dimethyl diphenylmaleate.

The addition of aryl groups with formation of derivatives of styrene or stilbene, and also condensation with ring closure, are explained as follows. The intermediate complex of the organochromium compound with acetylene is formed by the gradual replacement of solvent molecules. The final reaction products depend on the number of acetylene molecules coordinated to the triarylchromium molecule. The monosubstituted complex gives styrene or stilbene, and the disubstituted complex gives polycyclic aromatic hydrocarbons (e.g. naphthalene derivatives) if the *ortho*-position of the aryl is available for ring closure. The trisubstituted complexes given benzene derivatives.

Another important factor influencing the mechanism of the process is the effect of electron-repelling groups on the delocalisation of the $\pi$ electrons of the alkynes. Thus in the presence of the electron-repelling [sic] methoxycarbonyl groups, the products of cyclic condensation are not obtained. The reaction of dimethyl acetylenedicarboxylate with triphenylchromium takes place with the addition of two aryl groups to the acetylene derivative.

Alkenes such as hexenes, isoprene, stilbene, and styrene do not react with triphenylchromium. If the alkene is able to form a complex with chromium derivatives, addition reactions are observed. These properties are shown by 2,2,1-bicyclic dienes, e.g. bicyclo[2,2,1]hepta-2,5-diene and conjugated alkenes (maleic anhydride). It has been shown that cyclisation of alkenes does not take place on phenylchromium complexes[80].

At the present time this field of study is developing rapidly, since by selecting suitable derivatives of the arylchromium and unsaturated compounds it is possible to extend the synthesis of a variety of condensed aromatic systems and other compounds.

Chromium derivatives obtained by reducing alkyl halides with chromium(II) perchlorate constitute a group apart. The reaction of benzyl chloride with an aqueous molar solution of chromium perchlorate in dilute perchloric acid gave a yellow-brown solution of the benzyl derivative of chromium $[Cr(CH_2C_6H_5)(H_2O)_5]^{2+}$. The solution oxidises in air with the formation of benzaldehyde. In the absence of air, 1,2-diphenylethane is formed, evidently by dimerisation of the benzyl radicals. The half-life at room temperature is about $1\frac{1}{2}$ days. A rapid reaction takes place with mercuric chloride with the formation of benzylmercury chloride and the chromium ion without change in the pH of the medium[81]:

$$[Cr(CH_2C_6H_5)(H_2O)_5]^{2+} + HgCl_2 + H_2O \longrightarrow C_6H_5HgCl + [Cr(H_2O)_6]^{3+} + Cl'.$$

Benzylpentaaquochromium(II) solutions are decomposed by sulphur dioxide but are stable towards carbon dioxide; reaction with hydrogen in the presence of palladium gives toluene.

Methyl chloride and methylene chloride are not reduced by chromium(II) perchlorate. Chloroform and carbon tetrachloride are very readily reduced under these conditions. In both cases the pale blue colour of bivalent chromium changes to red within a few minutes. Carbon tetrachloride reacts with chromium(II) perchlorate to form unstable solutions, which have not been more closely studied. It is suggested that the reduction of chloroform takes place according to the following mechanism

$$CHCl_3 + 2[Cr(H_2O)_6]^{2+} \rightarrow [CrCl(H_2O)_5]^{2+} + [Cr(CHCl_2)(H_2O)_5]^{2+} + 2H_2O,$$
$$CHCl_3 + Cr^{2+} + 5H_2O \rightarrow [CrCl(H_2O)_5]^{2+} + \dot{C}HCl_2,$$
$$\dot{C}HCl_2 + Cr^{2+} + 5H_2O \rightarrow [Cr(CHCl_2)(H_2O)_5]^{2+}.$$

The chloroform derivative was not isolated in the pure state. The bond between chromium and the $CHCl_2$ group is evidently similar to a covalent bond of weak polar character. Unlike the benzyl derivative, the chloroform derivative does not react with mercuric chloride, oxygen, or sulphur dioxide[82], but it is reduced by hydrogen in the presence of a palladium catalyst. No tetrachloroethane or dichloroethylene is formed on heating; instead, the chloride ion is liberated. No volatile organic compounds are obtained.

An increase in the strength of the transition metal $\sigma$ bond, particularly that between chromium and carbon, is observed when a $\pi$-cyclopentadienyl group is introduced into the molecule. This is clearly illustrated for the case of organochromium compounds. Mixed cyclopentadienyl-nitrosyl derivatives of chromium with alkyl and aryl groups attached by $\sigma$ bonds are known. These are obtained via the sodium derivative $\pi$-$C_5H_5Cr(NO)_2Na$ by reaction with alkyl or aryl halides:

$$\pi\text{-}C_5H_5Cr(NO)_2Na + RX \rightarrow \pi\text{-}C_5H_5Cr(NO)_2R.$$

This method was used to prepare methyl, ethyl, and cyclopentadienyl derivatives containing σ bonds, and also the compound with R = $CH_2Cl$.[83,84] These compounds are diamagnetic, coloured, crystalline, or oily (R = $C_2H_5$ or $C_6H_5$) substances which are readily soluble in organic solvents and can be sublimed in a high vacuum. They decompose slowly in air. The stability of the compounds decreases in the order $C_6H_5 > CH_3 > C_2H_5$.

### Molybdenum and Tungsten

Molybdenum and tungsten halides react with phenyllithium or Grignard reagents; in a number of cases, only the dimerisation product biphenyl could be isolated[3]. Compounds of the type $(C_6H_5)_2Mo(OH, X)$, $C_6H_5MoO_2OH$, $C_6H_5Mo_2O_4H_4$, $(C_6H_5)_3Mo_2O_7H_7$, and $(C_6H_5)_2Mo_3O_9H_4$ may, however, be formed as intermediate products[84]. Analogous tungsten derivatives were obtained from $WCl_6$ or $W(OC_6H_5)_6$ with phenyl compounds of lithium or magnesium[85]. The properties of these molybdenum and tungsten compounds resemble those of the phenyl derivatives of chromium, but the former are less stable, so that they could not be isolated in the pure state.

Mixed π-cyclopentadienyl-carbonyl compounds of molybdenum and tungsten, containing a σ bond between the metal and the radical, have recently been reported. In these derivatives, stabilisation of the metal–carbon bond is due to the influence of the π-cyclopentadienyl group. σ-Substituted π-cyclopentadienyl-tricarbonyl compounds of molybdenum and tungsten have been obtained from the hydrides by reaction with diazomethane:

$$\pi\text{-}C_5H_5Mo(CO)_3H + CH_2N_2 \rightarrow \pi\text{-}C_5H_5Mo(CO)_3CH_3 + N_2,$$

or by reaction of the sodium salt of the π-cyclopentadienyl-tricarbonyl compound of the metal with alkyl halides[26,86]:

$$\pi\text{-}C_5H_5M(CO)_3Na + RI \rightarrow \pi\text{-}C_5H_5M(CO)_3R + NaI,$$

where R = methyl, ethyl, or isopropyl for M = Mo, and R = methyl or ethyl for M = W.

These compounds were isolated in 75–85% yield. They are relatively stable yellow crystalline substances with melting points from 80° to 150°. The stability of the compounds in air decreases in the order methyl > ethyl > isopropyl. The methyl compound of tungsten is more stable than that of molybdenum. All the compounds are insoluble in water and are slowly decomposed by acids and bases. Halogens bring about quantitative rupture of the alkyl–metal bond according to the equation

$$\pi\text{-}C_5H_5Mo(CO)_3CH_3 + I_2 \rightarrow \pi\text{-}C_5H_5Mo(CO)_3I + CH_3I.$$

The compounds react neither with $FeCl_2$ in tetrahydrofuran solution nor with maleic anhydride in benzene. Data obtained by infrared, ultraviolet, and nuclear magnetic resonance spectroscopy have established that all these derivatives have a cyclopentadienyl–metal π bond and a metal–radical σ bond.

The reaction of tungsten pentabromide with an ethereal solution of phenyllithium in a current of pure nitrogen gave crystalline tungsten compounds to which the formula $(C_6H_5)_3W.3C_6H_5Li.3(C_2H_5)_2O$ was at first ascribed[87]. This compound is a black substance which is readily soluble in benzene and readily ignites in air. According to recent data[88], the composition corresponds to the formula $(C_6H_5)_4W.2C_6H_5Li.3(C_2H_5)_2O$.

## GROUP VII

### Manganese and Rhenium

The stoichiometric coupling of a phenylmagnesium halide in the presence of manganese(II) chloride in ethereal solution gives biphenyl in quantitative yield[73]. Catalytic coupling (Kharasch's reaction) in the $C_6H_5MgX + C_6H_5X +$ + 3–5 mole % $MnX_2$ system produces 21% of biphenyl. The action of manganese bromide on ethylmagnesium bromide in the ratio 1 : 2 at 25° gave 63% of ethane and 29% of ethylene[42]. It was suggested that unstable intermediate organomanganese derivatives are formed, and this was confirmed by subsequent work. The reactions of phenylmagnesium iodide with manganese iodide in the ratio 3 : 1 in ethereal solution takes place with the formation of brown precipitates consisting of a mixture of the phenyl derivatives of manganese $(C_6H_5)_2Mn$ and $C_6H_5MnI$, which are unstable in air[3].

The reaction of alkyl and aryl Grignard reagents (methyl-, ethyl-, and benzyl-magnesium bromides, etc.) with manganese halides gives brownish oily liquids which are insoluble in organic solvents and unstable in air, and react readily with iodine in tetrahydrofuran or chloroform solution. With benzylmagnesium bromide, 1,2-diphenylethane was obtained. In other cases also, the manganese compounds could not be isolated in the pure state[89]. Replacement of the organomagnesium compound by RLi made it possible to obtain individual products. The reaction of methyllithium with manganese iodide gave methylmanganese iodide in the form of a brown oil, insoluble in ether:

$$CH_3Li + MnI_2 \rightarrow CH_3MnI + LiI.$$

Reaction with another molecule of methyllithium gives colourless amorphous dimethylmanganese:

$$CH_3MnI + CH_3Li \rightarrow (CH_3)_2Mn + LiI.$$

Dimethylmanganese was obtained as a spontaneously inflammable yellow powder, exploding on impact. It is evidently polymeric. Diphenylmanganese, like the dimethyl derivative, is polymeric, but it can be crystallised from tetrahydrofuran.

Dimethylmanganese readily reacts with manganese iodide according to the scheme

$$(CH_3)_2Mn + MnI_2 \rightarrow 2CH_3MnI.$$

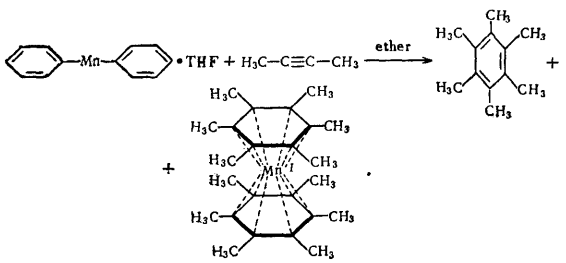
The reaction with excess of methyllithium gives the colourless amorphous complex $Li[Mn(CH_3)_3]$, insoluble in ether. This compound also reacts with $MnI_2$ to form dimethylmanganese and methylmanganese iodide:

$$(CH_3)_2Mn + CH_3Li \rightarrow Li[Mn(CH_3)_3],$$
$$Li[Mn(CH_3)_3] + MnI_2 \rightarrow (CH_3)_2Mn + CH_3MnI + LiI,$$
$$Li[Mn(CH_3)_3] + 2MnI_2 \rightarrow 3CH_3MnI + LiI.$$

Other complex products obtained were $Li[Mn(C_2H_5)_3]$ (a yellow amorphous powder, insoluble in ether), and also $Li[Mn(n\text{-}C_4H_9)_3]$, $Li[Mn(C_6H_5)_3]$, $Li[Mn(p\text{-}CH_3C_6H_4)_3]$, and $Li[Mn(p\text{-}CH_3OC_6H_4)_3]$.[89]

Diphenylmanganese can be obtained by the reaction of phenylmagnesium bromide with manganese chloride, or of phenyllithium with manganese iodide at -50° in tetrahydrofuran solution[90]. Dimethylmanganese forms a fairly stable pale yellow-green precipitate. Mesitylmagnesium bromide reacts with manganese chloride in the molar ratio 2 : 1 in

tetrahydrofuran solution to give a precipitate apparently consisting of dimesitylmanganese, but its structure has not been established. The substance is insoluble in organic solvents, very sensitive to the action of moisture and air, and does not react with alkynes, in particular but-2-yne. Diphenylmanganese similarly does not react with but-2-yne in tetrahydrofuran solution. When two volumes of diethyl ether are added to a tetrahydrofuran solution of diphenylmanganese, cyclic trimerisation of but-2-yne to hexamethylbenzene and the corresponding $\pi$ complex takes place:



$Mn^{II}$ is not as good an oxidising agent as $Cr^{III}$, so that the valency state of the manganese in this complex is unity, and this makes the complex isoelectronic with the zerovalent chromium complex[91]. The ability of phenylmanganese to coordinate solvent molecules is lower than that of the chromium compound[90]. Condensation with the formation of naphthalene derivatives is not observed. The fact that diphenylmanganese does not react with butyne in tetrahydrofuran solution is regarded as proof of the comparative stability of the phenyl–manganese bond. This is also illustrated by Tsutsui's data on the relative stabilities of the tetrahydrofuran addition compounds of diphenyl- and dimesityl-manganese[73]: the former decompose when the solvent is boiled, whereas the latter is quite stable at this temperature. This confirms Tsutsui's general hypothesis that the dimesityl derivatives of transition metals are generally more stable than the corresponding phenyl analogues.

Diphenyl- and dimethyl-manganese are decomposed by gaseous hydrogen. The solvent plays an important part in this process. In toluene, diphenylmanganese is unaffected when left to stand and agitated with hydrogen for 24 h, whereas in tetrahydrofuran at 20°, reaction begins rapidly with the formation of benzene and a black powder evidently consisting of the pyrophoric metal[27]. The quantity of hydrogen used corresponds to 0.85 mole per mole of substance; the reaction takes place according to the equation

$$(C_6H_5)_2Mn + H_2 \xrightarrow[20^\circ]{THF} Mn + 2C_6H_6.$$

The reduction of dimethylmanganese takes place in analogous fashion.

Stable organic derivatives of pentacarbonyl manganese, containing $\sigma$ bonds, are known. The donor carbonyl groups joined to the metal increase the strength of the $\sigma$ bond between manganese and substituents such as methyl, benzyl, and allyl, and also acetyl, benzoyl, and other acyls. The methyl derivative has been prepared by reaction of the sodium salt of pentacarbonyl manganese with dimethyl sulphate or methyl iodide[92]:

$$NaMn(CO)_5 + CH_3I \rightarrow CH_3Mn(CO)_5 + NaI.$$

Methylpentacarbonylmanganese forms colourless crystals which melt at 95°, are stable in air, and volatilise in a current of gas. The diamagnetic $CH_3Mn(CO)_5$ can be obtained by the action of diazomethane on the "carbonyl hydride"[94]:

$$HMn(CO)_5 + CH_2N_2 \rightarrow CH_3Mn(CO)_5 + N_2.$$

With carbon monoxide, methylpentacarbonylmanganese is converted into an acyl derivative, the process being reversible:

$$CH_3Mn(CO)_5 + CO \underset{t}{\overset{500\ atm,\ 20^\circ}{\rightleftharpoons}} CH_3COMn(CO)_5.$$

The acetyl derivative — a volatile white crystalline product of m.p. 54–55° — can be obtained in 51% yield by reaction of the sodium salt of pentacarbonyl manganese with acetyl chloride[92].

$\sigma$-Benzylpentacarbonylmanganese is prepared by a method analogous to that used for the methyl analogue. It is a pale yellow solid melting at 37.5–38.5°, stable to the action of air in the solid state, and less volatile in steam than the methyl derivative[92]. The phenyl-substituted product (m.p. 95–96°) has been obtained by the decarbonylation of benzoylpentacarbonylmanganese:

$$C_6H_5COMn(CO)_5 \rightarrow CO + C_6H_5Mn(CO)_5.$$

The presence of alkyl–manganese and acyl–manganese bonds is proved by the formation of the alkyl bromide or acyl bromide respectively on bromination[92].

$\sigma$-Allylpentacarbonylmanganese — an oily lemon yellow liquid which can be distilled *in vacuo* — has been obtained in 82% yield by the action of allyl chloride on the sodium salt of pentacarbonyl manganese in tetrahydrofuran solution[93]. It can be converted into $\pi$-allyltetracarbonylmanganese with the liberation of ~1 mole of carbon monoxide, by pyrolysis in a sealed tube at 80° for 12 h.

In Cotton's review[3] it is noted that methylmagnesium iodide in ether reacts vigorously with rhenium trichloride. After hydrolysis of the reaction mixture and removal of the solvent by distillation, fractionation at 60° gave trimethylrhenium in the form of a colourless oil, which burns with the formation of $Re_2O_7$. When this work was repeated, large quantities of methane and ethane were obtained[95] but no organorhenium compound was isolated. Like manganese, rhenium forms stable derivatives of the metal pentacarbonyl, containing an alkyl–metal $\sigma$ bond[96].

## GROUP VIII

### Iron

Covalent compounds of $Fe^{2+}$ and $Fe^{3+}$ have not been isolated in the pure state. Their possible formation in solution during the reaction of iron halides with organometallic compounds of lithium, magnesium, zinc, etc. has been reported[3]. This is indicated by change in colour of the reaction solutions, absorption of hydrogen and acetylene[97], and reduction of the iron. The organic radicals of the organometallic reactants dimerise or disproportionate in the process. Thus the reaction of methyllithium with $FeCl_2$ at ordinary temperatures gives 56% of methane and 24% of ethane[42].

The greatest number of attempts to prepare iron derivatives has been made with the alkyl and aryl organomagnesium compounds. Ethylmagnesium bromide reacts with $FeCl_2$ at 35° to give 49% of ethane and 40% of ethylene. Phenylmercury iodide in the presence of the halides of iron and other metals of Group VIII ($RuCl_3$, $OsCl_3$) undergoes

53–99% conversion into biphenyl[42]. The action of iron(III) chloride on phenylmagnesium bromide in the molar ratio 2 : 1 under ordinary conditions gives chlorobenzene in 40% yield[28].

Reduction of the metal during the synthesis, noted above, may indicate decomposition of intermediate unstable organometallic compounds of iron. In the reaction with phenylmagnesium bromide, the $Fe^{3+}$ is reduced to $Fe^{2+}$, and in a number of cases reduction to metallic iron takes place. Liberation of highly dispersed metal was observed when the temperature was raised above -40° in a reaction mixture having the composition $6C_6H_5MgBr + 2FeCl_3$.[98]

When the organomagnesium compound was replaced by $C_2H_5ZnI$, decomposition of the intermediate organoiron compounds did not take place. In this case the change in the ratio $Fe(OH)_2/Zn(OH)_2$ with time was studied by hydrolysed specimens of ethereal solutions of the reaction mixture $C_2H_5ZnI + FeI_2$. It was established that the ratio increased gradually and that after 6 h no ethylzinc iodide remained in solution. On hydrolysis of the final solutions, the quantity of ethane and $Fe(OH)_2$ corresponded to the formation of ethyliron iodide as intermediate product[99]:

$$2\,C_2H_5FeI + HI \xrightarrow{H_2O} 2C_2H_6 + Fe(OH)_2 + FeI_2.$$

This compound could not be isolated in the pure state.

Indirect indications of the possible formation of iron derivatives were obtained in the reaction of $FeCl_3$ or $FeCl_2$ with tetraethyllead, tetraethylsilicon, triphenylbismuth, etc.[101]. The reported formation of organoiron compounds by the reaction of pure iron with alkyl bromides is extremely doubtful[100].

Reports of the preparation of diaryl derivatives of iron by reaction of the corresponding mercury derivatives with iron powder at 120–125° [102] were found to be erroneous[103]. The tetrahydrofuran addition compounds of diphenyliron and dimesityliron are more stable, but these compounds are also decomposed at temperatures below -10°.[73]

The more stable mixed $\pi$-cyclopentadienyl compounds of the type $\pi$-$C_5H_5Fe(CO)_2R$, containing a $\sigma$ bond between the metal and the methyl, ethyl, phenyl, or cyclopentadienyl groups, have been isolated in the pure state[26,104]. The methyl derivative was obtained in 50% yield by the reaction of a methylmagnesium halide with a halogeno-$\pi$-cyclopentadienyldicarbonyl compound of iron in ethereal solution:

$$\pi\text{-}C_5H_5Fe(CO)_2I + CH_3MgI \rightarrow \pi\text{-}C_5H_5Fe(CO)_2CH_3 + MgI_2.$$

The yield of this compound is increased to 70% in the reaction of an alkyl halide with the sodium salt of the $\pi$-cyclopentadienyl derivative. When ethyl iodide is used, the ethyl derivative is formed in 60% yield. The yield of the phenyl analogue is only 2–5%.

The action of cyclopentadienylsodium on the bromide $\pi$-$C_5H_5Fe(CO)_2Br$ in tetrahydrofuran solution gave the compound $\pi$-$C_5H_5Fe(CO)_2$-$\sigma$-$C_5H_5$, in which the second cyclopentadienyl group is joined to the metal atom by a simple $\sigma$ bond.

These compounds are diamagnetic coloured products with definite melting points[26]. They are soluble in organic solvents, sublime readily in a high vacuum at 25–50°, and have characteristic odours. In solution, all the compounds are decomposed by air. The stability of the organoiron compounds decreases in the order phenyl > methyl > ethyl. These compounds are insoluble in water and do not react with it; they are decomposed by acids and bases. The action of acids gives the cation $[Fe(\pi\text{-}C_5H_5)(CO_2)]^{2+}$ (possibly hydrated), which yields characteristic Reinecke's salts. The action of iodine leads to quantitative formation of the iodide and the corresponding aryl or alkyl iodide. With the exception of the $\sigma$-cyclopentadienyl derivative, these compounds do not react with maleic anhydride. The reaction with the latter leads to a rapid change in colour, but the adduct obtained with maleic anhydride is unstable and cannot be isolated and identified.

## Cobalt

Coupling of $C_6H_5MgX$ takes place readily in the presence of added cobalt(II) chloride. The stoichiometric coupling of 0.03 mole of phenylmagnesium iodide with 0.01 mole of $CoCl_2$ gave 98% of biphenyl[42]. In the catalytic coupling, the yield of biphenyl is slightly lower and amounts to 86%.

The first papers on the preparation of organometallic compounds of cobalt of the type $RCoX_3$ and $R_2CoX_2$ appeared during 1949–1951. It was reported that the reaction of organomagnesium derivatives with cobalt bromide or iodide gave products with R representing methyl, ethyl, propyl, isopropyl, 1-naphthyl, and 2-naphthyl[105-107]. The compounds were obtained as coloured products decomposing at 65–160°. Some of their properties appeared to contradict the assumed formulae. For example, hydrolysis of a naphthyl derivative with water or dilute acids yielded chiefly binaphthyl. This gave the impression that the naphthyl groups were joined to one another in the same way as the phenyl groups in Hein's polyphenylchromium compounds. At the same time, doubt was cast on the possibility of formation of quadrivalent cobalt compounds under the conditions of the reducing medium in Grignard reactions[3].

The preparation of diallylcobalt, proposed as an additive to drying oils, has been reported in the patent literature[108,109], but there is no information on the methods of synthesis and the properties of this compound.

The formation of organometallic compounds of cobalt is indicated by the abnormal reactions of organomagnesium compounds in the presence of added cobalt salts. Kharasch and his coworkers have shown that the addition of 2–5 mole % of $CoCl_2$ to a Grignard reagent leads to a change in the mechanism of the reactions from ionic to free-radical[110-114]. An analogous but less marked effect is produced by iron(II) chloride and nickel(II) chloride. These results were attributed to the existence of intermediate unstable organocobalt compounds, which decompose with the formation of a cobalt subhalide; the latter brings about chain decomposition of the aryl or acyl halides:

$$RMgX + CoCl_2 \rightarrow RCoCl + MgXCl,$$

$$RCoCl \rightarrow R^{\cdot} + {}^{\cdot}CoCl,$$

$${}^{\cdot}CoCl + R'X \rightarrow R'^{\cdot} + CoXCl,$$

$$n\,R'^{\cdot} \rightarrow R'H + R'_2 + \text{other products.}$$

The conditions for the decomposition of RCoX may characterise the relative stability of the alkyl–cobalt and aryl–cobalt bonds. The reaction mixture of methylmagnesium bromide with added cobalt chloride loses its ability to bring about the dimerisation of phenyl radicals from bromobenzene after being heated for $1\frac{1}{2}$ h.[110] Coupling takes place quantitatively with a freshly prepared ethereal solution. Under the same conditions, phenylmagnesium bromide containing added $CoCl_2$, without preliminary heating, gives 98–99% of biphenyl from the phenyl radicals

of bromobenzene, but after heating for $1\frac{1}{2}$ h the yield of biphenyl amounts to only 50%. This indicates that the methyl–cobalt bond is less stable than the phenyl–cobalt bond. Contrary to Kharasch's opinion, however, the formation of symmetrical organocobalt compounds by the action of $CoCl_2$ on an organomagnesium compound is now considered more probable [115]:

$$2C_6H_5MgBr + CoCl_2 \rightarrow MgBr_2 + MgCl_2 + (C_6H_5)_2Co,$$

$$(C_6H_5)_2Co \rightarrow C_6H_6 + C_6H_4 + Co.$$

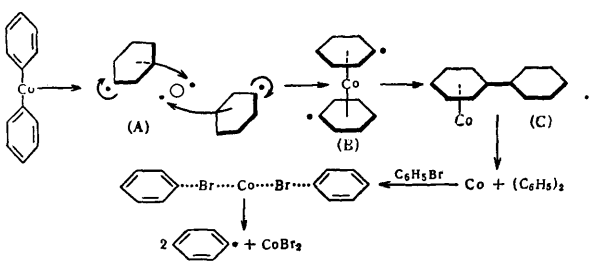
Decomposition of these compounds takes place with the separation of finely divided metallic cobalt, which brings about the chain reaction.

Proof of the existence of diaryls of cobalt is provided by the ability of phenylmagnesium bromide solutions containing $CoX_2$ to absorb hydrogen. The formation of benzene and cobalt hydride in the process is attributed to hydrogenation of the intermediate unstable diarylcobalt [97]:

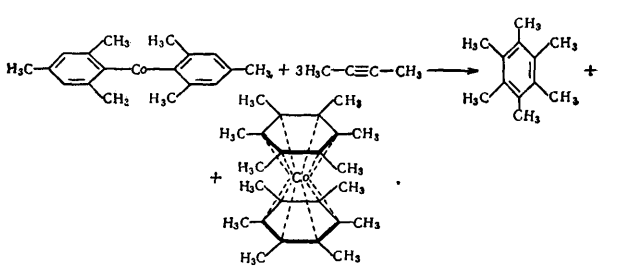
$$(C_6H_5)_2Co + 2H_2 \rightarrow CoH_2 + 2C_6H_6.$$

Finally, it has been possible to isolate diphenylcobalt and dimesitylcobalt in the form of the tetrahydrofuran addition compounds [74,90]. The dimesityl compound was obtained by the reaction of mesitylmagnesium bromide with cobalt chloride in tetrahydrofuran solution. The product is a yellow-green powder which is stable in the form of the tetrahydrofuran addition compound at -10° but which begins to decompose rapidly at room temperature. The presence of a mesityl–cobalt bond was proved by the quantitative formation of mesitylmercury chloride on reaction with mercuric chloride [90].

Tsutsui describes the conversion of the diarylcobalt compounds into the $\pi$ complexes. The unstable diphenylcobalt formed initially undergoes gradual rearrangement with rotation of the aromatic rings via the $\pi$-radical hybrid (A) and the diradical $\pi$ complex (B) to the half-sandwich $\pi$ complex (C): [73]




Dimesitylcobalt catalyses the cyclic condensation of but-2-yne. The reaction takes place between -30° and -50° in tetrahydrofuran solution, with the formation of hexamethylbenzene (the yield varies in the range 50–100%, calculated on the organocobalt compound) and the $\pi$ complex bishexamethylbenzenecobalt, the yield of which (20%) is independent of the alkyne concentration [91]:




The exceptional catalytic properties of dimesitylcobalt in this reaction are due to the unusual electronic structure of the $\pi$ complex.

The organocobalt compounds confirm the general hypothesis that the complexes of organic derivatives of the transition metals are more stable than the diaryls. Stabilisation of the aryl–cobalt bond is observed in the complexes of a diarylcobalt with phosphines [116]. The *trans*-planar complexes of dimesitylcobalt and bismethylnaphthylcobalt with phenyldiethylphosphine $[C_6H_5P(C_2H_5)_2]_2CoR_2$ have a very small or no dipole moment, in conformity with their structure.

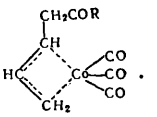
A methyl–cobalt bond is present in the mixed carbonyl of cobalt obtained by reaction of the sodium salt of the carbonyl with methyl iodide [117]:

$$Na[Co(CO)_4] + CH_3I \rightarrow CH_3Co(CO)_4 + NaI.$$

A number of interesting reactions of this unstable product have been described. Methyltetracarbonylcobalt readily undergoes rearrangement to acetyltricarbonylcobalt, and treatment of the latter with carbon monoxide leads to the formation of the acyltetracarbonylcobalt:

$$RCo(CO)_4 \rightleftarrows RCOCo(CO)_3 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} RCOCo(CO)_4.$$

Alkyl- and acyl-tetracarbonylcobalts react with conjugated dienes — butadiene, isoprene, cyclopentadiene, etc. — to form complexes of the type [118]




The same type of complex, with a bond between cobalt and the alkene, like that in the alkene complexes of platinum [119], has been obtained by reaction of the potassium salt of cobalt carbonyl with butadiene [120]. Study of the proton resonance, infrared, and ultraviolet spectra indicate that the compound is diamagnetic and contains no conjugated diene.

## Nickel

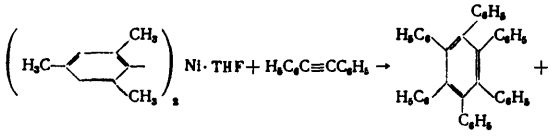
A great deal of indirect data indicates that the simplest organonickel compounds exist in solution, but these have not been isolated in the pure state [121–123]. The most noteworthy reaction is the coupling of phenyl Grignard reagents, which takes place readily in the presence of nickel salts. With aliphatic organomagnesium compounds, liberation of ethylene, acetylene, etc. is observed. In the presence of gaseous hydrogen, a freshly prepared reaction suspension of phenylmagnesium bromide in ether containing added $NiCl_2$ absorbs 2 moles of hydrogen per gramme-atom of nickel to give pyrophoric black nickel hydride [124]. It was suggested that the latter was produced by reduction of the hypothetical diphenylnickel formed in the initial stage:

$$NiCl_2 + 2C_6H_5MgBr \rightarrow (C_6H_5)_2Ni + MgCl_2 + MgBr_2,$$
$$(C_6H_5)_2Ni + H_2 \rightarrow 2C_6H_6 + NiH_2.$$

The instability of diphenylnickel is indicated by the following facts. If the reaction suspension containing $NiCl_2$ is kept for some time before the reaction of hydrogen, the yield of hydride is decreased considerably. After standing for 4 h at room temperature the system does not absorb hydrogen; no nickel hydride was found in the reaction products.

The formation of phenyl and mesityl compounds of nickel is indicated by the deep colour produced by the action of nickel chloride on the corresponding organomagnesium compound in tetrahydrofuran solution. The reddish brown colour is attributed to the tetrahydrofuran addition compounds of diphenylnickel and dimesitylnickel. Thus reaction of 0.01 mole of $NiCl_2$ in 50 ml of tetrahydrofuran with 0.02 mole of RMgBr between -30° and -70° gives tetrahydrofuran addition compounds which cannot be isolated in the pure state because of their low thermal stability. They begin to decompose at temperatures below -10°.[73]

The thermally unstable tetrahydrofuran addition compounds of $R_2Ni$ are used in solution for the characteristic reactions involving cyclisation of disubstituted alkynes. Diethylnickel converts diphenylacetylene into tetraphenylcyclohexadiene[125]. Reaction of diphenylacetylene with the tetrahydrofuran addition compound of dimesitylnickel gives hexaphenylbenzene and a nickel-containing polymer. At an original component ratio of 1 : 4 the chief reaction product is the polymer, which is precipitated from solution as a dark orange, insoluble, amorphous precipitate:



$$+ [(H_5C_6C{\equiv}CC_6H_5)_4Ni]_n.$$

With increase in the ratio from 1 : 4 to 1 : 6, the chief reaction product becomes hexaphenylbenzene, which can be isolated in yields corresponding to 1.7–2.0 moles per mole of the organonickel compound[74,91]. Cyclisation of this type is attributed to the formation of an intermediate cyclobutadiene compound.

The complexes of $R_2Ni$ with triethyl- or triphenyl-phosphines $(R'_3P)_2NiR_2$ and $(R'_3P)_2Ni(R)X$ are more stable. These compounds can be obtained by the reaction of the corresponding dihalide with an organomagnesium compound in liquid ammonia[116]. They are brightly coloured products, usually yellow-brown, with characteristic melting points. The derivatives with R = phenyl, *o*-tolyl, *o*-chloro- and *o*-bromo-phenyl, *o*-methoxyphenyl, mesityl, biphenylyl, pentachlorophenyl, and naphthyl, and R′ = phenyl, ethyl, propyl, and mixtures of these, have been isolated.

The thermal stability of these complexes depends to a marked extent on the nature of the radical from the organomagnesium compound, increasing in the order alkyl < phenyl < *m*- and *p*-substituted phenyl < *o*-substituted phenyl[126]. The alkyl complexes are less stable and have not been isolated in the pure state. The phenyl derivative decomposes rapidly in ethanol solution and melts with decomposition at 125–130°. The symmetrical mesityl compound melts at 148–150°, and the unsymmetrical compound sublimes *in vacuo* without decomposition at 150°.

The influence of *ortho*-substituents is due to steric hindrance to free rotation of the aryl groups about the nickel–carbon bond. The electronic systems of the aromatic rings undergo more energetic interaction with the *d* orbitals of the metal.

These compounds are diamagnetic and symmetrical, and have a low dipole moment. With the symmetrical and unsymmetrical derivatives, *trans*-planar arrangement of the groups relative to the nickel atom is observed. The chemical reactions indicate the mobility of the metal–radical bond, which is readily broken by hydrogen chloride with formation of a hydrocarbon and an unsymmetrical product:

$$trans\text{-}[(R'_3P)_2NiR_2] + HCl \rightarrow trans\text{-}[(R'_3P)_2Ni(R)Cl] + RH.$$

In the unsymmetrical derivatives, the chlorine atom is readily replaced by bromine or iodine atoms or nitro- or thiocyanato-groups[126].

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The above review shows that organic compounds of metals of the transition periods, containing a covalent metal–carbon bond, form a special class of compounds. Unlike the organometallic compounds of non-transition elements, which exhibit different characteristic chemical properties according to the groups of the Periodic System, the alkyls and aryls of the transition metals show a number of common chemical properties. Thus, for example, the covalent metal–carbon bond is readily broken by the action of hydroxyl-containing compounds, such as water, alcohols, acids, etc. The reaction of alkyls and aryls of the transition metals with halogens and halides is characteristic. These reactions are often used as analytical tests to prove the presence of an element–radical σ bond. Another typical property of most of these derivatives is their ready oxidation by oxygen and other oxidising agents.

The most characteristic property of these compounds — their thermal instability — is due to the presence of the incomplete electron sublevel of the central transition metal atom. The general characteristics of the electronic structure of the transition elements and the associated types of hybridisation involved in the formation of σ bonds have been examined more than once by Krause and von Grosse[1], Zeiss[4], Jaffé[127], and other workers.

The presence of vacant *d* sublevels in the transition metal atom makes possible the filling of these levels by various electron-donating ligands, such as amines, phosphines, ethers, and also carbonyl, nitrosyl, π-cyclopentadienyl, etc. These mixed sandwiches, carbonyls, or complexes with phosphines and other ligands are generally more stable to heat and also to oxidation and the action of other agents.

These compounds are of considerable interest in the study of the nature of the chemical bond. The intensified development of this field, however, is due not only to the theoretical importance of the subject but also to its considerable value in applied chemistry.

This review has not dealt with the exceptionally important problems associated with the use of catalytic systems based on organometallic derivatives of the transition metals. The mechanism of the stereoregular polymerisation of alk-1-enes depends to a marked extent on the properties of the intermediate covalent compounds of titanium, vanadium, and other transition metals[28,128,129]. Brief mention has been made of the interesting processes involving the cyclisation of disubstituted acetylenes with the participation of compounds of chromium, nickel, cobalt, etc.[77,78,91,130].

This young and rapidly developing field of chemistry dealing with the organometallic compounds of the transition metals promises to provide much of both theoretical and practical interest in the future.

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# ADDITION OF α-CHLOROALKYL ETHERS TO UNSATURATED COMPOUNDS

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## 1. INTRODUCTION

In his review of the addition of alkyl halides to olefins Arbuzov[1] dealt in some detail with the El'tekov[2] and Kondakov[3,4] reaction, and Summers[5] reviewed the preparation and reactions of α-chloro-ethers, covering the literature up to 1955; however, in neither review did the addition of α-chloro-ethers to unsaturated compounds receive much attention. Nevertheless, in recent years much interesting work on the electrophilic addition of chloro-ethers to multiple bonds has appeared. In the present paper we have attempted to collect and classify the considerable material which has now accumulated on this subject.

## 2. ADDITION OF α-CHLOROALKYL ETHERS TO OLEFINS

α-Chloroalkyl ethers are much more reactive than alkyl halides, and they behave analogously to hydrogen halides. Cocker et al.[6] associate the activity of the labile chlorine atom in α-chloro-ethers with the simultaneous existence of a carbonium ion and an oxonium ion:

$$R-\overset{+}{C}H-\ddot{O}-R' \longleftrightarrow R-CH=\overset{+}{\ddot{O}}-R'.$$

Chloromethyl ether undergoes rapid hydrolysis and alcoholysis in aqueous and alcoholic solutions, yielding formaldehyde and a dialkoxymethane respectively. The rapidity of such processes has led many workers to conclude that the reactions are unimolecular, and this has been confirmed kinetically[7]. The rate-determining step is ionisation of the chloro-ether to produce a mesomeric carbonium ion, which rapidly adds on a hydroxide or alkoxide ion from the solvent:

$$CH_3-\ddot{O}-CH_2-Cl \xrightarrow[\text{slow}]{} CH_3-O-\overset{+}{C}H_2 + Cl^-,$$

$$ROH + CH_3O-\overset{+}{C}H_2 \xrightarrow[\text{fast}]{} CH_3OCH_2OR + H^+$$

(R = H or alkyl).

At room temperature in anhydrous solvents (or in the absence of a solvent), α-chloroalkyl ethers add to olefins in the presence of acidic catalysts by an ionic mechanism

in almost every case[8]. Various catalysts may be used, e.g. bismuth trichloride[9,10], mercuric chloride[11], or, most frequently, zinc chloride[9,11].

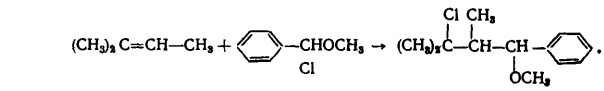
Scott in 1935 was the first to show[12] that chloromethyl ethers add to propene in the presence of bismuth trichloride to form 3-chloro-1-methoxybutane; the addition follows the Markovnikov rule:

$$CH_3{-}CH{=}CH_2 + CH_3OCH_2Cl \xrightarrow{BiCl_3} CH_3CHCl{-}CH_2CH_2OCH_3.$$

Straus and Thiel[11] investigated the addition of chloromethyl ethers to isobutene in the presence of mercuric chloride, and obtained the corresponding chloro-ethers (I):

$$(CH_3)_2C{=}CH_2 + ROCH_2Cl \xrightarrow{HgCl_2} (CH_3)_2CCl{-}CH_2CH_2OR. \qquad (I)$$

They also found that the $\alpha$-chlorobenzyl ether can add to olefins under these conditions[11]:

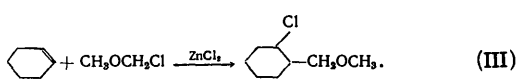


Mamedov, Zeinalov, and Pishnamez-zade[13-15] developed a simple method for the preparation of $\gamma$-halogeno-ethers (II) by addition of various chloro- or bromo-methyl ethers to olefins in the presence of zinc chloride:

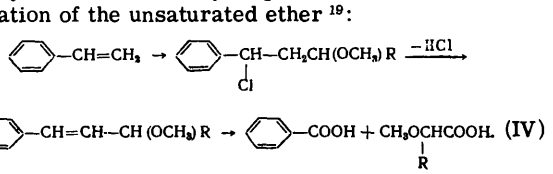
$$R{-}CH{=}CH{-}R' + R''OCH_2X \rightarrow \underset{X}{\overset{}{R}}CH{-}\underset{R'}{\overset{}{C}}H{-}CH_2OR''. \qquad (II)$$

The product yield is lower with ethylene than with its homologues. Certain of the resulting $\gamma$-halogeno-ethers possess acaricidal and insecticidal properties[16].

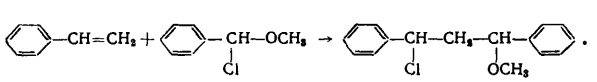
Chloromethyl ethers also add to cycloalkenes in the presence of zinc chloride. Straus[11] and Nenitzescu[17] obtained 1-chloro-2-methoxymethylcyclohexane (III) from cyclohexene and chloromethyl ether:



$\alpha$-Chloroalkyl ethers add to styrene to form the corresponding chloro-ether[18,19]; the structure of the product (IV) is proved by the removal of hydrogen chloride and subsequent oxidation of the unsaturated ether[19]:



$\alpha$-Chlorobenzyl ether also adds to styrene[11]:



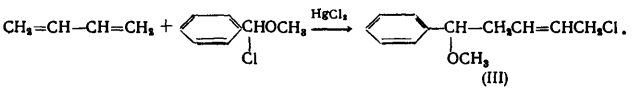
## 3. ADDITION OF $\alpha$-CHLOROALKYL ETHERS TO CONJUGATED DIOLEFINS

The addition of chloromethyl ethers to butadiene was accomplished in 1935–1936 by Scott[12] and Straus[11] in the presence of mercuric chloride or zinc chloride, giving a mixture of two isomeric chlorides, the 1,2-addition product 3-chloro-5-methoxypent-1-ene (I) and the 1,4-addition product 1-chloro-5-methoxypent-2-ene (II):

$$CH_2{=}CH{-}CH{=}CH_2 + CH_3OCH_2Cl \xrightarrow{ZnCl_2} \underset{(I)}{CH_3OCH_2CH_2CHCl{-}CH{=}CH_2} + \underset{(II)}{CH_3OCH_2CH_2CH{=}CHCH_2Cl}.$$

When distilled under normal conditions the 1,2-addition product isomerised completely into the 1,4-addition product.

In the reaction of $\alpha$-chlorobenzyl methyl ether with butadiene the only product is that of 1,4-addition (III):[11]



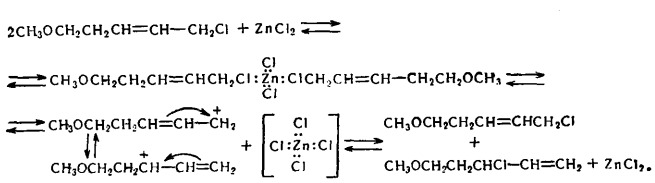
Pudovik, Arbuzov, and coworkers[20,21] investigated the addition of chloromethyl ethers to butadiene in some detail, and studied the resulting alkoxyalkyl chlorides; similar results were also obtained by other workers[22]. The total yield is 75%, comprising 75–80% of 1,2-addition product and 25–20% of 1,4-addition product. Under the influence of the zinc chloride catalyst there is mutual isomerisation of the alkoxyalkyl chlorides, so that a mixture is obtained containing 55% of the 1,4-addition product and 45% of the 1,2-addition product:

$$ROCH_2CH_2CH_2CHCl{-}CH{=}CH_2 \xrightarrow{ZnCl_2} ROCH_2CH_2CH{=}CHCH_2Cl.$$

In the absence of catalyst, both isomers remain unchanged for at least one year: i.e. they do not isomerise[20].

The action of 10% zinc chloride causes 90–93% isomerisation of the 1,2-addition product to the 1,4-addition product, the reverse process occurring only to the extent of 4–7%.[20] Pudovik and Arbuzov also show that in the absence of catalysts the alkoxyalkyl chlorides do not isomerise at 100°, while at 140° the 1,2-addition product is quantitatively isomerised into the 1,4-addition product.

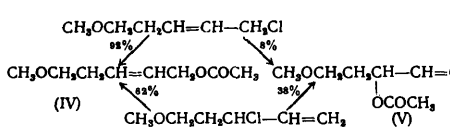
In the presence of zinc chloride the mutual isomerisation of the two isomeric chlorides is represented as follows[20]:



Meisenheimer and Schmidt[23] show that the allylic rearrangement can also occur under the influence of various chance factors (composition of the glass, contamination).

From the above, it may be said that chloromethyl ethers add to butadiene almost exclusively in the 1,2-position, but since the 1,2-addition products are very readily isomerised into the 1,4-addition products under the experimental conditions, the 1,4-isomer predominates in the final reaction product.

Allylic rearrangements occur not only with the products of the addition of chloromethyl ethers to butadiene, but also in the preparation of their derivatives. For example, with sodium acetate 1-chloro-5-methoxypent-2-ene gives the normal substitution product (IV) in 92% yield and the isomeric product (V) in 8% yield, while 3-chloro-5-methoxypent-1-ene gives 62% of the isomeric product (IV) and only 38% of the normal product (V):[24]

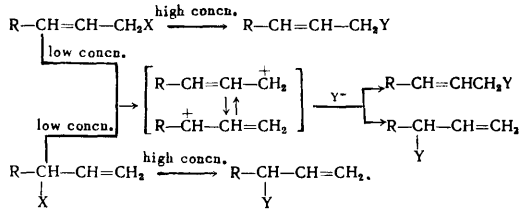


Both isomeric chlorides react analogously with sodiomalonic ester[25], phenylmagnesium bromide[26], and ammonium thiocyanate[22], but with alcohols in the presence of potassium hydroxide 1-chloro-5-methoxypent-2-ene gives the corresponding normal product, a 1,5-dialkoxypent-2-ene, in almost quantitative yield[8].

There have been many examples of the production of two isomers, depending on the reaction conditions, in the nucleophilic substitution of the chlorine in allyl chlorides, and various explanations for this have been proposed[27-33]. Prevost[30] considers it to be the result of ionisation of the rearranging molecule to produce the corresponding carbonium ion:

$$R{-}CH{=}CH{-}CH_2Cl \rightarrow R{-}\overset{+\delta}{C}H{-}CH{-}\overset{+\delta}{C}H_2.$$

It has been shown that nucleophilic substitution in allenic systems can take place by either a unimolecular or a bimolecular mechanism[34]: if the attacking reagent is added in small portions, the reaction proceeds by a unimolecular mechanism, either of the isomeric chlorides producing a mixture of the isomeric products corresponding to the two isomeric carbonium ions; while if the attacking reagent is added in high concentrations, it is mainly the normal reaction products which are formed:

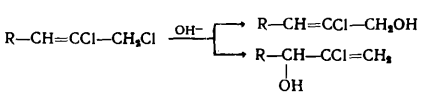


However, allylic systems do exist where no rearrangement occurs. For example, no isomeric products are obtained when the primary chlorine atom of 5-alkoxy-1,3-dichloroalk-2-enes (VI) is hydrolysed to give the corresponding alcohols or react to produce ethers, amines, etc.[35,36]:

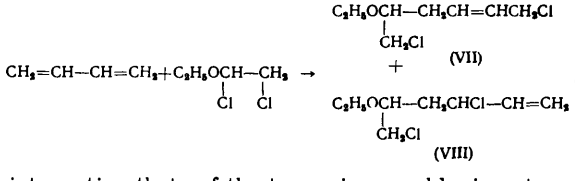
$$ROCH_2CH_2CCl{=}CH{-}CH_2Cl \xrightarrow{Y^-} ROCH_2CH_2CCl{=}CHCH_2Y.$$
(VI)

Y=OH, N<; OR'

Some allylic rearrangement occurs in the hydrolysis of 1,2-dichloroalk-2-enes, the isomeric chloro-alcohols being obtained in addition to the normal products[37]:

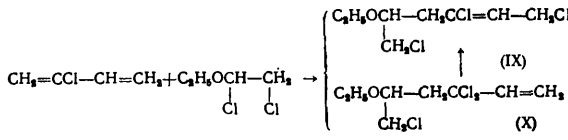


Pudovik[38] was the first to treat 1,2-dichlorodiethyl ether with butadiene in the presence of zinc chloride, obtaining 74% of the 1,4-addition product (VII) and 26% of the 1,2-addition product (VIII):



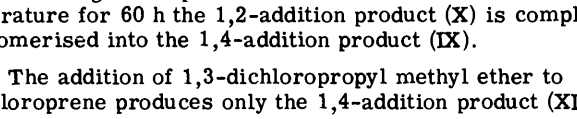
It is interesting that, of the two primary chlorine atoms in the 1,4-addition product (VII), only the $\alpha$-chlorine atom can react further, the $\gamma$-chlorine atom being unreactive[38].

In the presence of zinc chloride 1,2-dichlorodiethyl ether also adds to chloroprene by 1,4- and 1,2-addition, forming 1,3,6-trichloro-5-ethoxyhex-2-ene (IX) and 3,3,6-trichloro-5-ethoxyhex-1-ene (X):[39]

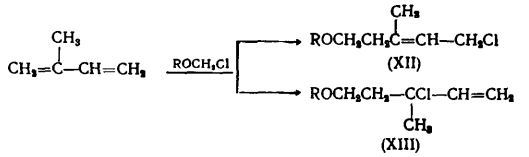


On standing in the presence of zinc chloride at room temperature for 60 h the 1,2-addition product (X) is completely isomerised into the 1,4-addition product (IX).

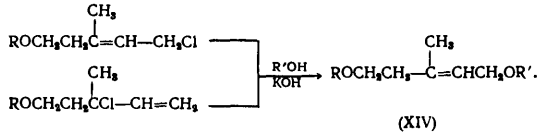
The addition of 1,3-dichloropropyl methyl ether to chloroprene produces only the 1,4-addition product (XI):[40]



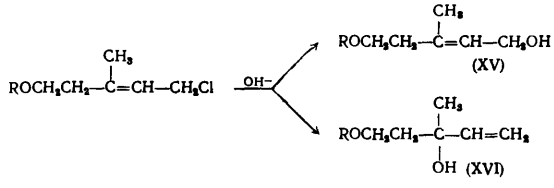
Chloromethyl ethers add to isoprene analogously to the above reactions, but the yield does not exceed 30–37%, and in the reaction products (XII) and (XIII) the 1,4-addition product (XII) predominates[41]. The mutual isomerisation of these two isomers is very rapid[41], and the equilibrium concentration of the 1,4-addition product (XII) is 90–92%



In the presence of potassium hydroxide the two isomers give the same product (XIV) with alcohols[41]:



Hydrolysis of 5-alkoxy-1-chloro-3-methylpent-2-enes (XII) with 15% aqueous potassium carbonate gives the two isomeric alkoxy-alcohols (XV) and (XVI):[42]



The addition of chloromethyl ethers to chloroprene in the presence of zinc chloride has been studied in some detail; the only product is that of 1,4-addition, the 5-alkoxy-1,3-dichloropent-2-ene (XVII):[35,43]:

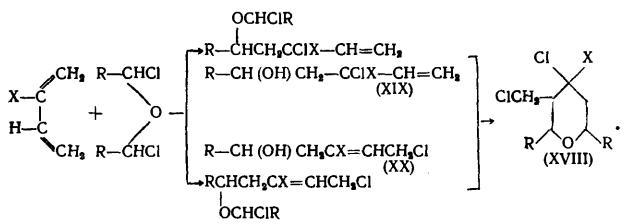
$$CH_2{=}CCl{-}CH{=}CH_2{+}ROCH_2Cl \xrightarrow{ZnCl_2} ROCH_2CH_2CCl{=}CHCH_2Cl.$$
(XVII)

These dichlorides are very reactive, and the primary chlorine atom takes part in all the reactions typical of alkyl halides[44-48].

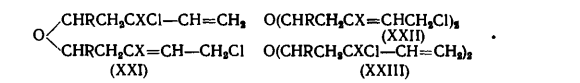
$\alpha$-Chloroalkyl ethers add to isoprene, chloroprene, and butadiene in the presence of zinc chloride in an analogous manner[40,49]:

$$CH_2{=}\underset{X}{C}{-}CH{=}CH_2{+}ROCHCl \rightarrow ROCH\underset{R'}{C}H_2C{=}CH\underset{R'}{C}H_2Cl.$$
(X=H; $CH_3$; Cl)

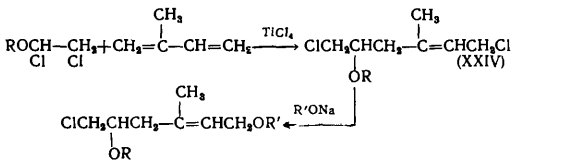
The addition of bis-$\alpha$-chloroalkyl ethers to chloroprene and isoprene in the presence of zinc chloride produces mainly the tetrahydropyran derivatives (XVIII):[50]



There are also obtained small amounts of chloro-alcohols (XIX) and (XX) produced by hydrolysis of the intermediate ethers, and products of the addition of the bis-$\alpha$-chloroalkyl ethers to two molecules of the diene (XXI)–(XXIII):[54]

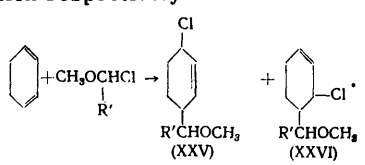


In the production of the vitamin A side-chain, a 1,2-dichloroethyl ether was added to isoprene in the presence of titanium chloride, to give the 1,4-addition product (XXIV),[51] only one primary chlorine atom of which undergoes further reaction:

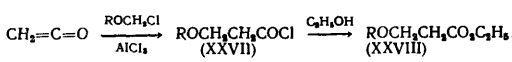


(R′ = $CH_3CO$ or Alk).

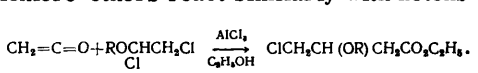
Chloromethyl ethers add analogously to cyclic conjugated dienes, e.g. cyclohexadiene, giving the two isomeric chlorides (XXV) and (XXVI), which are the products of 1,4- and 1,2-addition respectively [11]:



Chloromethyl ethers add to ketens in the presence of aluminium chloride. However, the expected alkoxylated acid chlorides (XXVII) have not been isolated, but have been treated with alcohol to give ethyl $\beta$-alkoxypropionates (XXVIII):[52]

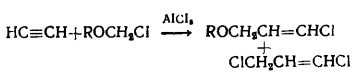


$\alpha\beta$-Dichloro-ethers react similarly with ketens [53]:



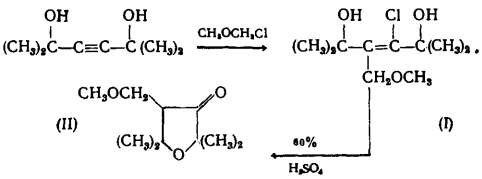
## 4. ADDITION OF $\alpha$-CHLOROALKYL ETHERS TO ACETYLENIC, VINYLACETYLENIC, AND DIVINYLACETYLENIC SYSTEMS

Chloromethyl ethers add to acetylene in the presence of aluminium chloride to give mainly 3-alkoxy-1-chloroprop--1-ene but with some 1,3-dichloroprop-1-ene [54]:



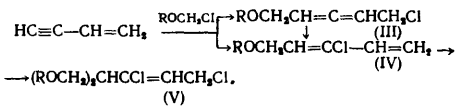
Phenoxymethyl chloride does not add to acetylene under these conditions [54].

Chloromethyl ethers add to the triple bond of tetramethylbutynediol in the presence of aluminium, tin, or zinc chloride to produce the corresponding chlorovinyl glycol (I), which when treated with 60% sulphuric acid forms tetrahydro-4-methoxymethyl-2,2,5,5-tetramethyl--3-oxofuran (II):[55]



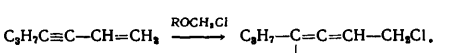
The addition of chloromethyl ethers to butyne-1,4-diols and their mono- and di-ethers proceeds analogously [55].

The addition of chloromethyl ethers to vinylacetylenic compounds has also been investigated. Dykstra [10] was the first to show that in the presence of bismuth trichloride they add to butenyne itself in the 1- and 4-positions. The product (III) can isomerise under the experimental conditions, or in the presence of cuprous chloride in 18% hydrochloric acid, and the resulting alkoxy-chloride (IV) can add a further molecule of chloromethyl ether under the given conditions, to form the dichloride (V):[56]

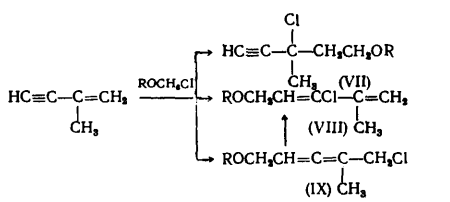


Zinc chloride produces the same reactions [56,57]. Dykstra prepared these chlorides in order to investigate their polymerisation, but the polymers obtained were not considered to be of good quality.

Under the conditions given above, chloromethyl ethers add to hept-1-en-3-yne to produce only the 1,4-addition product (VI), the isomeric chloride not being obtained. The product (VI) does not isomerise either under the experimental conditions or under the influence of cuprous chloride in 18% or 36% hydrochloric acid [56]:

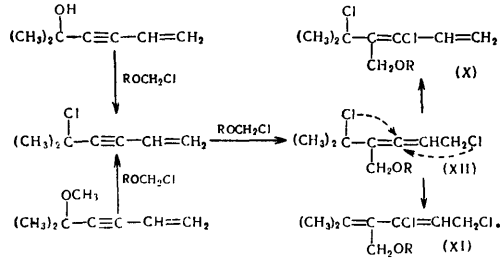


With 2-methylbut-1-en-3-yne, however, addition under the above conditions produces the three difficultly separable alkoxy-chlorides (VII)–(IX):[58]



The addition of chloromethyl ethers to 2-methylhex-5--en-3-yn-2-ol, to its methyl ether [59], or to 5-chloro-5--methylhex-1-en-3-yne [60] produces, in all cases, the same mixture of the two isomeric dichlorides (X) and (XI). Apparently the alkoxy- or hydroxy-group is first replaced by chlorine from the chloromethyl ether to give the corresponding chloro-compound, and the latter then undergoes

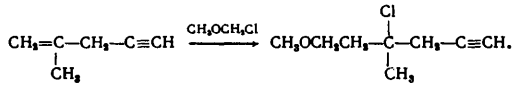
1,4-addition to the chloromethyl ether (as it does to hydrogen chloride[61]) to form the intermediate allenic dichloride (XII), which under the experimental conditions isomerises to produce a mixture of the two dichlorides (X) and (XI):



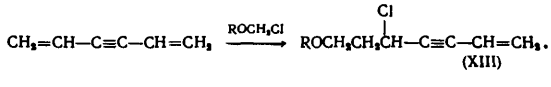
Unlike the ethers of dimethyl(vinylethynyl)carbinol [2-methylhex-5-en-3-yn-2-ol], those of primary and secondary vinylethynylcarbinols add chloromethyl ethers normally, i.e. by 1,4-addition, producing an allenic chloride which is not isomerised under the experimental conditions or under the influence of cuprous chloride in 18% or 36% hydrochloric acid[59]:



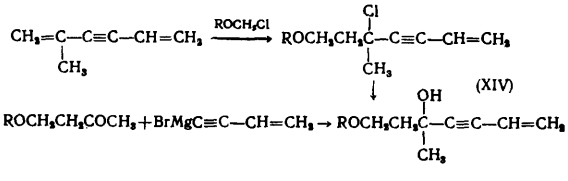
The addition of chloromethyl ethers to allylacetylenes [pent-1-en-4-ynes] has not been investigated; there is only one patent, describing the addition to 2-methylpent-1-en-4-yne, which takes place at the double bond according to Markovnikov's rule[62]:



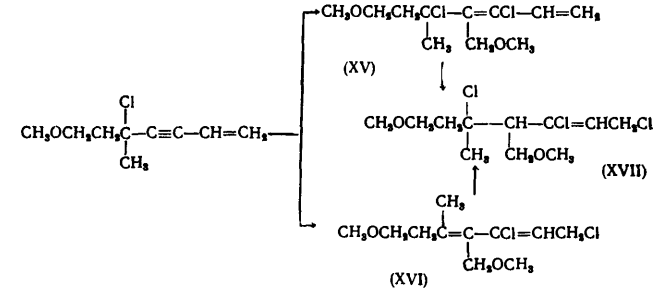
In the presence of zinc chloride chloromethyl ethers add to hexa-1,5-dien-3-yne in the 1,2-position to form a 7-alkoxy-5-chlorohept-1-en-3-yne (XIII):[63]



The addition of chloromethyl ethers to homologues of hexa-1,5-dien-3-yne, e.g. the 2-methylhexadienyne, is a selective process occurring at the double bond which is richer in electrons: i.e. it takes place by an electrophilic mechanism[64]. Hydrolysis of the resulting vinylacetylenic alkoxy-chloride (XIV) gives the corresponding vinylacetylenic carbinol, which has also been prepared by condensation of the appropriate 2-alkoxyethyl methyl ketone with but-3-en-1-ynyl bromide[65]:



A second molecule of the chloromethyl ether adds to the alkoxy-chloride (XIV) to give a mixture of the two isomeric dichlorides (XV) and (XVI), which with hydrogen chloride in the presence of cuprous chloride produce the same trichloride (XVII):



Certain derivatives of the two dichlorides (XV) and (XVI) have also been obtained[64].

The addition of α-halogeno-ethers to unsaturated compounds opens up great possibilities for the production of new halogen compounds of various types of structure. The ease and simplicity of production of these chlorides allow them to be used as starting materials for the preparation of new insecticides and fungicides, high-boiling solvents, plasticisers, etc. Certain of the α-chloro-ethers and new products obtained from them have already found practical application as insecticides[16,66], water-repellent agents in the textile industry[67,68], and for the treatment of wool to render it stable to washing[69,70].


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# THE DEVELOPMENT OF CATALYTIC SYNTHESES OF ORGANIC COMPOUNDS FROM CARBON MONOXIDE AND HYDROGEN

B. K. Nefedov and Ya. T. Eidus

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## INTRODUCTION

The catalytic synthesis of hydrocarbons and oxygen-containing compounds from carbon monoxide and hydrogen, particularly on an industrial and semi-industrial scale (Fischer–Tropsch hydrocarbon synthesis, synthesis of alcohols), is of great practical and theoretical interest[1-7]. The most recent reviews in this field were published by one of us in 1950–1951.[1,2] In the present review the main

advances during the past decade in the development of syntheses based on the catalytic reduction of carbon monoxide are considered†.

## I. FISCHER–TROPSCH SYNTHESIS OF HYDROCARBONS

The object of the synthesis of hydrocarbons from carbon monoxide and hydrogen, discovered in Germany in 1925 and adopted there industrially at the end of the 1930's, was to obtain liquid fuel[5,8,9]. Between 1936 and 1942 more than fifteen plants were set up in different countries (Germany, Japan, France) in which cobalt catalysts were used, mainly at atmospheric pressure[10]. In the post-war years intensive study of the process continued in the United States, Great Britain, West Germany, Japan, and India and also in the Soviet Union, Poland, East Germany, and China. A number of new plants were constructed, for example in South Africa and the United States, in which valuable chemical products (compressed gas, alcohols, solvents, paraffin wax) were obtained, in addition to liquid fuel, at moderate pressures in the presence of cobalt and iron catalysts[11–16]. At the same time new methods of obtaining cheap starting materials and highly productive and stable catalysts were developed, and new technological schemes of synthesis appeared[11,17–23].

### 1. Iron Catalysts

Iron catalysts have a number of advantages over cobalt catalysts: they are cheap and readily available, and they enable the synthetic process to be intensified by factors of 10–20; they are active and stable over a comparatively wide range of temperature and pressure with different $H_2$ : CO ratios in the starting gas.

(a) Methods of preparation. The first iron catalysts were prepared by the thermal decomposition of nitrates, and they contained activating copper and alkali additives[24,25]. However, *precipitated* iron catalysts were found to be considerably more active, especially when they contained activating additions of copper, alkalis ($K_2CO_3$, KOH, $Rb_2CO_3$), alkali-metal borates and silicates, several difficultly reducible oxides (MnO, MgO, $Al_2O_3$, $ThO_2$, CaO, $TiO_2$), and also cobalt and nickel[1,26–34]. The mechanical strength of the carriers was increased by depositing magnesium oxide, silica, kieselguhr, pumice, dolomite, diatomite, infusorial earth, and activated charcoal on them[16,35]. On the best iron catalysts (100 Fe, 5–25 Cu, 0.08–2 alkalis) at 200–280° and 1–30 atm, a CO–$H_2$ mixture (0.5–2 : 1) at a space velocity of ~ 100 $h^{-1}$ gave, per cubic metre at s.t.p., 100–130 g of liquid products, with a total yield of all products of 140–160 g $m^{-3}$. The hydrocarbons obtained at 10 atm and 212–218° in the presence of iron-copper catalysts promoted by silicates (10–20% on the Fe content), with a total yield of 131–134 g $m^{-3}$ consisted of 52–55% of solid paraffins with boiling points above 300°.[36] Active catalysts for the synthesis of the lower hydrocarbons were prepared on carriers of finely ground natural minerals containing over 10% of soluble silicates[37].

In recent years, in connection with the development of highly efficient synthetic processes, fused, sintered, and cemented iron catalysts have been intensively studied[1,16,38].

Fused catalysts are prepared by roasting powdered electrolytic iron or iron carbonyl vapour in oxygen with the subsequent addition of activators to the melt, or by fusing magnetic iron oxide with these activators[39–43]. Fused iron catalysts of the contact type used in ammonia syntheses began to be employed in the synthesis of hydrocarbons as early as the 1930's.[3,44] Later in Germany the Synthol process was developed in which a similar catalyst of composition 100 Fe : 4.9 $Al_2O_3$ : 0.9 $K_2O$ : 2.9 CaO was used; this had an activity approaching that of precipitated iron catalysts. Similar catalysts were also developed in the United States[16]. After reduction with hydrogen at 450–500°, they gave yields of hydrocarbons of up to 114–117 g × × $m^{-3}$ at 247–254°, 7–8 atm, and a space velocity (1 CO : 1 $H_2$) of 100–300 $h^{-1}$. However, all these catalysts were unstable.

Bashkirov and his coworkers found that fused iron catalysts, promoted by alumina, silica, and potassium carbonate, and reduced with hydrogen and carbon monoxide at 900–1150°, have higher activity and stability than those reduced at lower temperatures[40–43,45]. At 300–310°, 20–25 atm, and a space velocity (1 CO : 1 $H_2$ mixture) of 1500 $h^{-1}$, 85% conversion was achieved with a total hydrocarbon yield of 140–150 g $m^{-3}$. The most active catalyst had the composition $Fe_3O_4$ + 4–7% $Al_2O_3$ + 4–6% $SiO_2$ + + 1–1.4% $K_2CO_3$; it was necessary to introduce the potassium carbonate in such a way that reaction with the silica was avoided. The stability increased sharply when 0.3–1% of chromium, vanadium, or titanium, or of both chromium and vanadium, was introduced into the catalyst; the duration of the working cycle reached 600 h. The addition of 0.5% of molybdenum or 1% of manganese had no effect on the activity, and the addition of silicon and tungsten had a deactivating effect.

Sintered and cemented catalysts are prepared by sintering iron or its oxides with binding additives — $Al_2(NO_3)_6$, $Na_2B_4O_7$, $Na_2SiO_3$, etc.[3,16,46–50] — and also by sintering precipitated iron–alumina catalysts[51]. Catalysts sintered in a hydrogen atmosphere are active at 20 atm and 300° without preliminary activation. A catalyst of 100 Fe + + 10 $Al_2O_3$ remained active for more than 1000 h; in the range of space velocities of 100–300 $h^{-1}$, the degree of conversion of carbon monoxide reached ~ 98%, and the mean total yield of hydrocarbons 140–145 g $m^{-3}$.

(b) Physical properties and preliminary treatment. Unreduced precipitated iron–copper catalysts have the structure of an iron oxide gel with small pores and a large surface area (up to 300 $m^2 g^{-1}$)[35,52–54], but unreduced fused and sintered iron catalysts have a magnetite structure[16,54] with a very small surface area (< 1 $m^2$ × × $g^{-1}$), and consist, according to X-ray analysis, of the oxides FeO and $Fe_3O_4$.[42] Promoters are uniformly distributed in the melt[40,42]; this is apparently due to the formation in the fusion process of iron aluminates, silicates, and possibly aluminosilicates, partly dissolved in the iron oxides and partly concentrated as crystals or amorphous layers between the grains of solid solution[40,42,55]. Thermomagnetic results show that the alkali-metal oxides also form solid solutions with magnetite[56], but there is evidence against this: over 70% of the surface is covered by alkali, which can be easily removed from the catalyst, and the properties of the catalyst are independent of whether the alkali has been added before or after fusion[16].

† The mechanism of these processes will be considered in a separate review.

Before use in synthesis the precipitated iron–copper catalysts are usually treated with hydrogen, carbon monoxide, ammonia, or mixtures of carbon monoxide and hydrogen. The method of treatment has no effect on the activity (Table 1), but materially affects the duration of further development of the catalyst, its selectivity, and its stability[3,16,57,58]. According to some data, when iron oxides are treated with hydrogen at 230–250° they are almost completely reduced to the metal; but according to other data[35] no metallic iron, or at most 1–2%, is observed after such treatment, and the catalysts consist to the extent of 50–60% of FeO and compounds of the spinel type — $FeO.Fe_2O_3(Fe.Fe_2O_4)$, $CuO.Fe_2O_3(Cu.Fe_2O_4)$, $MgO.Fe_2O_3$, or $MnO.Fe_2O_3$ [59] — which is evidently explained by differences in the degree of reduction of the iron oxides depending on the duration of reduction. Treatment with carbon monoxide or a mixture of carbon monoxide and hydrogen gives magnetite and Hägg's carbide, and treatment with ammonia gives magnetite and iron nitrides[54]. Catalysts treated with hydrogen and particularly with ammonia promote the formation of products of lower molecular weight (and also considerable quantities of alcohols) than do catalysts treated with a mixture of carbon monoxide and hydrogen. Nitrided catalysts were less stable than those treated with hydrogen or a mixture of carbon monoxide and hydrogen. The greater the alkali content and the lower the copper content of catalysts, the higher the temperature and the longer the time required for reduction. When the starting gas contained carbon monoxide, the temperature and duration of treatment could be decreased[57]. Reduction by a gas containing carbon dioxide, and particularly water vapour, had a deleterious effect on activity. Treatment with a mixture of carbon monoxide and hydrogen gives catalysts that are insensitive to sulphur compounds[60]. After precipitated catalysts have been treated with a mixture of hydrogen and carbon monoxide, their surface area has decreased from ~300 to ~20 $m^2 g^{-1}$,[35,53,61] but the surface area of catalysts precipitated on a carrier evidently remains unchanged or slightly increases[10].

Fused catalysts are reduced by hydrogen at 375–500° in 25–60 h,[16,62-64] or at ~1000° in 1.5–6 h[41-43,65-67] at atmospheric or higher pressure (up to 10 atm). In this case also water vapour or carbon dioxide has a deleterious effect on the activity of the catalysts[63]. In reduction at 450° the surface area of the catalysts and the volume of the pores increase linearly with the degree of reduction up to ~80% reduction[62]. Pores with a mean diameter of ~333 Å are formed. With a degree of reduction of over 80% the surface area increases more rapidly than the pore volume. With reduction between 99.5% and 100% there is some decrease in the surface area. At 550° catalysts having a mean pore diameter of 830 Å are formed. With reduction in the range 400–650°, the particle size of the catalyst does not change; the porous structure is formed by removal of the oxygen from the iron oxides. The volume of the pores increases and the surface area decreases[62,64]. The reduction process becomes more rapid with increasing temperature. The surface area of reduced fused catalysts is 1–50 $m^2 g^{-1}$.[10,62] Promoters stabilise the structure produced on reduction, but they do not prevent diminution in the surface area with increasing temperature. In the course of reduction the promoters are extruded on to the surface of the $\alpha$-iron crystals, in which they are insoluble[42,68]. $\alpha$-Iron, $\alpha$-quartzite, $\gamma$-alumina, and compounds of the andalusite type have been detected in reduced samples of fused catalysts. Extraction with hot water improved the activity of sintered catalysts; the improvement is due to the removal of sulphur compounds present as impurities and to the formation of a finely dispersed highly active iron oxide by decomposition of the ferrites formed in the preparation of the catalysts[49,50].

TABLE 1. The effect of preliminary treatment at 250° on the activity of precipitated iron–copper catalysts[16].

| Preliminary treatment | Duration of treatment, h | Activity of catalyst | |
|---|---|---|---|
| | | temp. of synthesis, °C | contraction of gas, % |
| No treatment | — | 251 | 64 |
| With nitrogen | 24 | 250 | 65 |
| With natural gas | 16 | 250 | 67 |
| With hydrogen | 17 | 250 | 65 |
| With carbon dioxide | 21 | 250 | 69 |
| With air | 16 | 248 | 67 |

The thermal conductivity of precipitated iron–copper catalysts is 2–3 times that of cobalt–thoria catalysts[69], and the conductivity of fused catalysts is greater than that of precipitated catalysts. The thermal conductivity of all catalysts approximately doubles in operation, as a result of saturation with reaction products. This is important because when a reactor is being brought into operation, the temperature and the gas charge must be increased slowly for effective removal of the heat of reaction. Only when the catalyst has become saturated with the reaction products (paraffin is sometimes poured over it for this purpose) and its thermal conductivity has been increased can the synthesis function under normal conditions.

(c) Development. Fused iron catalysts, reduced at ~1000°, are inactive immediately on reduction, and acquire a high activity only after the starting gas has been passed over them for 7–50 h.[65-67] Precipitated and fused catalysts are at once activated at 375–500°, but it is only in the process of synthesis that the active catalyst surface is formed; its structure and phase composition are changed as a result of the chemical reaction of iron compounds with starting reagents and reaction products[35,70-72]. Metallic iron, iron carbides, and iron oxides do not separately catalyse the synthesis of organic compounds from carbon monoxide and hydrogen[65,72]. In the initial period of the synthesis a number of competing reactions occur on the catalyst surface between its components and the gases in the reaction mixture; these include carbidation of the iron, hydrogenation of carbides, oxidation of the iron by water, reduction of the iron oxides by carbon monoxide and hydrogen, etc. Dynamic equilibrium is established between the surface phases[70,73-77]. In the course of these reactions, proceeding at the interphase boundaries of the surface, molecules of carbon monoxide and hydrogen are activated and, when the necessary geometrical relationship with the surface arises, they interact[66,72]. To acquire such properties, catalysts reduced at 375–500°, either carbided[78-80] or nitrided[80-86], do not require a long activation process. The formation of their active surface apparently consists in the rapid production of the phase combination necessary for the synthesis. In the formation of the surface and then in the synthesis, water vapour and carbon dioxide have a deleterious effect on the activity and selectivity: oxidative deactivation occurs with change in the phase composition[70,73,76,87,88].

(d) Catalysts based on natural ores. Work has been carried on for a long time on the use of natural

minerals or ores containing iron or its oxides as catalysts in the reduction of carbon monoxide. After reduction with hydrogen at 450° these proved to be active at 230–300° and 7 atm with a space velocity of starting gas ($CO_2 + H_2$, 1 : 1) of ~ 1000 $h^{-1}$.[3,16,89-92] Krivorog ochre haematite ($79Fe_2O_3$, $7Al_2O_3$, $1.0SiO_2$), Khallilovo ore ($56Fe_2O_3$, $12Al_2O_3$, $10SiO_2$), red mud, a by-product of the aluminium industry ($55.4Fe_2O_3$, $20.3Al_2O_3$, $12.5SiO_2$, $4.8CaO$), titanomagnetite ($50Fe_2O_3$. $.24FeO.3Al_2O_3.3SiO_2.13TiO_2$), and magnetic iron ore ($60Fe_2O_3.14FeO.3Al_2O_3.6SiO_2.6CaO + MgO$) have been used[93]. After reduction at 800–1000° and saturation with potassium carbonate or sodium borate solution, the catalysts work stably at 20–40 atm, 300–320°, and a space velocity of 500–1500 $h^{-1}$ (with a 1 : 1 mixture of carbon monoxide and hydrogen), giving a yield of liquid products up to 90 g $m^{-3}$. For catalytic activity, iron ores must have a high content of iron oxides and an alkali additive. Oxides in the ore that are difficult to reduce serve as structural promoters. The catalytic properties of iron ores are improved by fusion, which leads to a more uniform distribution of the oxide promoters and the removal of some compounds that lower activity. Such catalysts are active in the same way as ordinary fused catalysts, but they are rapidly destroyed by the deposition of carbon.

(e) Industrial methods of synthesising hydrocarbons from carbon monoxide and hydrogen in the presence of iron catalysts. The intensive investigation of iron catalysts led to the development of a highly efficient process accomplished by different technological methods (Table 2).[46,94-99] The earliest of these, in which the process was carried out *in the gas phase* with stationary precipitated iron–copper catalysts, was inefficient. Its disadvantages were: (1) low efficiency because of the low space velocity of the starting gas necessitated by the difficulty of removing the heat of reaction; (2) the narrow temperature range of the reaction; (3) non-uniform distribution of temperature and composition of the reaction mixture along the layer of catalyst, which led to choking up by coke formation and oxidation of the catalyst by water vapour; and (4) the ratio in which hydrogen and carbon monoxide were consumed differed from the ratio in the starting gas, and this led to a decrease in the theoretical yield of product. The problem of effectively removing the heat of reaction was partly solved by the use of fused, sintered, or cemented catalysts, operating at high degrees of conversion of the gas and over a wide range of space velocities, and also by recirculating the effluent gases. When recirculation is used, the reaction, which ordinarily proceeds at constant temperature and pressure in the region of kinetic control, passes to the external diffusion region, because of changes in the concentrations of carbon monoxide and hydrogen in the gas, its linear velocity, and the hydrodynamic conditions[35,97,100,101]. When the coefficient of recirculation is greater than unity, the reaction passes into the internal diffusion region. With recirculation[102,103], or increase in the linear velocity of the starting gas[13], the productivity of the process is increased 6–8 times and the yield of products approaches the theoretical. On fused catalysts the optimal consumption ratio of $H_2$ : CO establishes itself at a space velocity of 100–50 000 $h^{-1}$ and a recirculation coefficient of 0–50.[102]

The best removal of heat is achieved with a *fluidised bed* of catalyst suspended in the gas phase. With this method the efficiency is 2–4 times that achieved with a stationary layer, there is a high degree of conversion of the starting gas, and the catalyst can be easily replaced or regenerated (Table 2).[1,46,63,104-107] Fused and sintered catalysts of particle size 2–100 μm are used; they are active for more than 350 h without regeneration. Such a process is operated at a works in South Africa. The precipitated catalyst ($86.6Fe + 5Cu + 8Mg + 0.4K_2O$) in a fluidised layer worked at a lower temperature and pressure, but its activity, selectivity, and stability were less than those of fused catalysts[63,107]. Catalysts in a fluidised

TABLE 2. Characteristics of processes for the synthesis of hydrocarbons from carbon monoxide and hydrogen on iron catalysts.

| Process | Synthesis in gas phase on stationary catalyst | | | Synthesis in gas phase on fluidised catalyst | | Synthesis in liquid phase with suspended catalyst | Synthesis in liquid phase with suspended catalyst | |
|---|---|---|---|---|---|---|---|---|
| Catalyst | pptd. Fe–Cu | fused $NH_3$-synthesis type | pelleted on powdered steel | pptd. Fe–Cu | fused $NH_3$-synthesis type | fused $NH_3$-synthesis type | pptd. Fe–Cu | fused $NH_3$-synthesis type |
| References | 22, 35 | 94, 104 | 97 | 63, 107 | 46, 104–107 | 108, 109 | 35, 111–115 | 104, 110, 116 |
| Pressure, atm | 1–10 | 21–42 | 30 | 5–15 | 20–30 | 20 | 8–20 | 21–42 |
| Temperature, °C | 175–230 | 250 | 230–310 | 250–320 | 300–340 | 255–265 | 220–290 | 265–305 |
| Space velocity, $h^{-1}$ | ~100 | up to 1045 | 300–1000 | 600–1200 | 500–2200 | ~300 | ~230 | up to 1000 |
| $H_2$ : CO in starting gas | 0.67–2 | 2 | 0.83–1.2 | 1.35–1.9 | 1.95–2.5 | 1–1.3 | 0.65–1.5 | 0.7–2.0 |
| Recirculation coefficient | 0–9 | 2–2.5 | 2–3.5 | nil | 1.5–13 | 1–2 | nil | up to 6 |
| Conversion, % | | | | | | | | |
| CO | 90–96 | up to 96 | 69 | 92–97 | 90–98 | — | 91 | up to 96 |
| $CO + H_2$ | 50–60 | up to 85 | 61 | 70–77 | 80–93 | 70 | 89 | up to 93.5 |
| $H_2$ : CO consumed | 0.63–1.52 | 1.56–1.88 | — | 0.99–1.04 | 1.7 | 0.99–1.22 | — | 1–1.57 |
| Yield, g $m^{-3}$ (at s.t.p.) | | | | | | | | |
| $C_1$ | 7–15 | 15–37 | | 10–34 | 20–63 | ~14 | | 12.7–22.6 |
| $C_2$ | | | 12–23 | | | 11–12 | 3–12 | |
| $C_3 + C_4$ | 22–51 | 34–59 | 11–27 | 40–70 | 55.8–64 | | 4–48 | 37–38 |
| Petrol (up to 200°) | 23–87 | | | | | 72 | 13–102 | 57–58 |
| Oil (200–320°) | 17–45 | 75–95 | 69 | 20–50 | 38–72 | 11–12 | 10–45 | 11.3–13.4 |
| Paraffin wax (>320°) | 17–60 | | | | | 16–23 | 2–150 | 16–30 |
| Overall yield of hydrocarbons, g $m^{-3}$ (at s.t.p.) | 157–186 | 140–170 | 93–119 | 140 | 159–170 | 124–135 | 162–182 | 125–139 |
| Yield of oxygen-containing compounds, g $m^{-3}$ (at s.t.p.) | 23–41 | 5–16 | 6 | — | 5–19 | 14–15 | 2–3 | 8–15 |
| Efficiency, kg $m^{-3}$ of catalysts per day | — | 1250 | 1970 | — | up to 4320 | — | 770–1000 | — |
| Cooling surface in reactor, $m^2$ per 1000 $m^3$ of converted gas per h | — | 235 | — | — | ~30 | — | 50 | — |

bed must have high mechanical strength. Polymeric products must not be formed, as their deposition on the surface of the catalyst would bring about defluidisation, so that a higher temperature is also required. However, this may greatly accelerate side-reactions of carbon monoxide with water (the water-gas reaction) and carbon formation, and lead to a decrease in the selectivity and stability of the catalysts. These undesirable effects may be prevented by carrying out the synthesis with hydrogen-enriched gas ($H_2 : CO = 1.95–2.5$) and by using circulation.

Highly active, selective, and stable nitrided catalysts are of considerable interest in this process[63]. Synthesis on these takes place at 260–275° and 15–25 atm with a starting gas consisting of $H_2 : CO = 1.2–1.3$. They had a working cycle without regeneration of over 1500 h.

In *liquid-phase* synthesis, precipitated and fused iron catalysts are used both stationary[108,109] and suspended in oil[35,104,110–116]. Hydrocarbon fractions of b.p. 200–450° and 300–450° were used as medium. The heat of reaction went to heat the circulating oil and evaporate its lighter components. The rise in temperature of the oil did not exceed 50 deg. Precipitated iron catalysts were very active, but were rapidly destroyed by the circulating oil. The less active and more stable fused catalysts (Table 2), however, did not work for more than 2–3 months, because of cementation and a sharp rise in hydraulic resistance. This disadvantage is eliminated when a catalyst of 6–20 mesh particle size forms a circulating or stationary suspension in the oil. According to the conditions of synthesis and the catalyst, the product may consist mainly of gasoline, diesel oil, or solid paraffins. The solubility of the gases and reaction products in the liquid phase plays an important part[112]. The process is characterised by good heat removal, high selectivity, flexibility, uniform loading of the catalyst, ease and simplicity of plant layout, and high efficiency.

Processes using a stationary layer of iron catalyst with circulating gas, but particularly in the liquid phase with the iron catalyst suspended in oil, are most selective (lowest yield of methane) and are characterised by high stability and productivity, good heat exchange, comparatively low reaction temperatures and pressures, and also great flexibility. Gasoline as the main product, or gasoline with diesel fuel, or solid paraffins can be obtained from gases with an $H_2 : CO$ ratio of 0.6–2.0, and consequently from effluent gases of a number of plants (Table 3). Considerable amounts of oxygen-containing compounds, mainly alcohols, are formed on fused and sintered catalysts[11,117–125]. The gasolines have much better engine characteristics than those obtained from carbon monoxide and hydrogen on cobalt catalysts.[3,11,21,118,126] After the addition of R-9 or polymer motor fuel (0.5–1.5 ml $kg^{-1}$) or after thermal treatment in the presence of alumina, commercial A-66 or A-70 motor fuels are obtained. Diesel fuel obtained on

TABLE 3. Composition and characteristics of products of industrial processes in semi-works trials of the synthesis of hydrocarbons from carbon monoxide and hydrogen on iron catalysts.

| Process | Synthesis in gas phase with stationery catalyst | | | Synthesis in gas phase on fluidised catalyst | Synthesis in liquid phase with suspended catalyst | | |
|---|---|---|---|---|---|---|---|
| | at atmospheric pressure | at moderate pressure | | | | | |
| Catalyst | pptd. Fe–Cu | | fused $NH_3$-synthesis type | fused $NH_3$-synthesis type | pptd. Fe–Cu | | |
| | I | II | | | I | II | III |
| References | 35 | 22, 35, 117–119 | 118,120–123 | 46, 124 | 35, 112 | | |
| Yield, wt. % on total $CH_2$ | | | | | | | |
| $C_1$ | 5.1 | 4.5–8.1 | 8.9 | 13.4–15.8 | | | |
| $C_2$ | 7.1 | | 7.8 | 12.2–12.3 | 6.2 | 1.7 | 1.6 |
| $C_3 + C_4$ | 6.1 | 15–30 | 29.8 | 24.5–25.1 | 17.0 | 6.8 | 2.2 |
| Petrol (190°) | 34.8 | 15–50 | 41.0 | 29–31 | 63.8 | 39.4 | 7.0 |
| Diesel fuel (190–310°) | 24.4 | 10–30 | 6.2 | 3–4 | 10.2 | 25.4 | 8.1 |
| Soft paraffin (310–450°) | 13.1 | | | | 2.3 | 18.0 | 32.6 |
| Hard paraffin (>450°) | 9.4 | 10–40 | 6.3 | 1.6–2.6 | 0.5 | 8.9 | 48.5 |
| Unsaturated compounds, % | | | | | | | |
| $C_3 + C_4$ | — | 50 | up to 83 | 85–86 | | 70–92 | |
| Petrol | 26 | 42–53 | 74–87 | 44–49 | | 62–95 | |
| Diesel fuel | — | 25.4 | 73–76 | — | | 30–80 | |
| Paraffin (>310°) | — | — | 75 | — | | 10–60 | |
| Engine characteristics | | | | | | | |
| 1. Petrol | | | | | | | |
| Octane No. (engine method) | 35 | 55–61 | 58 | 73.8 | | 73 | |
| After treatment with $Al_2O_3$ | — | — | — | 74.9 | | 81 | |
| With addition of R-9, mg $kg^{-1}$ | | | | | | | |
| 0.5 | — | 67.0–68.3 | — | — | | — | |
| 1.0 | — | 71.7–73.2 | — | — | | — | |
| 1.5 | — | 73.8–77.0 | 68 | — | | — | |
| 2. Diesel fuel | | | | | | | |
| Cetane rating | — | 85 | 50 | — | | 70 | |
| Pour point, °C | — | —4 | —24 | — | | —11 | |
| Content of oxygen compounds in reaction water, % | | | | | | | |
| Acids | — | 0.31–0.47 | 1.2–1.3 | 3.1–3.9 | | — | |
| Alcohols | — | 6.1–14.7 | 4.3–9.2 | 9.1–10.4 | | — | |
| Aldehydes | — | 0.129 | 0.1–0.6 | | | — | |
| Ketones | — | | 0.6–2.2 | | | — | |

iron catalysts is of low quality, and can be used only as a component of high-quality diesel fuels [126].

A gas-phase process on fluidised iron catalysts is used for the preparation of high-quality motor fuels, although it is less selective than the previous two, and requires higher temperatures and pressures and the use of a hydrogen-enriched starting gas [46].

The synthesis of hydrocarbon fuels from carbon monoxide and hydrogen is of definite value for countries that have no, or very limited, natural oil sources [11,18,19,21,127]. However, it is more expedient to obtain from these gases raw materials for organic synthesis in the form of unsaturated hydrocarbons and oxygen-containing compounds [45,118,128]. For the synthesis of $C_2$–$C_4$ unsaturated hydrocarbons [129] or a mixture of liquid and gaseous olefins [130–134], iron catalysts in a stationary or fluidised layer are recommended, with addition to the starting gas of halogens, hydrogen halides, or organic halogen compounds that give hydrogen halides on dissociation. The catalyst may be promoted with iron halides or alkali-metal halides [134], with lead [135,136], and also by the addition of 0.02–0.5 wt.% of sulphur [129,137,138]. The process operates at high pressure, 295–400°, and a space velocity of starting gas (2.25 CO : 1 $H_2$) of 3100 $h^{-1}$.

## 2. Oxide Catalysts

(a) Metal oxides. Oxides that are difficult to reduce — $ThO_2$, $Al_2O_3$, $SiO_2$, ZnO, etc., — are known as promoters of nickel, cobalt, and iron catalysts in the synthesis of hydrocarbons from carbon monoxide and hydrogen. Pichler and Ziesecke found that, at temperatures of ~450° and pressures of over 100 atm, liquid and gaseous aliphatic hydrocarbons, mainly with branched structures, can be synthesised from carbon monoxide and hydrogen on these oxides [139–142]. Thoria, zirconia, and ceria were found to be active [139,143,144], as were also the mixed catalysts $ThO_2$–$Al_2O_3$, $ThO_2$–ZnO, and ZnO–$Al_2O_3$. [143] In the presence of these catalysts at 400–450° and 250 atm, 70–80% conversion of carbon monoxide was achieved; the total yield of hydrocarbons was 105 g $m^{-3}$, of which up to 57 g $m^{-3}$ represented liquid hydrocarbons. At 30 atm the degree of conversion of carbon monoxide and the yield of products were small. At increased temperatures (above 450°) the gaseous products increased, and below 375° alcohols were mainly formed. When potassium carbonate, kieselguhr, or iron was added to $ThO_2$ or $ThO_2$–$Al_2O_3$, the activity of these catalysts was diminished and methane formation was increased [143]. The reaction products contained large amounts of unsaturated aliphatic hydrocarbons, over 90% of which had branched structures; small amounts of aromatic hydrocarbons and naphthenes were found. Catalysts consisting of the oxides of aluminium, tungsten, zirconium, uranium, and the rare earths, with the addition of zinc oxide, chromic oxide, or copper, have been proposed for the preparation of high quality motor fuel from carbon monoxide and hydrogen; they are active at pressures above 100 atm and temperatures above 350–400°. [145] On oxides of molybdenum, tungsten, chromium, manganese, vanadium, and magnesium promoted with 1–5% of potassium carbonate the degree of conversion of carbon monoxide at 30 atm and 400–470° was 87–92%, but gaseous products were mainly formed. Oxides of titanium and strontium, and also metal oxides that are easily reduced, e.g. PbO, $SnO_2$, and CdO, were inactive [146,147]. Catalysts prepared from bauxites by impregnation or fusion with potassium carbonate and borax, and containing $Fe_3O_4$, are active at 280° and 20 atm with a gas mixture (1CO : 1$H_2$) at a space velocity of 1250 $h^{-1}$; these operated for more 120 h without loss in activity, giving a yield of $C_2$ and higher hydrocarbons up to 110 g $m^{-3}$. [148]

(b) Silicic acid catalysts. Promoted silicic acid catalysts form a large group of oxide catalysts for the reduction of carbon monoxide; they are prepared both from soluble silicates and from natural silicate-containing minerals [144]. Silicon dioxide with 2% of potassium carbonate, potassium hydroxide, or sodium borate is active at 350–450° and 20–40 atm after preliminary treatment [146,148]. The degree of conversion of carbon monoxide with a gas mixture (1 CO : 1 $H_2$) at a space velocity of 100–300 $h^{-1}$ was 80–95%; the yield of hydrocarbons was 110–130 g $m^{-3}$, up to 65 g $m^{-3}$ being liquid. At temperatures above 450° more liquid products and much gas were obtained, and at 500° methane was the main product. The addition of small quantities of alumina promoted the reaction, but the oxides of magnesium, calcium, tungsten, and thorium were inactive [144].

Natural silicate minerals are active at 350–470°, pressures above 20 atm, and a space velocity (1 CO : 1 $H_2$) of 100–300 $h^{-1}$. [149,154] Alkaline additives (potassium and sodium carbonates, potassium hydroxide) generally increased the activity and promoted the formation of hydrocarbons of higher molecular weight. The minerals rhodonite (Mn, Ca)$[Si_2O_6]$, kaolin $Al_2[Si_2O_5](OH)_4$, montmorillonite (Mg, Ca)O.$Al_2O_3$.5$SiO_2$.7$H_2O$, nontronite $H_2Fe_2Si_2O_5.H_2O$, and microcline $K[AlSi_3O_8]$ were virtually inactive. The minerals beryl $Be_3Al_2[SiO_3]_6$, dumortierite $HBAl_8Si_3O_{20}$, spodumene (Li, Na)$Al[Si_2O_6]$, and albite $Na[AlSi_3O_8]$ gave methane as the main product with a high conversion of carbon monoxide. Liquid hydrocarbons were formed only in the presence of almandite $Fe_3Al_2[SiO_4]_3$, diopside $CaMg[Si_2O_6]$, actinolite $Ca_2(Mg, Fe)_5[Si_4O_{11}](OH)_2$, gedrite, anthophyllite $(Mg, Fe)_7[Si_4O_{11}]_2(OH)_2$, talc $Mg_3[Si_4O_{10}](OH)_2$, biotite $K(Mg, Fe)_3[Si_3AlO_{10}](F, OH)_2$, and kieselguhr.

The most active minerals were talc and kieselguhr; these gave yields of liquid products of 75 and 95 g $m^{-3}$ with total yields of 130 and 140 g $m^{-3}$ respectively. The reaction started only at 320°. The optimum temperature of the reaction was 350–450° on kieselguhr, and 415–450° on talc. Above 450° methane formation and coking up sharply increased. At atmospheric pressure the reaction did not occur even at temperatures above 450°; the optimum pressure was 20–40 atm. Increasing the pressure to 200 atm reduced the yield of liquid hydrocarbons, and increased the formation of oxygen-containing products and coke.

Alkaline additives ($K_2CO_3$, $Na_2CO_3$, KOH, $Na_2B_4O_7$, etc.) and also the salts $KNO_3$, $KMnO_4$, etc. are activators. With salts the efficacy of the cations diminished in the order K > Na > Li. Carbonates, nitrates, and fluorides were the most effective, but chlorides, bromides, and sulphates deactivated the catalysts. The degree of conversion of carbon monoxide and the total yield of hydrocarbons increased continuously as the potassium carbonate content increased from 0 to 10%. With further increase up to 50%, the yield of products decreased and the stability of the catalyst diminished. The activity of talc catalysts depends largely on preliminary thermal treatment. The best results are obtained by preliminary heating to 600°. According to X-ray analysis, this promoted the removal of all adsorbed interplanar and interstitial water without destroying the

structure of the talc. At 850–1000° the structure was destroyed, and the surface area was reduced by a factor of 2–3. Talc roasted at 600° together with an alkaline additive had a low activity, apparently because of sintering of the particles and reduction of the surface area.

The maximum total yield and also yield of liquid hydrocarbons were observed with 54–60% of CO in the starting gas. As the space velocity is increased in the range 100–1650 $h^{-1}$, the efficiency of the catalysts continuously increases, but its stability falls sharply. Silicate catalysts are regenerated by air at 450°. Gaseous and liquid hydrocarbons, oxygen-containing compounds, water, and carbon dioxide are formed on silica catalysts. The content of oxygen-containing compounds, mainly alcohols and carbonyl compounds, in the products of the reaction on kieselguhr catalysts is small (5–8%); on talc it reaches 80%. The hydrocarbons, which are mostly volatile below 170°, contain 60–70% of unsaturated compounds and consist mainly of aliphatic hydrocarbons with branched structures. The content of aromatic hydrocarbons does not exceed 6–10%. The octane number of the motor fuel obtained from carbon monoxide and hydrogen on silicic acid catalysts reaches 76–81.

A characteristic feature of natural silicate minerals is their crystalline structure, which is based on different arrangements in space of $[SiO_4]^{4-}$ tetrahedra. Only lower, mainly gaseous hydrocarbons are formed on silicates with single or double tetrahedra, but liquid hydrocarbons are formed on silicates with a layer structure.

Oxide catalysts therefore constitute a new class of catalyst for the reduction of carbon monoxide. They form neither carbides nor carbonyls with the latter, but decompose it, promoting its conversion by water vapour. They are not oxidised by water and carbon dioxide, but under the conditions of the synthesis they may perhaps react with carbon dioxide to form carbonates. The reduction of carbon monoxide on oxide catalysts proceeds at high temperatures (350–500°) and pressures (20–600 atm) with the formation of hydrocarbons, mainly with branched structures.

According to the semi-contact hypothesis on the hydrogenation of carbon monoxide to branched hydrocarbons [155], oxide catalysts are not capable of activating hydrogen directly, which leads to an increased concentration of CHOH groups together with $CH_2$ groups on the surface of the catalyst. Branched compounds are formed by catalytic dehydration and condensation, in which the hydroxy-groups on the secondary carbon atoms react with hydrogen atoms of the hydrocarbon chain.

## II. DIRECTED SYNTHESES OF ORGANIC COMPOUNDS FROM CARBON MONOXIDE AND HYDROGEN

The Fischer–Tropsch synthesis of hydrocarbons from carbon monoxide and hydrogen on catalysts based on iron, cobalt, and nickel is not selective [5]. For this reason, the directed syntheses of valuable chemical products from carbon monoxide and hydrogen are of great interest.

### 1. Synthesis of Higher Hydrocarbons

(a) Ruthenium catalysts. As early as 1938, a yield of hydrocarbons of 140–150 g $m^{-3}$ (60–70% solid paraffin) was obtained from a mixture of $1CO + 2H_2$ on finely divided metallic ruthenium at 180–200° and 100–800 atm. [156,157] At the present time, in connection with the development of radio-electronic and other processes, the demand for synthetic paraffins with a number of properties superior to those of petroleum paraffins has greatly increased. New work has been done on the synthesis of solid paraffins in the presence of ruthenium catalysts [158–160]. It was found that, as the temperature increased in the range 165–275°, the degree of conversion of the starting gas continuously increased, but the yield of paraffins passed through a maximum at 170–180°. Increasing the total pressure to 1500 atm and reduction of the contact time promoted the formation of solid paraffins, their content in the reaction products reaching up to 65%. At the same time the optimum reaction temperature was lowered. The maximum yield of solid and liquid hydrocarbons was obtained from a 1 : 2 mixture of carbon monoxide and hydrogen. More liquid and gaseous hydrocarbons were formed on ruthenium with the addition of 20% of thorium, aluminium, and magnesium oxides. However, it was later shown that the addition of small amounts of metal oxides, for example 1.5% of magnesium oxide, led to a sharp increase in the yield of solid hydrocarbons. Preliminary treatment of the catalysts with hydrogen at 220–420° led to a 20% reduction in activity, but sharply increased the selectivity, apparently by the formation of a definite microstructure with pores of 400–1000 Å diameter and a total surface area of 7–15 $m^2\ g^{-1}$. Catalysts containing traces of alkali and having a pore diameter of 1200–1600 Å were much less selective. Catalysts nitrided at 250–300° with the formation of ruthenium nitrides gave mainly liquid and gaseous hydrocarbons, but catalysts nitrided at 400–450° had high selectivity and stability to oxygen and gave products containing 93–95% of solid paraffins.

Therefore the conditions for activating ruthenium catalysts for very selective synthesis of solid paraffins having m.p. 50–140° have now been established.

(b) Modified cobalt catalysts. Thorium dioxide in cobalt catalysts for the synthesis of hydrocarbons from carbon monoxide and hydrogen may be replaced by zirconium or titanium dioxide [161]. Such catalysts, after preliminary reduction with hydrogen at 400° for 12 h, operated at 190° and atmospheric pressure with yields of liquid hydrocarbons of 150–170 g $m^{-3}$ of starting gas (1 CO : 2 $H_2$). With a pressure of 10 atm on catalysts of composition 100Co : $6ZrO_2$, or $TiO_2$ : 10MgO: 200 kieselguhr, the reduction of carbon monoxide in the first 144 h proceeded, as at atmospheric pressure, with the formation mainly of liquid hydrocarbons. Then solid paraffins began to be mainly formed having m.p. 70–98°, with an average yield of ~92 and a maximum yield of 116 g $m^{-3}$. The catalysts worked for over 800 h with no loss in activity [162].

(c) Molybdophosphoric catalysts. Solid paraffins are obtained from mixtures (10 : 1 to 1 : 5) of carbon monoxide and hydrogen at 125–350° and 450–500 atm in the presence of molybdophosphoric acids $P_2Mo_xO_y$ ($x$ = 20–24 and $y$ = 31–60) and their salts $M_yP_2Mo_xO_z$ (M is a metal — Li, Na, K, Rb, Cs, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Mg, Mn, Fe, Co, Ni — $y$ = 2–10, $x$ = 20–26, and $z$ = 37–65). [163,164] The following acids and salts have been used as catalysts $P_2Mo_{22}O_{39}$, $P_2Mo_{21}O_{47}$, $P_2Mo_{22}O_{48}$, $Ni_2P_2O_5(Mo_2O_5)_{11}$, $Co_3P_2O_5(Mo_2O_5)_{22}$, $Fe_3P_2O_5(Mo_2O_5)_{10}$, $Cu_3P_2O_5(Mo_2O_4)_{12}$, and $Zn_3P_2O_5(Mo_2O_3)_{12}$. The catalyst, used in 1.5–30% quantities, was first reduced in hydrogen at 400° for 17–19 h. The synthesis was carried out in cyclohexane, methanol,

decahydronaphthalene, tetrahydronaphthalene, aromatic hydrocarbons, or cyclohexanone as diluents.

### 2. Synthesis of Ethylene

Ethylene is a valuable raw material for organic synthesis in industry [165], and for this reason, attempts have been made to prepare it from carbon monoxide and hydrogen [166-170]. This synthesis was first carried out by Orlov in 1908 at 95–100° and atmospheric pressure on nickel–palladium catalysts [171,172]. According to modern patent information, ethylene is formed on iron catalysts promoted by compounds of copper, titanium, manganese, chromium, molybdenum, aluminium, thorium, cerium, and zirconium, and containing 20–50% of aluminium, magnesium, and zinc silicates. The reaction occurs at atmospheric or slightly increased pressure, 470–600°, and a space velocity of circulating gas mixture of 500–5000 $h^{-1}$ ($CO : H_2$ 1 : 1–2, circulation coefficient 0.5–5). It is necessary to add to the reaction zone small amounts of ammonium chloride or fluoride or other compounds that form hydrogen halides under the reaction conditions [166]. The following catalysts have also been proposed [168]: (1) zinc and chromic oxides with the addition of magnesium oxide; the chromic oxide may be replaced by the oxides of vanadium, niobium, tantalum, molybdenum, or tungsten, and the zinc oxide by oxides of cadmium, copper, or silver; (2) one of several metals in Group VIII of the Periodic System or their compounds; (3) the oxide or hydroxide of aluminium and/or the oxides of silicon, titanium, zirconium, hafnium, thorium, cerium, vanadium, or rare-earth elements; and finally (4) carbonates, oxides or hydroxides of the alkali metals. The catalysts may be deposited on a carrier of kieselguhr, silica gel, or clay. On a catalyst of composition $51Zn + 0.13Cr_2O_3 + 0.64Co + 0.04K_2O + 100Al_2O_3$ at atmospheric pressure, a temperature of 430°, and a space velocity of 350 $h^{-1}$, 25 litres of $C_2H_4$ and 2 litres of $C_2H_6$ were obtained per cubic metre of gas (1 $CO : 1\ H_2$). A catalyst of 3% CuO on $Al_2O_3$ is active at 20–40 atm and 250°. [169] Ethylene is also formed by passing a gas mixture (1–3 $CO : 1\ H_2$) at 350–550° and atmospheric pressure through a copper tube at a space velocity of 370–2500 $h^{-1}$. [170]

### 3. Synthesis of Alcohols

As early as 1913 it was discovered in the Badische Anilin- und Soda-Fabrik that a mixture of alcohols, aldehydes, ketones, and acids with a small admixture of hydrocarbons is formed from carbon monoxide and hydrogen at 300–400° and 100–200 atm in the presence of cobalt and osmium oxides deposited on asbestos and activated by alkalis [173]. Fischer and Tropsch set up the Synthol process operating at 400–450° and 100–150 atm in the presence of iron oxide promoted by alkali; this gave a complex mixture of alcohols, aldehydes, ketones, and acids from carbon monoxide and hydrogen [174]. Later, in Germany the Synthol process with fused iron catalysts, of the type used in ammonia synthesis, at 190–220° and 20 atm was used to obtain a liquid product (yield 170–180 g $m^{-3}$) containing 60–70% of alcohols from a $1\ H_2 : 1–1.3$ CO mixture [5,175,176]. The products obtained on precipitated iron–copper catalysts at 180–220° and 30 atm also contained a large amount of oxygenated compounds, comprising 75–80% of alcohols and ethers and 25–20% of carbonyl compounds, or under slightly different conditions, 80% of alcohols and 20% of ethers and carbonyl compounds [177]. The alcohols were primary with only a small amount of branching.

An important step forward in the synthesis of alcohols from carbon monoxide and hydrogen was the development of zinc–copper and zinc–chromium catalysts, in the presence of which methyl alcohol is selectively formed [178-181]. Methanol is synthesised industrially at 300–325 atm, 325–375°, and a space velocity of circulating gas (1 $CO : 2\ H_2$) of 10 000 $h^{-1}$. When the starting gas contained stoichiometric proportions of carbon monoxide and hydrogen, difficulty was encountered in controlling the reaction temperature. The process was considerably improved by reducing the concentration of carbon monoxide in the circulating gas to 5–6%. [182,183] It was found possible to combine the synthesis of methanol with degradative hydrogenation processes in vapour and liquid phases and with the ammonia synthesis; this made the product cheaper.

The synthesis of higher alcohols from carbon monoxide and hydrogen is thermodynamically more favoured than the synthesis of methanol [5,184]. Displacement of the reaction towards the production of higher alcohols is promoted by a higher temperature (above 400°), a lower space velocity of starting gas, and alkaline additives in the catalyst. Higher alcohols were formed at 380–490°, 150–250 atm, and a space velocity (of $H_2 : CO = 5–1 : 1$) of 2000–20 000 $h^{-1}$ on modified oxide catalysts. [184] The alcohol content of the reaction product reached 60% with methanol and primary isobutanol predominating [184-185]. At lower temperatures the reaction product contained up to 20% of ethanol. Selective catalysts for the synthesis of ethanol are obtained on the basis of Group VIII metals [186-191].

In the presence of fused iron catalysts [188-191], promoted by oxides that are difficult to reduce ($ZrO_2$, $Al_2O_3$, ZnO, $TiO_2$, $V_2O_5$, $Cr_2O_3$) and alkaline additives, at 150–180°, 200 atm, and a space velocity of 300–2000 $h^{-1}$, a yield of liquod product of 160–170 g $m^{-3}$ was obtained from a 1 CO : : 2 $H_2$ gas mixture. The product contained 85–100% of oxygen-containing compounds, 80–90% of which were normal alcohols and 5–10% carbonyl compounds. Ethanol and unsaturated hydrocarbons have been synthesised from a $3\ CO_2 : 1\ H_2$ gas mixture at 200–350 atm, 335–370°, and a space velocity of circulating gas of 10 000–20 000 $h^{-1}$ on fused iron catalysts with oxide ($K_2O$, $Al_2O_3$, $SiO_2$, MnO, etc.) additives [190].

Natural mineral talc with the addition of barium aluminate and potassium carbonate may be used as catalyst in the synthesis of oxygen-containing compounds [149-154,192]. The reaction product obtained at 430°, 30 atm, and a space velocity of 500 $h^{-1}$ with a mixture (1 : 1) of carbon monoxide and hydrogen contained up to 80% of alcohols and carbonyl compounds. After supplementary hydrogenation it consisted of a mixture of alcohols with n-propyl and isopropyl alcohols predominating.

## III. KÖBEL–ENGELHARDT SYNTHESIS OF ORGANIC COMPOUNDS FROM CARBON MONOXIDE AND WATER VAPOUR

The synthesis of hydrocarbons from carbon monoxide and water vapour, discovered by Kölbel and Engelhardt in connection with a study of the mechanism of the Fischer–Tropsch synthesis on iron catalysts, proceeds according to the following overall reaction [35,70,193]

$$3CO + H_2O = 2CO_2 + CH_2 + 58.4\ \text{kcal mole}^{-1}. \quad (1)$$

This discovery became practicable after it had been shown experimentally that the formation of carbon dioxide is due to a secondary water-gas reaction[87,88]

$$CO+H_2O \rightleftarrows CO_2+H_2+9.5 \text{ kcal mole}^{-1}. \quad (2)$$

Water is formed by the primary reduction of carbon monoxide:

$$CO+2H_2=CH_2+H_2O+39.4 \text{ kcal mole}^{-1}. \quad (3)$$

On examination of the thermodynamics of the reduction of carbon dioxide to higher hydrocarbons[194-196]

$$CO_2+3H_2=CH_2+2H_2O+29.9 \text{ kcal mole}^{-1} \quad (4)$$

of the Fischer–Tropsch synthesis with the separation of water (3) or $CO_2$

$$2CO+H_2=CH_2+CO_2+48.9 \text{ kcal mole}^{-1}, \quad (5)$$

and of the interaction of carbon monoxide and water vapour by reaction (1), it was found that at 200–250° conditions are much more favourable for the formation of hydrocarbons from carbon monoxide and water vapour (1) than for the Fischer–Tropsch reaction (3). All the reactions examined are formally derived from the Fischer–Tropsch reaction (3), when account is taken of the water-gas reaction (2). The formation of hydrocarbons from carbon monoxide and water is possible at temperatures up to ~500°.

Kölbel–Engelhardt catalysts have as basis metals of Group VIII — iron, cobalt, nickel, or ruthenium — and they do not differ in composition and method of preparation from Fischer–Tropsch catalysts[113,197-202]. Optimum conditions for the synthesis of hydrocarbons from carbon monoxide and water vapour are given in Table 4. In addition to the formation of hydrocarbons, side-reactions also occur: these include the water-gas reaction, the decomposition of carbon monoxide

$$2CO \rightarrow C+CO_2, \quad (6)$$

methane formation

$$CO+3H_2 \rightarrow CH_4+H_2O, \quad (7)$$

and oxidation of iron present in the catalyst. These side-reactions can be kept to a minimum by changing the conditions of the process and the composition of the catalysts.

TABLE 4. Conditions and yield of products in synthesis of hydrocarbons from carbon monoxide and water vapour.

| Conditions | Catalyst based on | | | | |
|---|---|---|---|---|---|
| | Fe | | Co | Ni | Ru |
| | stationary layer | liquid-phase synthesis | | | |
| Temperature, °C | 220—240 | 240—280 | 200—240 | 190—205 | 160—199 |
| Pressure, atm | 1—100 | 15—20 | 1—10 | 2.5 | 50—110 |
| Space velocity of initial vapour–gas mixture, $h^{-1}$ | 10—100 | — | 10—50 | — | 16—48 |
| Initial $CO:H_2O$ ratio | 3:1—2:1 | 3:1,15 | 3:1—1:1 | 2:1 | — |
| Degree of conversion of CO, % | 92—98 | 93 | 86—97 | 50—60 | 34—71 |
| Yield, g $m^{-3}$ CO | | | | | |
| $C_1$ | 4—12 | } 22 | 2—4 | 25.0** | } 2.8—4.4 |
| $C_2$ | 11—14 | | } 204 | 0.3 | |
| $C_3$ and higher | 140—190 | 160 | | 74.7 | 66—142 |
| Total hydrocarbons | 160—210 | 182 | 206—208 | 100 | 70—145 |

* Duration of reaction, h.

** Composition of products of synthesis, %.

The addition of alkaline agents to the catalyst considerably diminishes methane formation, and the addition of oxides that are difficult to reduce prevents the formation of carbon[194-196]. In the presence of iron and cobalt catalysts the formation of hydrocarbons proceeds most smoothly in the temperature range 200–240°, 93–98% of the carbon monoxide being converted into liquid products. At temperatures below 200° only the water-gas reaction occurs. At temperatures above 240° the formation of methane and carbon is accelerated, and the proportion of carbon monoxide that goes to form liquid products decreases[195,203,204]. Increasing the space velocity at atmospheric pressure leads to a decrease in side-reactions and in the total yield of liquid hydrocarbons. It has been found that, in general, the maximum space velocity, expressed in $hour^{-1}$ with 90% conversion of carbon monoxide, should be 9–12 times the total pressure expressed in atmospheres. In contrast to the Fischer–Tropsch synthesis, increasing the total pressure leads to an increase in catalyst efficiency and to a weakening of side-reactions. To ensure normal operation of the synthesis it is necessary to adhere to a stoichiometric $CO:H_2O$ ratio in the gas mixture of 3:1 for the preparation of hydrocarbons and of 2:1 for the synthesis of oxygen-containing compounds. An excess of carbon monoxide leads to an increase in coke formation, especially at atmospheric pressure[203], and an excess of water vapour leads to oxidation and deactivation of the catalysts[196,203,205,206]. Iron catalysts are the most easily oxidised, and for these the $CO:H_2O$ ratio should not be less than 2:1. The stability of the catalysts is increased by treating them with a 3 CO : 1 $H_2$ mixture at 220°; cobalt catalysts are treated at 200° and a space velocity of 80 $h^{-1}$, or with ammonia at 200° and 300 $h^{-1}$.[206]

The reaction products obtained under optimum conditions are saturated and unsaturated aliphatic hydrocarbons mixed with small quantities of oxygen compounds. The reaction products obtained on iron and cobalt catalysts contain 50–70% of olefins. On nickel catalysts the main products are saturated hydrocarbons[207,208]. When the partial pressure of the water vapour is increased, the molecular weight of the products and their content of unsaturated compounds decrease; a total pressure up to 16 atm with a 1 CO : 1 $H_2O$ mixture as starting gas has no effect on the degree of saturation of the reaction products[203]. An increase in pressure to 100 atm promoted the formation of ~30% of oxygen-containing compounds, mainly alcohols. In the presence of ruthenium catalysts[209], as in Pichler's synthesis[156,157], solid paraffin hydrocarbons with a mean molecular weight of 500–7000 are formed. Gases, free from catalyst poisons, containing even small amounts of carbon monoxide, such as blast-furnace and other industrial gases, may be used as raw materials in the synthesis of hydrocarbons from carbon monoxide and water vapour[194-196,210]. The synthesis is carried out on a very large scale in the presence of iron catalysts in the liquid phase with a space efficiency of 272 kg of hydrocarbons ($C_3$ and higher) per day per cubic metre of reaction space[113]. Petrol, diesel fuel, or solid paraffin can be obtained as the main product according to the conditions of the process and the composition of the catalyst. In all cases the products contained 70–80% of unsaturated hydrocarbons.

As kinetic measurements have shown, the process by which hydrocarbons are synthesised from carbon monoxide and water vapour consists of a series of very fast successive water-gas (2) and carbon monoxide reduction (3) reactions[208,211-214]. When the time of contact with iron, cobalt, and nickel catalysts is increased, the content of carbon

dioxide and hydrocarbons in the reaction mixture increases, while that of carbon monoxide and water vapour falls continuously. The hydrogen content passes through a maximum, which decreases as pressure increases, and increases with increase in the $H_2O:CO$ ratio. In the region of high partial pressures of carbon monoxide and water vapour, the rate of formation of hydrogen according to Eqn. (2)

$$r_1 = k_1 P_{CO}^a P_{H_2O}^b, \quad (8)$$

predominates over the rate of its disappearance by reaction (3)

$$r_2 = k_2 P_{CO}^c P_{H_2}^d. \quad (9)$$

As the partial pressures of carbon monoxide and water vapour decrease, the rate of formation of hydrogen decreases, but the rate at which it enters into reaction increases. The two rates become equal when the reaction products contain the maximum amount of hydrogen as a function of the time of contact. As the partial pressures of carbon monoxide and water vapour are further decreased, $r_2$ becomes greater than $r_1$. The numerical values of the exponents of the partial pressures — $a$, $b$, $c$, and $d$ — in Eqns. (8) and (9) depend mainly on the surface concentrations, and differ little with iron, cobalt, and nickel catalysts (Table 5),

The rate constants $k_1$ and $k_2$ are determined by adsorption factors and differ from one another in different ways with different catalysts. With iron catalysts $k_1 > k_2$, with cobalt catalysts $k_1 \simeq k_2$, and the ratio of the rate constants of the hydrogen formation and consumption reactions decrease in the sequence

$$\left(\frac{k_1}{k_2}\right)_{Fe} > \left(\frac{k_1}{k_2}\right)_{Co} > \left(\frac{k_1}{k_2}\right)_{Ni}. \quad (10)$$

After hydrogen has been formed by reaction (2) it is desorbed into the gas phase to the extent of two-thirds on iron catalysts, one-third on cobalt catalysts, and one-sixth on nickel catalysts. The synthesis of organic compounds from carbon monoxide and hydrogen has many features in common with the synthesis from carbon monoxide and water vapour; they are both based on the catalytic reduction of carbon monoxide by hydrogen. They occur on the same catalysts, they are accompanied by the same side-reactions, and their apparent activation energies are closely similar. The reaction products from the two processes have virtually the same fractional composition, but the products of the carbon monoxide and water vapour synthesis contain more olefins and oxygen-containing compounds. The temperature in the synthesis from carbon monoxide and water vapour is ~30 deg higher than in the Fischer–Tropsch synthesis. Material advantages of the synthesis of hydrocarbons and oxygen-containing compounds from carbon monoxide and water vapour are the insignificant amount of methane formation and the possibility of using cheap technical and effluent gases containing small amounts of carbon monoxide and large admixtures of inert gases.

TABLE 5. Reaction order of formation and consumption of hydrogen on iron, cobalt, and nickel catalysts in the synthesis of hydrocarbons from carbon monoxide and water vapour.

| Catalyst | Total pressure, atm | Reaction $CO+H_2O=H_2+CO_2$, $r_1=k_1 P_{CO}^a P_{H_2O}^b$ | | Reaction $CO+2H_2=CH_2+H_2O$, $r_2=k_2 P_{CO}^c P_{H_2}^d$ | |
|---|---|---|---|---|---|
| | | $a$ | $b$ | $c$ | $d$ |
| Fe | 11 | 0.5 | 0.2 | 0.2 | 1.5 |
| Co | 21 | 1.0 | 0.3 | −0.3...+0.3 | 1.0 |
| Ni | 5 | 0 | 0.6 | 0 | 0.6 |

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The synthesis of hydrocarbons and oxygen-containing compounds has thus been further developed in the last ten years. New technological schemes have been worked out, and cheap, readily obtainable, and effective catalysts have been developed on the basis of iron. A new method of reducing carbon monoxide with water vapour has been worked out; with this process effluent gases can be used and valuable products can be obtained. Interesting results have been obtained in putting into practice directed synthesis of oxygen compounds, mainly alcohols, macromolecular solid paraffins, and ethylene.


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# SOME REGULARITIES IN THE POLYMERISATION OF BIFUNCTIONAL MONOMERS

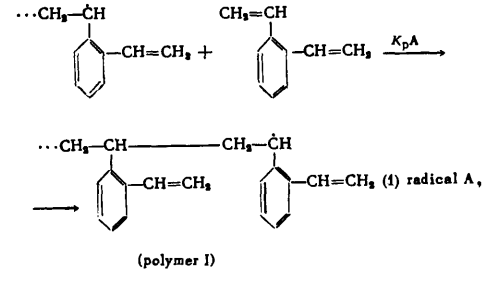
V. V. Amerik and B. A. Krentsel'

The development of processes of linear and stereospecific polymerisation, which has considerably extended the range of polymerisable compounds and opened up new possibilities for controlling the growth of macromolecules, has given rise to a natural interest in the polymerisation of bifunctional monomers. Several new regularities have been discovered in the polymerisation of these monomers, which are of scientific and practical importance.

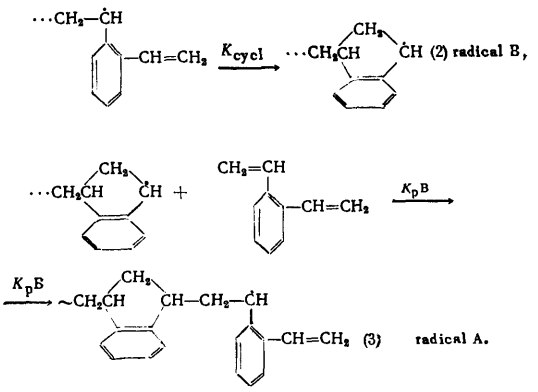
In the polymerisation of the simplest symmetrical bifunctional monomer, butadiene, either 1,2- or 1,4-addition is possible. A polymer chain of desired structure can be obtained by using a definite type of catalyst. The polymerisation of bifunctional compounds in which the two carbon–carbon double bonds differ in electron density is still more influenced by the type of catalyst (cationic or anionic) and by the solvent.

If a bifunctional compound containing a heteroatom attached to one of the double bonds is used as monomer, the structure of the resulting polymer depends not only on the nature of the catalyst and the solvent but also on the temperature of polymerisation. In spite of several investigations published in the literature, these questions are still far from being completely elucidated.

The polymerisation of bifunctional compounds containing two double bonds in the *ortho*-position has been studied with *o*-divinylbenzene as example [1]. This monomer was polymerised by a radical mechanism (with $\alpha\alpha'$-azoisobutyronitrile as initiator) in benzene solution. The resulting soluble polymer still contained double bonds, as was confirmed by their spectra and by bromination in carbon tetrachloride. Therefore the following three reactions can be assumed for growth of the polymer chain:




(polymer I)



The mole fraction of monomer units containing unchanged vinyl groups is given by the equation

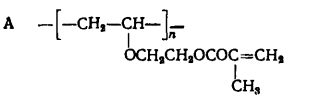
$$-\frac{dm}{dM}=\frac{2[M]}{2[M]+r_c}\quad r_c=\frac{K_{cycl}}{K_pA},$$

where [M] is the molar concentration of monomer and $m$ the concentration of polymer (I). It is obvious from this equation that the content of monomer units containing unchanged vinyl groups will depend on the initial concentration of the monomer, since $r_c$ is constant.

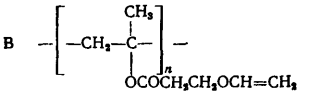
If the polymer contains one vinyl group per monomer unit, the content of polymer (I) is taken as 100%. Usually, however, it was always less than 100%, varying from 30% to 90% depending on the conditions of polymerisation. The content of monomer units containing vinyl groups falls with a decrease in the concentration of monomer in the initial mixture and with a rise in the temperature of polymerisation, since conditions favouring the cyclisation reaction (2) are produced. This fact is explained by the difference in activation energy between the bimolecular growth in the polymer chain (1) and the intramolecular cyclisation (2). Addition of *o*-divinylbenzene in the growth reaction occurs in the same way as with styrene. The growing radical A has a rather larger delocalisation energy than the styrene radical, while the cyclic radical B possesses a far smaller delocalisation energy. Hence a higher activation energy is required for intramolecular cyclisation than for addition of the monomer. The thermal polymerisation of *o*-divinylbenzene therefore results in formation of a linear polymer containing five-membered rings. Chain growth takes place mainly in conformity with Eqn. (1).

Various bifunctional monomers containing two or more carbon–carbon double bonds have been synthesised[2], and found to differ greatly in their tendency to form growing ions or free radicals depending on the mode of initiation of the reaction. Vinyl ethers of phenols containing the unsaturated side-chain $CH_2:CHOCH_2CH_2OR$, where R represents phenyl, allylphenyl, methylallylphenyl, 2-allyl-4-chlorophenyl, or but-2-enyl, were subjected to low-temperature polymerisation in the presence of boron trifluoride. Linear polymers were obtained, whose infrared spectra confirmed that the vinyloxy-group was involved in the polymerisation. This is explained by the greater electron density on the vinyloxy-bond and the greater reactivity of the latter compared with the allyl functional group.

The unsuccessful attempt to polymerise the resulting oligomers at the allyl double bond by using radical initiators is explained by the so-called degradation mechanism of chain transfer[3]. The radical which is formed is strongly stabilised by delocalisation of the unpaired electron. Polymerisation of 2-vinyloxyethyl methacrylate with cationic and anionic catalysts gave polymers of varying structures. This compound $CH_2:C(CH_3)COOCH_2CH_2OCH:CH_2$ contains two types of double bonds, the electron-rich vinyloxy-bond and the electron-deficient methacrylate double bond[4]. Chain growth takes place differently with cationic and with anionic catalysts, giving polymers of structures A and B respectively



(cationic catalyst),

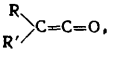


(anionic catalyst).

The polymerisation of 2-vinyloxyethyl methacrylate over tin(IV) chloride has been described[5]. The infrared spectra of the polymer obtained by polymerisation in solution in carbon tetrachloride at 0° showed complete disappearance of the 1780 $cm^{-1}$ band characteristic of the vinyloxy-group, while the bands at 1000–1650 $cm^{-1}$ characteristic of the methacrylate double bond remained. Consequently the resulting polymer had structure A. Polymerisation of 2-vinyloxyethyl methacrylate on a Ziegler catalyst at -20° gave a polymer of structure B, soluble in benzene. Polymerisation on the same catalyst at +25° gives a mixture of A and B polymers (see Table 1).

It can be assumed from these results that the nature of the active centres in Ziegler catalysts depends not only on the proportions of the components but also on the temperature of polymerisation. This is probably the reason for the contradictory results obtained by many authors in attempting to classify these catalysts as anionic or cationic.

A no less interesting class of bifunctional compounds are those in which a carbon–carbon double bond is accompanied by a carbonyl double bond. Among such monomers are keten, dimethylketen, biketen, and acrylaldehyde. The presence of cumulative carbon–carbon and carbonyl double bonds in ketens

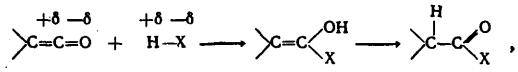


makes them highly reactive towards polar and non-polar molecules. The latter add on at the carbon–carbon double bond, and polar molecules at the carbonyl double bond. In many reactions, however, the products of addition to the

TABLE 1. Polymerisation of 2-vinyloxyethyl methacrylate on various catalysts.

| Catalyst | Solvent | Temp., °C | Conversion, % |
|---|---|---|---|
| $SnCl_4$ | $CCl_4$ | −20 | 90A |
| $TiCl_4$ + Al(iso-$C_4H_9$)$_3$ | $C_6H_{12}$ | −20 | 13B |
| Al/Ti 1.2 : 1 | | | |
| $TiCl_4$ + Al(iso-$C_4H_9$)$_3$ | $C_6H_{12}$ | +25 | 12A |
| Al/Ti 1.2 : 1 | | | 2B |
| Li tri-n-butylamine | $(C_4H_9)_3N$ | −25 | 30B |
| Triethylboron | $C_6H_6$ | 25 | 12A |

carbonyl group, which are in the enolic form, pass into carbonyl compounds:

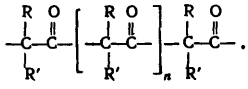


where HX is a substance containing polar groups.

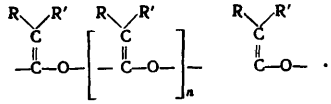
Structural units retaining the original form can therefore be observed only when keto–enol rearrangement in the reaction products is impossible, i.e. in the polymerisation of ketens. Linear and regular polymers of ketens may contain two structural units



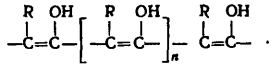
Regular "head-to-tail" addition of $\alpha$-monomer units gives macromolecules having an $\alpha$-ketonic structure



Similar addition of $\beta$-monomer units gives a polyacetal structure

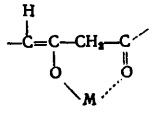


If R and R′ are hydrogen atoms, the $\alpha$-ketonic structure is in equilibrium with the enolic structure



In most cases only products of low molecular weight were isolated in the polymerisation of keten (see Table 2).

Natta and his coworkers[9] have attempted to polymerise keten using Friedel–Crafts catalysts ($ZnCl_2$, $AlCl_3$) and organometallic catalysts (triethylaluminium and butyllithium, di-n-butylzinc), and have obtained compounds having a chelate type of structure

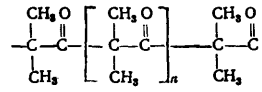


where M represents the metal. Degrees of conversion were low owing to deactivation of the catalyst.

Chelate structures are not formed if hydrogen atoms are not present in the monomer. At an early date Staudinger observed[7,10] the polymerisation of dimethylketen in the presence of trimethylamine as catalyst at -80°. The polymer had no regular chemical structure, and was completely converted into the monomer over the temperature range 100–200°.

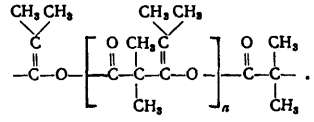
Polymers of dimethylketen having a regular structure have been obtained[9,11] with several types of catalysts — (1) acidic catalysts, which in most cases act by a cationic mechanism, and have the formula $AlX_nR_{3-n}$, where X is a halogen, R is an alkyl or an aryl radical, and $n$ = 1–3; and (2) catalysts of anionic type, containing metals of small ionic radius and possessing electronegativities not exceeding 1.6, such as triethylaluminium, diethylberyllium, ethyllithium, etc. (see Table 3).

With the first group of catalysts dimethylketen yields a white polymer of 60–80% crystallinity. The polymer is soluble only in strongly polar solvents of high boiling point. It melts close to 250°, and is thermally stable up to 300°, within which temperature limits it is not depolymerised to the monomer. Intense absorption bands in the region of 5.9 $\mu$m in the infrared spectra, and in the region of 259 m$\mu$m in the ultraviolet spectra, indicate the presence of carbonyl groups in the polymer, which suggests an $\alpha$-ketonic structure



(I)

The dimethylketen polymer (II), obtained in the presence of catalysts of the second group, differs markedly in structure from polymer (I). Its infrared and ultraviolet spectra confirm its polyester structure, since the absorption band due to carbonyl groups is weak, while a band is observed in the region of 5.74 $\mu$m, which is characteristic of ester groups



(II)

The structures of polymers (I) and (II) are confirmed also by chemical methods.

TABLE 2. Products of the polymerisation of keten.

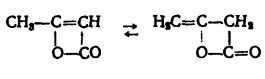
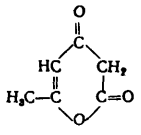
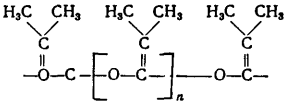
| Conditions of polymerisation | Products obtained | Ref. |
|---|---|---|
| 0–50°, no catalyst |  | 6 |
| 70–120°, pyridine as catalyst |  | 7 |
| -78° in acetone solution | $(C_2H_2O)_4$ | 8 |

TABLE 3. Polymerisation of dimethylketen in the presence of various catalysts at -78°.

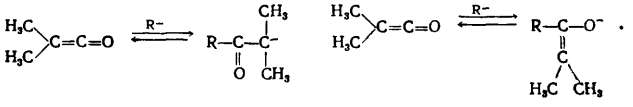
| Catalyst | Solvent | Conversion, % | Time, min | Structure of polymer | | |
|---|---|---|---|---|---|---|
| | | | | polyketone | polyester | polyacetal |
| $AlBr_2^*(C_2H_5)_2O$ | toluene | 18 | 360 | + | | |
| $AlBr_3$ | ether | 22 | 1800 | + | | |
| Na–naphthalene | toluene | 32 | 1440 | | + | |
| Na–naphthalene | dimethylformamide | 55 | 1440 | | | + |
| $C_2H_5ONa$ | toluene | 100 | 10 | | | + |
| Na–naphthalene | toluene | 93 | 3 | | | + |
| $C_4H_9Li$ | tetrahydrofuran | 86 | 12 | | | + |
| $C_4H_9Li$ | toluene | 18 | 1440 | | + | |
| $Al(C_2H_5)_3$ | toluene | 8 | 1440 | | + | |
| $BrMgC_2H_5$ | toluene | 15 | 1440 | + | + | |
| $Zn(C_2H_5)_2$ | – | 10 | 1440 | | + | |
| $(C_2H_5)_2NH$ | toluene | 35 | 1440 | | + | + |

* Polymerisation carried out at -50°.

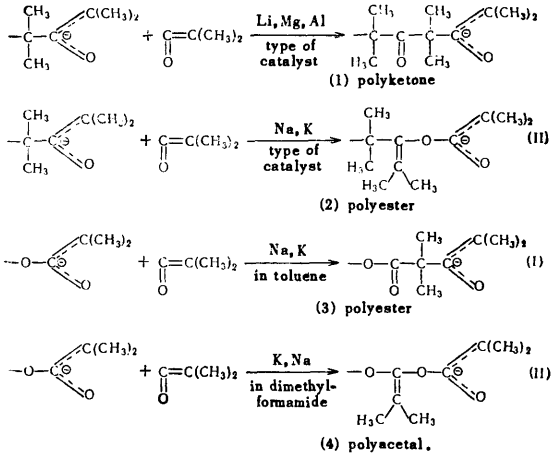
Polymers of dimethylketen which have a predominantly polyacetal structure have been obtained [11,12] by polymerisation in the presence of anionic catalysts ($C_4H_9Li$, $C_4H_9OLi$, Na–naphthalene, $C_2H_5ONa$). The polarity of the solvent influences the structure of the polymer obtained [12]. When dimethylketen is polymerised in the presence of the sodium–naphthalene complex as catalyst in toluene solution, polymers of polyester structure are obtained. Replacement of toluene (dielectric constant $\epsilon = 2.379$) by dimethylformamide (35.0) results in formation of a polymer of polyacetal structure. The infrared spectra of these polymers exhibit a band characteristic of carbon–carbon double bonds, and the products of acid alcoholysis and of hydrogenolysis in the presence of lithium tetrahydroaluminate indicate the presence of acetal links



The various reactions in the polymerisation of dimethylketen can be explained by postulating the following scheme for initiation and growth of the polymer chain [11,13,14]

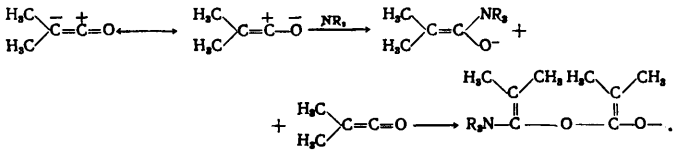


The following four types of reaction can be postulated in the stage of chain growth

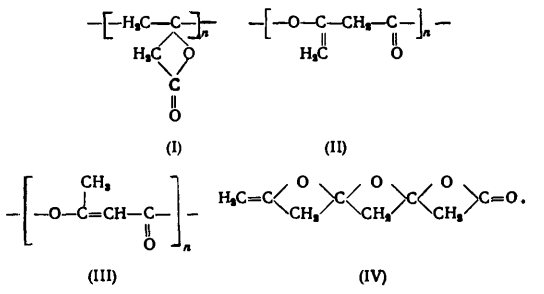



The driving force in the reaction of ketens with nucleophilic reagents is electrostatic interaction of the polarised keten molecule with electron-rich centres [15]. The anion (1) usually reacts with the next molecule of dimethylketen through the more electronegative oxygen atom according to Eqn. (2). The ester ion (II), under the influence of the oxygen atom, reacts more readily with the next monomeric molecule through the carbanion structure according to Eqn. (3). Polymerisation is also possible at the same time according to Eqns. (2) and (3) in the presence of catalysts containing sodium and potassium ions in toluene solution, which results in the formation of polyesters. Polyacetals are obtained, according to Eqn. (4), predominantly in polar solvents, such as dimethylformamide and triethylamine, which stabilise the enolic structure (II) by solvation. Japanese authors [14] give data on the polymerisation of dimethylketen in the presence of tertiary aliphatic amines. A more detailed study has shown [16] that the catalytic activity of tertiary amines increases with their dissociation constant. Increase in the polarity of the solvent results in an increased content of polyacetal structure in the polymer (see Table 4).

Polymerisation of dimethylketen in toluene also yields a considerable quantity of polyacetal structure, which represents an exception to the general rule of the effect of solvent polarity on polymer structure. It is interesting that, in dimethylformamide solution, dimethylketen polymerises in the absence of a catalyst. Dimethylformamide is probably sufficiently basic to initiate the polymerisation of dimethylketen in the absence of any other catalyst. In any case, rise in temperature results in a decrease in the proportion of polyacetal structure in the resulting polymer. The suggested mechanism of polymerisation when a series of amines are used as catalysts is that the first stage involves nucleophilic attack by the bases on the carbonyl group:



The influence of conditions on the polymerisation of biketen and the structure of the resulting polymer has been studied in less detail. The following four polymer structures can be imagined [17,18]




At room temperature biketen yields a dimer.

Fairly recently [19] a polymer of biketen of molecular weight ~ 1630 has been obtained in the presence of mercuric chloride as catalyst. It has the polyester structure (II).

TABLE 4. Effect of nature of solvent on polymerisation of dimethylketen at -40°; 50 ml of solvent, 0.4 vol. % of $(C_2H_5)_3N$.

| Solvent | Dimethylketen, ml | Time of reaction, min | Yield of polymer, % | $\frac{D_{5.85\,\mu m}^{*}}{D_{5.66\,\mu m}}$ |
|---|---|---|---|---|
| Cyclohexanone | 10 | 30 | 70 | 4.7 |
| Acetone | 10 | 15 | 65 | 11.7 |
| Diethyl ketone | 10 | 15 | 65 | 9.0 |
| Acetonitrile | 10 | 15 | 83 | 6.3 |
| Diethyl ether | 10 | 15 | 4 | (a) |
| Dimethylformamide (b) | 10 | 15 | 100 | 5.3 |

* $D_{5.85\,\mu m}$ = intensity of absorption band characteristic of polyacetal structure;

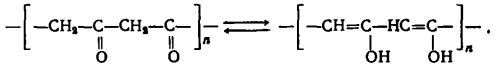
$D_{5.66\,\mu m}$ = intensity of absorption band characteristic of isolated polyester links.

(a) Mixture of polyester and polyacetal structures obtained.

(b) No catalyst present.

A polymer of polyester structure is also obtained[20] from biketen in the presence of aluminium ethoxide.

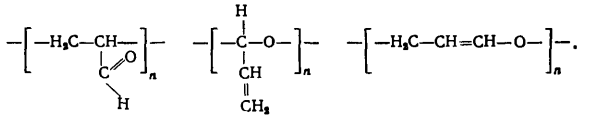
In the presence of boron trifluoride an amorphous polymer has been obtained[21,22] whose structure differs from those suggested previously. The molecular weight is comparatively low (2080) and the infrared spectra support a β-diketone structure



In ethylene glycol solution the ketonic form of the polymer is in equilibrium with the enolic form. This structure is confirmed also by the product obtained on reaction with phenylhydrazine, whose infrared spectrum has a band in the range 1600–1500 $cm^{-1}$, which is characteristic of the –C=C–C=N– grouping.

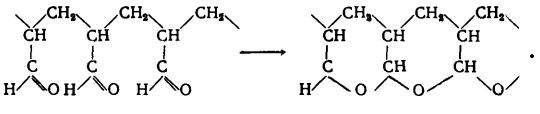
It is difficult to polymerise keten under these conditions, but the use of benzonitrile as catalyst has enabled a polymer of β-diketone structure to be obtained[22].

In the acrylaldehyde molecule, in contrast to dimethylketen, the two double bonds, carbon–carbon and carbon–oxygen, are conjugated. In the Diels–Alder reaction, acrylaldehyde acts as a diene[23,24], which suggests the formation of polymers having the structures



Several workers[25–27] have investigated the polymerisation of acrylaldehyde and studied the properties of the resulting polymers. Cationic polymerisation in the presence of aluminium chloride, zinc chloride, and ether complexes of boron trifluoride in various solvents (at 0–30°) yields soluble polymers containing reactive aldehyde groups (15–20%).

Koton and his coworkers have investigated[28] the polymerisation of acrylaldehyde in the presence of gaseous boron trifluoride with various additives over the range 0–80°. They obtained a vitreous polymer containing no free aldehyde groups. It is evident that the aldehyde group plays an active part in the polymerisation. The polymer is insoluble in organic solvents, but dissolves readily in sulphuric acid. Polymerisation takes place by a "head-to-tail" mechanism, all the aldehyde groups being located on the same side of the chain, which favours cyclisation through the $-C\overset{O}{\underset{H}{<}}$ group:



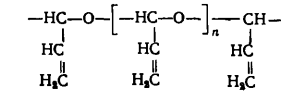
The cyclic structure of the polymer is indicated by its high thermal stability, while the absence of cross-linked structures is confirmed by the sharp melting point. Cyclisation does not occur on polymerisation on dilute solution.

Acrylaldehyde undergoes polymerisation in the 1,4-position in the presence of metallic sodium in boiling benzene[29]. The resulting polymer contains 5 mole % of aldehyde groups and 10–15% of double bonds.

Infrared and nuclear magnetic resonance data confirm that the polymer has the structure

$$[CH_2-CH=CH-O-CH_2-CH=CH-O]_n.$$

Anionic polymerisation of acrylaldehyde in the presence of various catalysts (see Table 5) between +25° and -78° yields polymers in whose infrared spectra the absorption band due to the carbonyl group (5.85 μm) has been considerably weakened or is completely absent[30]. The quantity of –C=C– double bonds, determined by hydrogenation of a solution of the polymer in glacial acetic acid, is 50–70%. Aldehyde groups were identified in the polymer by treating it with phenylhydrazine and then determining the nitrogen content. The proportion of aldehyde groups in polyacrylaldehyde obtained in the presence of anionic catalysts varies from 1% to 9%. The nature of the solvent affects not only the rate of polymerisation but also the chemical structure of the product. A decrease in the temperature of polymerisation and an increase in the polarity of the solvent decreases the quantity of free carbonyl groups in the polymer, which has the polyacetal structure



The epoxypropionaldehyde molecule, like that of acrylaldehyde, contains a reactive carbonyl group, but the position of the vinyl group is occupied by a heterocyclic ring, which can be regarded as a functional group. This aldehyde polymerises readily under the influence of catalysts of various types[20]. Thus triethylaluminium at -78° yields a polymer of polyacetal structure

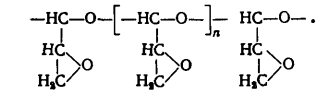
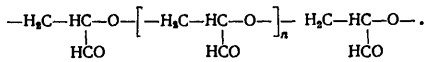


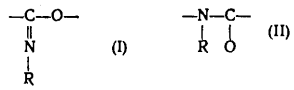
TABLE 5. Polymerisation of acrylaldehyde.

| Solvent | ml | Acrylaldehyde, ml | Catalyst | mole % | Time, min | Temp., °C | Yield of polymer, % |
|---|---|---|---|---|---|---|---|
| Petroleum ether | 25 | 5 | n-$C_4H_9Li$ | 0.5 | 300 | -20 to 30 | – |
| Toluene | 25 | 5 | n-$C_4H_9Li$ | 1.0 | 780 | -20 to -30 | 16 |
| Toluene | 30 | 5 | n-$C_4H_9Li$ | 1.0 | 600 | room temp. | 91 |
| Toluene | 25 | 5 | $C_6H_5MgBr$ | 4.5 | 60 | room temp. | trace |
| Diethyl ether | 30 | 5 | $(C_6H_5)_3CNa$ | 0.5 | 180 | -20 | 36 |
| Diethyl ether | 25 | 5 | $CH_3ONa$ | 1.0 | 240 | -30 | 46 |
| Dimethoxymethane | 45 | 5 | K–benzophenone | 0.5 | 150 | -30 | 33 |
| Tetrahydrofuran | 25 | 5 | Na–naphthalene | 0.5 | 840 | -78 | 5 |
| » | 45 | 5 | Na–naphthalene | 0.5 | 285 | -50 | 79 |
| » | 145 | 5 | Na–naphthalene | 1.0 | 240 | -50 to 60 | 66 |
| » | 50 | 5 | K–benzophenone | 0.5 | 150 | -50 to 60 | 55 |
| » | 30 | 5 | $(C_6H_5)_3CNa$ | 1.0 | 180 | -30 to -40 | 93 |
| » | 25 | 5 | $CH_3ONa$ | 1.0 | 150 | -40 | – |
| » | 25 | 5 | sodamide | 1.0 | 180 | -40 | 54 |
| » | 45 | 5 | Na | 1.0 | 225 | -50 | 48 |
| » | 15 | 5 | piperidine | 1.0 | 105 | 0 | 40 |
| » | 20 | 5 | $C_4H_9MgBr$ | 2.0 | 480 | room temp. | trace |
| 1,2-Dimethoxyethane | 20 | 5 | Na–naphthalene | 1.0 | 120 | -40 | 86 |
| Acetonitrile | 40 | 5 | $CH_3ONa$ | 1.0 | 25 | -35 | 48 |
| Methyl acetate | 30 | 5 | $CH_3ONa$ | 1.0 | 120 | -40 to 50 | 65 |
| No solvent | – | 15 | n-$C_4H_9MgBr$ | 5.0 | 1440 | room temp. | 30 |

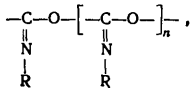
With aluminium isopropoxide, however, a polymer of polyepoxide structure is obtained



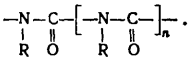
Isocyanates give dimers and trimers [31] in the presence of bases, triethylamine and pyridine. Two fundamental polymer structures



are possible on the stereospecific polymerisation of isocyanates. Regular opening of the carbonyl double bond gives a macromolecule of polyacetal structure

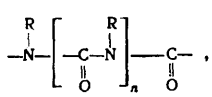


whereas regular opening of the carbon–nitrogen double bond yields an amide structure



Natta and others have obtained polymers of phenyl and butyl isocyanates by low-temperature polymerisation [32,33]. Only traces of polymers were formed in the presence of catalysts of cationic type, but with the corresponding anionic catalysts crystalline polymers of these isocyanates were formed (see Table 6).

The presence in the infrared spectra of an intense band characteristic of disubstituted amides suggests that the polymer has a polyamide structure



where R represents phenyl or butyl. Polymers having the polyacetal or mixed structure were not obtained.

Analysis of the above results on the polymerisation of bifunctional monomers enables the following general conclusions to be drawn:

1. In the polymerisation of a bifunctional compound containing double bonds differing in electron density, the structure of the resulting polymer is determined to a considerable extent by the choice of catalyst (anionic or cationic).

TABLE 6. Polymerisation of phenyl and n-butyl isocyanates.

| Isocyanate | Catalyst | Solvent | Temperature, °C | Conversion, % |
|---|---|---|---|---|
| Phenyl | $AlBr_3$ in heptane | toluene | −60 | trace |
| Butyl | | toluene | −78 | – |
| Phenyl | $C_2H_5Li$ in benzene | $CS_2$ | −78 | 34.5 |
| Butyl | | $CS_2$ | −78 | 76.0 |
| Phenyl | | toluene | −78 | 45 |
| Butyl | $C_2H_5Li$ | toluene | −78 | 43 |

2. Growth of the polymer chain is determined not only by the reactivity of each bond but also by the polar effect. In the polymerisation of dimethylketen, for example, a polyester structure is formed: i.e. there is a strongly marked tendency for alternating polymerisation at the carbon–carbon and the carbonyl double bond. This results in formation of a characteristic copolymer.

3. Decrease in the temperature of polymerisation of monomers containing carbon–carbon and carbonyl double bonds results in increased specific gravity in the polymer of polyacetal structure. The structure of the polymer is probably determined by the thermodynamics of the process. At lower temperatures polymerisation becomes possible with a small heat of reaction: i.e. a polymer of mixed and polyacetal structure can be formed.

4. The polarity of the solvent affects not only the rate of polymerisation but also the structure of the polymer chain. An extreme case is provided by dimethylformamide, in which dimethylketen polymerises in the absence of a catalyst.


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# THE FREE-RADICAL COPOLYMERISATION OF ETHYLENE

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## I. INTRODUCTION

Copolymerisation has now acquired considerable importance as a method which makes it possible to alter the properties of a polymer in a required direction. By selecting different combinations of ethylene with appropriate monomers, it is possible to vary over a wide range such properties of the polymer as its strength, elasticity, melting point, adhesive properties, solubility, etc.[1,2] Copolymers of ethylene can be prepared both by free-radical copolymerisation and by ionic copolymerisation. The free-radical process, in particular, is of considerable interest, since in this case the number of monomers which can be used with ethylene is much greater than for ionic copolymerisation. The ionic process is carried out chiefly with monoalkene and diene hydrocarbons, whereas the copolymerisation of ethylene by the free-radical mechanism can be carried out not only with these hydrocarbons but also with a large number of compounds of different types, including halogenated alkenes, vinyl esters and ethers, acrylic monomers, and even compounds which do not polymerise independently, such as sulphur dioxide and carbon monoxide[1,2]. Moreover, the presence of different functional groups (e.g. acetate and carbonyl groups) in the copolymers prepared by radical copolymerisation makes it possible to convert these polymers, by means of chemical reactions, into a number of new copolymers (binary or ternary in the case of partial replacement of the functional groups) which cannot be obtained by direct copolymerisation with ethylene.

The present review deals with copolymers of ethylene prepared by radical copolymerisation, and covers the literature up to September 1964. Work published before 1959 is mentioned only briefly, since this has been described in detail in monographs devoted to polyethylene[1,2], and more recent work is examined in greater detail.

## II. GENERAL PROBLEMS OF THE COPOLYMERISATION OF ETHYLENE

Copolymers of ethylene, with such readily polymerised monomers as styrene, vinyl acetate, and acrylic acid, were first prepared as early as 1930,[3] i.e. before polymers of ethylene itself had been prepared. In the presence of peroxo-compounds under conditions of low pressure, a small quantity of ethylene was introduced into the polymer. However, the copolymerisation of ethylene with unsaturated compounds of different types[4] was described for the most part after the discovery of polyethylene. Styrene, isobutene, methyl acrylate, n-butyl acrylate, methyl methacrylate, vinyl acetate, butadiene, etc. were proposed as secondary components. The copolymerisation was carried out by a method analogous to that used for the polymerisation of ethylene, by the block method under conditions of high pressure (1000–2000 bars) and relatively high temperature (100–300°), in the presence of oxygen or peroxo-compounds as initiators[5-9]. It has been shown comparatively recently that it is possible to copolymerise ethylene under the influence of ionising radiation with alkenes[10], vinyl chloride, vinyl acetate, and carbon monoxide[11].

Colombo and Steinberg[12-14] describe the radiation copolymerisation of ethylene with a large number of monomers — propene, but-1-ene, *cis*- and *trans*-but-2-ene, isobutene, isoprene, vinyl chloride, chlorotrifluoroethylene, vinyl acetate, allyl acetate, allyl alcohol, acrylonitrile, methyl methacrylate, styrene, divinylbenzene, vinylpyrrolidone, methyl vinyl ketone, and carbon monoxide. In a number of cases, however, the data on the composition and properties of the resulting copolymers, given by Colombo and Steinberg, are of doubtful accuracy, since the copolymerisation was carried out to high degrees of conversion. On the basis of the data given below on the relative activities of monomers, it may be assumed that, in the case of copolymerisation with methyl methacrylate, methyl acrylate, vinylpyrrolidone, methyl vinyl ketone, and also possibly with propene and allyl acetate, the reaction products contained polyethylene.

Kolesnikov and his coworkers[15,16] showed that it is possible to copolymerise ethylene with certain monomers (vinyl chloride, styrene, vinyl acetate, acrylonitrile, and methyl methacrylate) under the influence of alkylborons.

The copolymerisation temperature for ethylene covers a very wide range, from -70° to 250°. The process is usually carried out at 180–250° in the case of initiation of copolymerisation by molecular oxygen[4] or within the range 50–150° for initiation by organic peroxides[5-9]. The use of $\gamma$-radiation[12] and alkylborons[16] makes it possible to carry out the copolymerisation at or below room temperature. The possibility is not excluded that at temperatures below 0° the process takes place partly or completely by an ionic mechanism. In particular, ethylene is known to polymerise by a cationic mechanism under the influence of $^{60}Co$ $\gamma$-radiation at -78°.[17,18]

The radical copolymerisation of ethylene is most frequently carried out at a pressure of ~ 1000 bars[4,8,9]. The use of such high pressures is apparently necessary in order to produce a high concentration of ethylene to ensure sufficiently rapid reaction and to obtain copolymers of optimum

molecular mass. It may be assumed, however, that this condition to some extent applies only to the copolymerisation of ethylene with a small quantity of a second component in the gas phase. In the case of copolymerisation in the liquid phase, pressure plays a smaller part and may be reduced to 100–300 bars[5,15,16].

The process is carried out, not only by block copolymerisation, but also in low-boiling organic solvents (e.g. benzene, toluene, or isooctane)[9,15,16], in water[7,8], and in emulsion[6].

Some idea of the physical properties of copolymers of ethylene can be obtained on the basis of a comparatively simple model consisting of a polymethylene chain in which hydrogen atoms have been replaced by different side-groups. The properties of the copolymers will be determined by the nature of the second component, its concentration in the copolymer, and the nature of the distribution of monomer units of the second component along the length of the chain.

The influence of the nature of the second component involves chiefly two factors, the polarity and the dimensions of the monomer units. The presence of polar units in the polyethylene chain brings about intermolecular and intramolecular interaction between the permanent and induced dipoles, leading to an increase in the rigidity and a rise in the melting point; at the same time there is a deterioration in the dielectric properties of the polymer, and its adhesion to various materials increases.

In the molecules of ethylene copolymers containing a small quantity of the second component, the units of the latter will generally be attached only to non-polar and unpolarised methylene groups, which have no significant influence on their dipole moment. In this case the dipole moment of the units can be taken as approximately equal to that of the corresponding hydrogenated compound. The dipole moments of compounds which are the hydrogenated analogues of the second components in ethylene copolymers are given in Table 1. In conformity with the data in Table 1, the greatest rigidity and highest melting point among the known types of ethylene copolymer are shown by the copolymers with carbon monoxide and sulphur dioxide.

TABLE 1. Dipole moments of various hydrogenated analogues of second components in copolymers of ethylene[19].

| Compound | Dipole moment, D |
|---|---|
| Hydrogenated analogues of methyl acrylate*, vinyl alcohol, methyl methacrylate**, ethyl acrylate, n-butyl acrylate, vinyl chloride, vinyl acetate, vinyl fluoride, and vinylidene chloride | 1.7–1.9 |
| 1,1-Difluoroethane (vinylidene fluoride) | 2.2 |
| Diethyl ketone (carbon monoxide) | 2.7 |
| Acetonitrile (acrylonitrile) | 3.3 |
| Succinic anhydride (maleic anhydride) | 3.8 |
| Diethyl sulphone (sulphur dioxide) | 4.4 |
| Ethylene carbonate (vinylene carbonate) | 4.7 |

* The dipole moment of the monomer unit of methyl acrylate attached to two monomer units of styrene in the copolymer of methyl acrylate with styrene is 1.61 D, and that of methyl methacrylate is 1.68 D. The production of induced dipoles in neighbouring phenyl groups possibly leads to a slight decrease in the dipole moments of the monomer units of methyl acrylate and methacrylate relative to those for the corresponding homopolymers[20,21].

** Shima's data[21].

The dimensions of the units of the second component influence the properties of the ethylene copolymer as follows. When side-groups whose dimensions differ little from those of the methylene groups are introduced into the polyethylene chain, the crystal structure of the polyethylene is not broken down: there is merely a change in some parameters of the crystal lattice, accompanied by a change in the physical properties of the polymer[22–25]. In particular, the melting points of these copolymers change monotonically with change in composition, from the melting point of polyethylene to that of the second homopolymer. This phenomenon, which is analogous to the formation of mixed crystals in the cocrystallisation of compounds of low molecular weight, has been termed isomorphism of monomer units in macromolecules[26]. Values of the van der Waals radii of some substituents are given in Table 2.[27] In conformity with these data, the formation of crystalline copolymers over a wide range of composition was observed in the copolymerisation of ethylene with tetrafluoroethylene and carbon monoxide†, and also in copolymers of ethylene with vinyl alcohol[22–25,28,29]. Determination of the crystal structure of copolymers of ethylene with vinyl alcohol led to a re-examination of previously held ideas on the nature of the crystallinity of high polymers[24,25].

If the dimensions of the side-groups are so great that packing of the copolymer molecules into the crystal lattice of polyethylene becomes impossible, the introduction of copolymer molecules into the polyethylene chain leads to a gradual decrease in the crystallinity of the copolymer. At a low concentration of the second component, the melting point of these copolymers falls rapidly, in agreement with Flory's formula[30]. At the same time there is a decrease in the hardness of the polymers and increases in their elasticity and solubility. At a low concentration of the second component the nature of these changes apparently depends chiefly on the quantity of added monomer and not on its nature. Thus the copolymers of ethylene with vinyl acetate, ethyl acrylate, *N*-vinylpyrrolidone, and *N*-vinylsuccinimide, obtained at 1000 bars and 70–90°, showed an approximately linear relationship between the logarithm of

TABLE 2. Van der Waals radii of substituents[27].

| Substituent | Van der Waals radius, Å |
|---|---|
| H | 1.17 |
| F | 1.35 |
| O | 1.35* |
| Cl | 1.80 |
| $CH_3$ | 1.90 |

* Bunn's data[24].

† The structure of the copolymer is

$$[(-CH_2CH_2-)_n-\underset{\underset{O}{\|}}{C}]_m$$

the modulus of rigidity and the molar content of the second component in the polymer, irrespective of the nature of the second component [31].

The influence of the dimensions of the unit of the second component on the crystallinity of the copolymers is clearly revealed on comparing the properties of the copolymers of ethylene with carbon monoxide and with propene (the latter copolymer was prepared on a Ziegler–Natta catalyst): the crystallinity of ethylene–carbon monoxide copolymers amounts to ~ 70% and is independent of the content of the second component; the crystallinity of ethylene–propene copolymers decreases linearly to zero with increase in the content of the second component from 0 to 15%. [32] This shows that carbonyl groups enter the polyethylene crystal lattice, whereas $CHCH_3$ groups break down the lattice‡.

The phenomenon of isomorphism of monomer units in macromolecules can be observed in the copolymers of ethylene and carbon monoxide. According to the data of Chatany et al. [34,35], copolymers obtained at room temperature in the gas phase have the crystal structure of polyethylene, but the lattice parameters change with increase in the carbon monoxide content.

Thus the two factors examined — the polarity and the dimensions of the unit of the second component — have opposite effects on the properties of the ethylene copolymers. If the unit of the second component is sufficiently large, steric factors predominate. For example, the copolymerisation of ethylene with small quantities of polar monomers such as vinyl acetate gives products whose rigidity and melting points are lower than those of polyethylene. On saponification of these copolymers, however, the opposite effects are observed, as a result of the replacement of the large acetate group by the comparatively small hydroxy-group, despite the fact that the dipole moment of the unit of the second component remains almost unchanged (see Table 1).

One of the most important factors influencing the properties of a copolymer is its composition. The nature of the dependence of the properties of ethylene copolymers on the relative proportions of the monomers is determined by the dimensions of the molecules of the second component. Where isomorphous crystalline structures are formed, we must expect a monotonic change in the properties of the copolymer with increasing content of the second component. If introduction of molecules of the latter leads to breakdown of the copolymer structure, the properties of the copolymer show a marked dependence on composition. The addition of even small quantities of monomers such as vinyl chloride and vinyl acetate leads to a marked fall in the melting point and the crystallinity of the copolymer. At a high concentration of the second component, the product acquires properties characteristic of the homopolymer of the second monomer. The influence of the composition of ethylene copolymers is not shown with all properties, however. In particular, the dependence of the temperatures of vitrification of ethylene copolymers on their composition is specific in character [36,37].

‡ Here and subsequently, conclusions regarding the crystallinity of copolymers are based on data obtained by X-ray structural analysis. However, structural criteria of crystallinity do not always agree with thermodynamic criteria [33]. Similarly no account is taken of the influence of intermolecular interaction in the molten state, the rigidity of the chain, and other factors on the kinetics of crystallisation and the tendency of the copolymers to undergo supercooling.

The dependence of the vitrification temperature of ordinary vinyl copolymers on their composition is described, to a first approximation, by the straight line joining the glass points of the corresponding homopolymers [38]. The vinyl chloride–vinyl acetate and vinyl chloride–acrylonitrile systems provide examples. It was to be expected that copolymers of ethylene would exhibit analogous properties, but they in fact exhibit quite different behaviour, as shown by Reding et al. [37] By means of a torsion balance and an apparatus for determining the maximum mechanical losses (Instron tester), they detected two glass points (two temperature transitions) in ethylene copolymers. The first, low-temperature transition takes place at -125° and is almost independent of the composition of the copolymers. The existence of this glass point was attributed [37] to the movement of segments comprising 3–5 $CH_2$ groups. The second, high-temperature transition is observed between -25° and +50°, and is independent of composition only at high ethylene contents (35–100 wt.%); at high concentrations of the second component, the glass point of the copolymer rises sharply, approaching linearly that of the corresponding homopolymer. It was not clear why the glass point of the copolymer remains unchanged over a wide range of compositions. Mandelkern et al. [39] suggested that in crystalline copolymers it is determined by the composition of the amorphous phase. Since in ethylene copolymers only the ethylene units crystallise with increase in the ethylene content, the composition of the amorphous phase remains constant, so that the vitrification temperature remains constant. A similar explanation for copolymers of ethylene with vinyl acetate was given by Nielsen [36], but, as correctly noted by Reding et al. [37], this explanation does not reflect the true situation, since with ethylene–vinyl acetate copolymers the last traces of crystallinity disappear at a content of the latter of 45 wt.%, whereas the glass point remains constant up to 65%. Reding and his coworkers suggest that the high-temperature transition in ethylene copolymers is associated with the localised movement of small segments of the main chain, attached to tertiary carbon atoms. This movement is independent of the nature of the remainder of the molecule. At a high concentration of the second component, as a result of steric hindrance or dipole–dipole interaction between the side-groups, this movement is transformed into movement of large sections of the macromolecules, including long sections of the chain and side-groups, analogous to that taking place in copolymers of the vinyl chloride–vinyl acetate type.

The two glass points of copolymers of ethylene with many monomers depend little on the nature of the second component [37].

It is evident that the properties of copolymers also depend on the distribution of the monomer units along the chain, which is determined by the product of the relative activities of the monomers (see Section III); if this quantity is close to unity, the monomer units are distributed irregularly; but with decrease in the magnitude of the product, the extent to which the monomers alternate increases. In particular, if the crystallinity of the copolymers is determined by the crystallisation of chain segments consisting of the units of only one monomer (e.g. ethylene), the crystallinity of such a copolymer increases with increase in the product of the relative activities of the monomers. This was confirmed for copolymers of ethylene with propene, having up to 10% crystallinity, obtained on Ziegler–Natta catalysts [40,41]. The crystallinity of ethylene copolymers has been studied by Killian [42].

The uses of ethylene copolymers have been dealt with in a number of reviews[43,44]. Some information on their applications is given in Section IV.

## III. THE REACTIVITY OF ETHYLENE IN RADICAL COPOLYMERISATION

Because of the experimental difficulties involved in carrying out copolymerisation under high pressures, data on relative activities have until now been published only for a comparatively small number of systems containing ethylene (Table 3). We ignore the values given by Pieski[55] for the relative activities in the copolymerisation of ethylene with styrene ($r_{ethylene} = 0.0069$, $r_{styrene} = 345$), since the conditions and methods of determination are unknown.

Since there is no conjugation of the double bond, the reactivity of ethylene as a monomer is low, so that the rate of attachment of ethylene molecules to both types of copolymer radical in copolymerisation with vinyl chloride, acrylonitrile, and n-butyl acrylate is less than the rate of attachment of molecules of the second component ($r_1 < 1$, $r_2 > 1$); the opposite relationship is observed in copolymerisation with vinyl fluoride.

If we take ethylene as standard monomer, the relative rates of attachment of monomers to copolymer radicals terminating in an ethylene group, in reactions of chain growth in the radical copolymerisation of ethylene, are given by the corresponding values of $1/r_1$. In Table 4 the values of $1/r_1$ for various monomers are compared with the relative rates of attachment of the same monomers to the methyl radical in the liquid phase at 65°, calculated from Szwarc's data given in Bagdasar'yan's monograph[56]. Since the relative activities generally depend little on temperature, the values of $r_1$ are taken from Table 3 without correction for temperature§. The relative rate of addition of propene to the methyl radical was calculated from the data of Mandelkern and Steacie[56] for a temperature of 175° (reaction in the gas phase). It can be seen from Table 4 that the relative reactivity of monomers towards both the methyl radical and copolymer radicals terminating in an ethylene group increases in the order propene < vinyl acetate < < tetrafluoroethylene < acrylonitrile. The values do not, however, show a quantitative relationship corresponding to Szwarc's equation[57] ($n$ not constant).

TABLE 4. Relative rates of attachment of monomers to the methyl radical and to copolymer radicals terminating in an ethylene group.

| Monomer ($M_i$) | $\frac{K_{CH_3^\cdot M_i}}{K_{CH_3^\cdot C_2H_4}}$ | $\frac{1}{r_1}$ | $n=\frac{\log\frac{K_{CH_3^\cdot M_i}}{K_{CH_3^\cdot C_2H_4}}}{\log 1/r_1}$ |
|---|---|---|---|
| Propene | 1.22 | 0.29 | —0.16 |
| Tetrafluoroethylene | 10 | 6.7 | 1.2 |
| Vinyl acetate* | 2.2 | 1.3 | 3.0 |
| Acrylonitrile | 91 | 50—1000 | — |

* The relative rate of attachment to the ethyl radical at 90° is 2.0; $1/r_1 = 0.93$.[48]

The relative rates of addition of propene to methyl and to copolymer radicals are quite different. The rate of attachment of propene to the methyl radical is greater than that of ethylene, whereas the opposite relationship is observed in the addition of these monomers to a copolymer hydrocarbon radical. The lower reactivity of propene in the latter case does not agree with the theory of ideal radical reactivity applicable to the reactions of hydrocarbons[58]. The reasons for the above discrepancies are not clear.

According to Alfrey and Price[58], the relative activities of monomers in copolymerisation reactions can be calculated by means of constants characteristic of individual monomers — the activity factor $Q$ and the polarity factor $e$ — which are calculated from experimental data. The values taken for styrene are $Q = 1.0$ and $e = -0.8$. A theoretical interpretation of the method of Alfrey and Price has

§ For vinyl acetate the value of $r_1$ at 70° has been taken.

TABLE 3. Experimental values of the relative activities and parameters for the copolymerisation of ethylene.

| Second component | Copolymerisation conditions | | Relative activities | | Ref. | $r_1 r_2$ | Copolymerisation parameters by methods of | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Alfrey and Price | | Kawabata et al. | | Spasskii and Karas* | |
| | temp., °C | pressure, b | $r_1$ (ethylene) | $r_2$ | | | $Q_1$ | $e_1$ | $Q_1$ | $e_1$ | $\alpha_1\beta_1$ | $\epsilon_1$ |
| Propene | 130—220 | 1000—1700 | 3.43±0.16 | — | 45 | — | — | — | — | — | — | — |
| But-1-ene | 130—220 | 1000—1700 | 3.25±0.38* | — | 45 | — | — | — | — | — | — | — |
| Oct-1-ene | 130—220 | 1000—1700 | 3.66±0,15 | — | 45 | — | — | — | — | — | — | — |
| Vinyl chloride | 70 | до 300 | 0.20±0.002 | 1.85±0.2 | 46 | 0.37 | 0.019 | —0.79 | 0.02 | —0.6 | — | — |
| Ditto | 90 | 1000 | 0.24±0.07 | 3.6 ±0.3 | 47,48 | 0.86 | 0.011 | —0.18 | 0.01 | 0.0 | — | — |
| Vinyl fluoride | 160 | 1000 | 4.4 ±0.8 | 0.16±0.05 | 48 | 0.70 | 0.035 | 0.68 | — | — | — | — |
| Tetrafluoroethylene | 40—200 | 70—200 | 0.15 | 0.85 | 49 | 0.13 | 0.010** | —0.21** | — | — | — | — |
| Vinyl acetate | 70 | 400 | 0.77±0.04 | 1.02±0.02 | 50 | 0.79 | 0.023 | 0.26 | 0.02 | 0.4 | 0.14 | —0.06 |
| Ditto | 130 | 400 | 0.97±0.03 | 1.02±0.02 | 50 | 0.99 | 0.022 | —0.13 | 0.02 | 0.0 | 0.22 | —0.29 |
| » | 90 | 1000 | 1.07±0.06 | 0.08±0.19 | 47,48 | 1.16 | 0.026 | —0.22 | 0.02 | —0.1 | 0.23 | —0.30 |
| Acrylonitrile | 20 | 10—45 | 0 | 4 | 51 | 0 | — | — | — | — | — | — |
| » | 18—50 | 100 | 0 | 7 | 51 | 0 | — | — | — | — | — | — |
| n-Butyl acrylate | 70 | 1000 | 0.03±0.01 | 11.9 ±2.5 | 48 | 0.36 | 0.015 | —0.01 | — | — | 0.26 | —0.34 |
| Carbon monoxide | 20 | 650 | 0.05 | 0*** | 13,52 | 0 | — | — | — | — | — | — |
| Ditto | 70 | 120—240 | 0.16±0.02 | 0 | 53 | 0 | — | — | — | — | — | — |
| » | 120—130 | 850—1000 | 0.15 | 0*** | 54 | 0 | — | — | — | — | — | — |
| | | | | | Mean | | 0.020 | —0.075 | 0.02 | —0.1 | 0.21 | —0.25 |

* Without correction for chain transfer via the alk-1-ene.
** Values taken from Young's summary[49].
*** Assumed by the authors of the works cited.

been given by a number of authors[60-69]. Despite certain difficulties associated with the interpretation of the physical significance of the polarity factor[66,67], this method is useful for a preliminary estimation of the behaviour of monomers in copolymerisation reactions. Table 3 gives the values of the parameters $Q$ and $e$ which we have calculated for ethylene; those for other monomers have been taken from Young's summary[49].

Since the Alfrey–Price method is semi-empirical in character, various modifications have been proposed. In particular, it appears more appropriate to take as standard monomer not styrene but ethylene, assuming for the latter $Q = 1$ and $e = 0$, since, of all monomers containing a carbon–carbon double bond, ethylene has the simplest molecular structure. The establishment of the true zero on the scale of polarity factors would make it possible to obtain more accurate values for the activity and polarity factors of various monomers. The relative activities for the copolymerisation of several monomers have been calculated by Zutty and Burkhart[47,48], using a $Q-e$ scale based on ethylene. Allowance must be made for the fact that these values correspond only to a pressure of about 1000 bars, at which the copolymerisation of ethylene was carried out, since the relative activities and hence the activity and polarity factors depend on pressure[47].

Kawabata et al.[66,67] consider it advisable to take $e = 0$ for styrene; the same conclusion has been reached by Bamford and Jenkins[65]. Values of the activity and polarity factors for ethylene which we have calculated using the method of Kawabata et al. are given in Table 3. Price[70], however, objects to the choice of zero for the polarity factor of ethylene or styrene. In his opinion, the polarity factor for ethylene should be negative, since the double bond in the ethylene molecules carries a negative charge; the zero on the scale of polarity factors should correspond to vinyl chloride, and this corresponds to a value of $e$ for styrene of -0.8. He refers, in particular, to the data of Zutty and Burkhart[48], who, on the basis of values of $Q$ and $e$ for other monomers taken from Alfrey et al.[59] and from Thompson and Raines[71], calculated for ethylene the mean values $Q = 0.03$ and $e = -0.43$. The mean value of the polarity factor which we have obtained for ethylene by the Alfrey–Price method is close to zero; at the same time, Young's summary gives for vinyl chloride $e = 0.20$. The value of the polarity factor can evidently vary over a fairly wide range, depending on the choice of data taken as a basis for the calculation.

In the method of Spasskii and Karas'[72], the activity factor $Q$ is replaced by the product of two quantities — a factor $\alpha$ representing the influence of the polarisability of the $\pi$ bonds, characterised by the refraction, and a factor $\beta$ representing the influence of the structure of the monomer, not taken into account by the refraction. Values of the parameters for the copolymerisation of ethylene, which we have calculated by this method, are given in Table 3.

From the mean values of the activity and polarity factors for ethylene (Table 3) we have calculated, by the methods of Alfrey and Price, Kawabata et al., and Spasskii and Karas', values of the relative activities for the copolymerisation of ethylene with monomers of different classes. The results of the calculation are given in Table 5, the copolymerisation parameters of the monomers having been taken from published data[49,66,67,72]. The order of magnitude is generally the same for the relative activities calculated by different methods; discrepancies are observed only with maleic anhydride and diethyl fumarate. Comparison of the calculated (Table 5) and experimental (Table 3) values of the relative activities for the copolymerisation of ethylene shows that the methods of calculation used are sufficiently accurate.

TABLE 5. Calculated relative activities for copolymerisation with ethylene.

| Second component | Relative activities by methods of: Alfrey and Price | | Kawabata et al. | | Spasskii and Karas' | |
|---|---|---|---|---|---|---|
| | $r_1$ ($C_2H_4$) | $r_2$ | $r_1$ ($C_2H_4$) | $r_2$ | $r_1$ ($C_2H_4$) | $r_2$ |
| Styrene | 0.02 | 25 | 0.02 | 50 | 0.03 | 33 |
| Butadiene | 0.01 | 43 | 0.02 | 64 | 0.02 | 58 |
| Isoprene | 0.01 | 41 | — | — | 0.01 | 75 |
| Vinyl chloride* | 0.44 | 2.1 | 0.32 | 2.5 | 0.28 | 1.3 |
| Vinylidene chloride | 0.09 | 9.4 | 0.04 | 6.5 | 0.01 | 5.4 |
| 1,1-Dichloro-2,2-difluoroethylene | 0.41 | 0.02 | — | — | — | — |
| Chlorotrifluoroethylene | 0.89 | 0.10 | — | — | — | — |
| Vinyl fluoride* | 1.50 | 0.11 | — | — | — | — |
| Tetrafluoroethylene* | 0.37 | 0.50 | — | — | — | — |
| Vinyl acetate* | 0.78 | 1.26 | 1.00 | 1.00 | 0.98 | 0.99 |
| Vinyl γ-methylvalerate | 0.49 | 1.32 | — | — | — | — |
| Vinyl stearate | 0.61 | 1.29 | — | — | — | — |
| Vinyl benzoate | 0.36 | 2.4 | — | — | — | — |
| Vinyl thioacetate | 0.07 | 2.1 | — | — | — | — |
| Ethyl vinyl ether | 0.68 | 0.45 | — | — | — | — |
| Methyl vinyl ketone | 0.03 | 21 | 0.00 | 15 | 0.01 | 19 |
| Maleic anhydride | 0.07 | 0.06 | — | — | 0.01 | 0.41 |
| Diethyl maleate | 0.30 | 0.28 | — | — | 0.10 | 0.46 |
| Diethyl fumarate | 0.03 | 5.8 | — | — | 0.01 | 0.91 |
| Vinylene carbonate | 2.9 | 0.25 | — | — | — | — |
| Acrylonitrile* | 0.03 | 6.4 | 0.01 | 2.9 | 0.00 | 5.6 |
| Methacrylonitrile | 0.02 | 27 | 0.01 | 6.8 | 0.00 | 21 |
| Methyl acrylate | 0.05 | 11 | 0.01 | 9 | 0.01 | 20 |
| Methyl methacrylate | 0.03 | 31 | 0.01 | 20 | 0.02 | 33 |
| Ethyl acrylate | 0.04 | 24 | — | — | — | — |
| Ethyl methacrylate | 0.04 | 27 | — | — | — | — |
| n-Butyl acrylate* | 0.04 | 8.3 | — | — | 0.03 | 14 |
| n-Butyl methacrylate | 0.03 | 35 | — | — | — | — |
| 2-Vinylpyridine | 0.02 | 52 | 0.01 | 23 | 0.03 | 35 |
| *N*-Vinylcarbazole | 0.05 | 4.0 | — | — | — | — |
| *N*-Vinylpyrrolidone | 0.16 | 2.1 | — | — | — | — |
| *N*-Vinylsuccinimide | 0.14 | 7.2 | — | — | — | — |

* The experimental values are given in Table 3.

The results of the calculations given in Table 5 naturally require experimental verification. These data may prove useful, however, in the planning of experiments on the radical copolymerisation of ethylene.

The production of a copolymer of uniform composition in high yield can be achieved only if the relative activities of the monomers used do not differ too greatly. The data in Tables 3 and 5 show that the most "convenient" monomers in this sense for copolymerisation with ethylene are fluoroalkenes, vinyl esters of aliphatic acids, and carbon monoxide.

In particular, considerable difficulties should be encountered in the copolymerisation of ethylene with small quantities of acrylic and, more particularly, methacrylic monomers. Copolymers of ethylene with ethyl acrylate, containing a small quantity of the latter, are, however, now being produced in the USA,[73] on equipment designed for the production of high-pressure polyethylene, i.e. as a continuous process. It is evident that it is much easier to keep the composition of the monomer mixture constant in this type of process than in a batch process.

Kawabata et al.[68,69], on the basis of the method proposed by Fukui and his coworkers[61,74,75] for the quantitative characterisation of the activation energy for growth reactions in vinyl polymerisation, have calculated the additional energies of conjugation in the transition state for reaction of the ethylene radical with various monomers ($E_{R\cdot M}$) and also of various radicals with ethylene ($E_{RM\cdot}$). If it is assumed, following these authors, that the preexponential factors for

the addition of different monomers to the same radical are equal, the relative activities of ethylene in copolymerisation with different monomers will be given by the equation

$$\ln r_1 = -q\frac{E_M}{RT},$$

where $E_M$ is the difference between the additional energies of conjugation for reaction of the ethylene radical with the second component and with ethylene, and $q$ is a proportionality coefficient. The polarity factors in reactions involving the ethylene molecule or the ethylene radical were taken as zero.

As will be seen from the results discussed below, however, the assumption that the preexponential factors for the copolymerisation of ethylene are equal is unjustified, so that the relative activities in the copolymerisation of ethylene with vinyl acetate and vinyl chloride (Table 3) do not correspond to the above equation. For many monomers, however, an approximately linear relationship is observed between $E_M$ and the values of the activity factors calculated on the scale proposed by Kawabata et al. ($Q$ = 1.0 and $e$ = 0 for styrene) or on the scale based on ethylene ($Q$ = 1.0 and $e$ = 0 for ethylene)[68,69,76].

## IV. COPOLYMERISATION OF ETHYLENE WITH VARIOUS MONOMERS

### (a) Copolymerisation with Hydrocarbons

The ionic copolymerisation of ethylene with alkene, alkyne, and diene hydrocarbons has been studied in considerable detail (particularly the copolymerisation of ethylene with propene and butenes on organometallic complexes or a chromium-oxide catalyst), but the free-radical copolymerisation of ethylene with these hydrocarbons has been little studied.

In early patents on the copolymerisation of ethylene[4,5,7], the second components included such alkenes as propene, butene, and methylpropene. No reliable proof of the formation of a copolymer was given, however. Later, solid high-molecular copolymers of ethylene with a small quantity of propene or octadec-1-ene were prepared at higher pressures, of 2000–2500 bars[77]. The copolymerisation was carried out by a continuous block method at ~ 200° in the presence of oxygen as initiator. The products obtained differed from polyethylene in their high content of vinyl groups, determined by infrared spectrophotometry. Thus polyethylene prepared by the usual high-pressure method contains 0.02–0.06 double bond per 1000 carbon atoms, whereas the copolymer of ethylene with propene contains 0.2–0.6 double bond[77].

According to Boghetich et al.[45], the only way in which the unsaturation of the polymer can increase is by chain transfer via the alk-1-ene:

$$\cdots CH_2{-}CH_2^{\cdot} + CH_2{=}CH{-}CH_3 \longrightarrow \cdots CH_2{-}CH_3 + CH_2{=}CH{-}CH_2^{\cdot},$$

$$CH_2{=}CH{-}CH_2^{\cdot} + CH_2{=}CH_2 \longrightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2^{\cdot},$$

since none of the four growth reactions in the copolymerisation of ethylene with alk-1-enes leads to an increase in the content of double bonds in the copolymer.

Boghetich et al.[45] give convincing proof of the copolymerisation of ethylene with alk-1-enes by a radical mechanism. Formation of a copolymer was confirmed by carrying out the copolymerisation of ethylene with $^{14}C$-labelled propene, but-1-ene, and oct-1-ene, and then determining the activity of the product. The copolymerisation was carried out at 1050–1750 bars and 130–200° under the influence of t-butyl peroxide and acetoxime. The values of the relative activity of ethylene in copolymerisation with different alk-1-enes (Table 3) are close to one another and lie in the range 3.4–3.6, with a correction for chain transfer; in other words, under the conditions studied, ethylene is a more active monomer than the alk-1-enes. Chain transfer was estimated from the decrease in molecular mass and the increase in unsaturation of the polymer with increase in the alk-1-ene content of the original mixture. The values of the chain-transfer constants are given in Table 6. Comparison of the data on the unsaturation and on the radioactivity of the copolymers shows that only a small quantity of alk-1-ene (< 10%) enters the copolymer by chain transfer, and that the predominant reaction is copolymerisation.

Study of the continuous copolymerisation of ethylene with propene in the presence of oxygen as initiator at 1500–1800 bars in the range 170–240° showed that the process can be carried out at a concentration of propene in the original mixture not greater than 15%.[78]

As stated in Section II, ethylene copolymerises under the influence of $^{60}Co$ $\gamma$-radiation with alkenes, styrene, isoprene, and divinylbenzene[10,12–14].

The copolymerisation of ethylene with styrene has also been carried out under the influence of tributylboron at 18–50°[15] and of triisobutylboron between -70° and 18°.[16] In the latter case, ethylene copolymerises with styrene much more slowly than with vinyl chloride and acrylonitrile. The low yield of copolymer was attributed to the fact that styrene, which is the more active monomer, does not polymerise readily in solution in the presence of alkylborons. Copolymers of ethylene with styrene dissolve readily in toluene, dichloroethane, and tetralin at room temperature, and have vitrification temperatures in the range 55–95°.[16] The copolymerisation of ethylene with 9-methylenefluorene has also been described[79].

The free-radical copolymerisation of ethylene with acetylene and diene hydrocarbons is carried out at high pressures (of about 1000 bars) and temperatures up to 200° under the influence of oxygen, organic peroxides[7,9,80–82], and $^{60}Co$ $\gamma$-radiation[10,12,13]. Among diene hydrocarbons, butadiene, isoprene[7,9,12,13,81], and norbornadiene[82] have been used. According to our calculations (Table 5), the relative activity of monomers such as butadiene and isoprene is much greater than that of ethylene, which is zero. Thus the content of the second component in the copolymer will always be greater than its content in the original mixture. A characteristic feature is that the copolymers of

TABLE 6. Chain-transfer constants for the copolymerisation of ethylene with alk-1-enes[45] (pressure 1400 bars, temperature 130°).

| Alk-1-ene | Chain-transfer constant from | |
|---|---|---|
| | infrared spectrophotometry | decrease in molecular mass |
| Propene | 0.011±0.003 | 0.015±0.003 |
| But-1-ene | 0.033±0.007 | 0.047±0.002 |
| Oct-1-ene | — | 0.036±0.002 |

ethylene with acetylene and diene hydrocarbons contain double bonds, by means of which vulcanisation can be carried out. The molecular mass of the ethylene–acetylene copolymers decreases with increase in the content of the latter [80].

Mortimer and Arnold [83] have shown that ethylene does not copolymerise with benzene in the presence of t-butyl peroxide at 1400 bars and 130°.

(b) Copolymerisation with Halogenated Alkenes

According to many patents, ethylene copolymerises with halogen-containing alkenes of different types: the comonomers are chlorine- and fluorine-containing compounds, and alkenes containing one, two, or more halogen substituents may be used. Copolymerisation is carried out chiefly at high pressures (700–1500 bars) and temperatures of 50–200° under the influence of peroxide initiators in the presence of water or in block. Under these conditions, copolymers of ethylene have been obtained with vinyl chloride [84,85], vinylidene chloride [86], vinylidene fluoride [87–89], tetrafluoroethylene [90], chlorotrifluoroethylene [91], 1-chloro-1-fluoroethylene [92], 1,1-dichloro-2,2-difluoroethylene [93], 3,3,3-trifluoropropene [94], and hexafluorocyclobutene [95]. With some monomers (tetrafluoroethylene [96] and 3,3,3-trichloropropene [97]) the copolymerisation initiated by organic peroxides was carried out at a relatively low pressure (up to 200 bars).

Ethylene copolymerises with vinyl chloride and chlorotrifluoroethylene under the influence of $^{60}Co$ $\gamma$-radiation [11–14,98]. The copolymerisation is usually carried out at room temperature. With chlorotrifluoroethylene, development of an explosive reaction is observed at a definite dose rate, of about 3000 J $kg^{-1}$ $h^{-1}$. [13,98] In the separate polymerisation of ethylene and chlorotrifluoroethylene under analogous conditions, no explosion was observed. Tabata and his coworkers [28,29,99,100] have shown that it is possible to carry out the radiation copolymerisation of ethylene and tetrafluoroethylene in the liquid state at -78°. They suggest that under these conditions the reaction proceeds in a homogeneous medium. A characteristic feature is that the copolymerisation takes place by a radical mechanism, whereas at this temperature ethylene polymerises only by a cationic mechanism [17,18].

The copolymerisation of ethylene with a number of halogen-containing alkenes (vinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride, and chlorotrifluoroethylene) has been carried out under the influence of alkylborons, e.g. triethylboron and tributylboron [16,101–105]. An important feature is that in this case the copolymerisation is carried out at extremely low temperatures, between -70° and -80°. [16,102]

Experimental relative activities for the copolymerisation of ethylene with vinyl chloride [46,48], vinyl fluoride [48], and tetrafluoroethylene [49] are given in Table 3; calculated values for copolymerisation with other halogen-containing alkenes are given in Table 5. A noteworthy feature is that the relative activity of vinyl fluoride and also, apparently, chlorotrifluoroethylene and dichlorodifluoroethylene, is much lower than that of ethylene, whereas the relative activity of vinyl chloride is much greater than that of ethylene. It may be assumed that vinylidene chloride has an even higher relative activity than vinyl chloride.

Duntov and Erusalimskii [46,106] have studied the copolymerisation of ethylene with vinyl chloride under the influence of azoisobutyronitrile at 70° and pressures up to 300 bars. According to their data, copolymerisation in the ethylene–vinyl chloride system is homogeneous under the conditions studied. The order of the initial reaction rate with respect to initiator at an equimolar monomer ratio is 0.5, indicating that the ethylene–vinyl chloride–initiator system is homogeneous. When the reaction was carried out to a high degree of conversion at a vinyl chloride content of 5 mole % (in this case the proportion of vinyl chloride in the copolymer varied between 13% and 17%, and the melting point of the copolymer, determined from thermomechanical curves, was 52–53°), the degree of copolymerisation was found to increase with increase in the degree of conversion; this is explained by the heterogeneity of the monomer–polymer system at the given monomer ratio. The relative activities determined by these authors are close to those established by Zutty and Burkhart [47] for the process at 90° and 1000 bars.

Kolesnikov et al. [16] studied the copolymerisation of ethylene with vinyl chloride in the presence of triisobutylboron at an ethylene pressure of 98 bars and temperatures from -70° (initial) to 18° (final) in toluene medium. The yield of copolymer increases with increase in the ethylene content of the original mixture. Their statement that under the conditions of this process ethylene is a more active monomer than vinyl chloride is open to doubt, since the composition of the original mixture of monomers was, in fact, unknown (the experiments were carried out over a wide temperature range, for the most part below the critical temperature of ethylene).

We must also expect differences in the properties of the copolymers of ethylene with fluorinated and with chlorinated alkenes. As noted above, replacement of hydrogen atoms in the polyethylene chain by fluorine atoms can take place without breakdown of the polyethylene lattice. Thus, for example, copolymers of ethylene with tetrafluoroethylene are crystalline throughout the composition range [28,29,99,100]. Analogous properties may be expected for copolymers of ethylene with other fluorine-substituted ethylenes. But the introduction of chlorine atoms into the polyethylene chain, because of their large dimensions (Table 2), should lead to breakdown of the crystal structure. Thus in the case of the copolymer of ethylene with vinyl chloride [16,84,85], the rigidity first decreases with increase in the vinyl chloride content, and then increases. Rubberlike products are formed in the intermediate composition range. The addition of small quantities of copolymer phasticises poly(vinyl chloride) [107].

The melting points of the copolymers of ethylene with tetrafluoroethylene rise sharply with increase in the content of the latter within the composition range close to polyethylene. An interesting feature is that, for the same fluorine content, the melting points of the copolymers are 100–140 deg higher than those of poly(vinyl fluoride) and poly(vinylidene fluoride) [28,29].

Thermostable oils are obtained by the copolymerisation of ethylene with tetrafluoroethylene in a tertiary hydrocarbon (telogen) medium under the influence of peroxo-compounds [108].

Tarutina [109] has studied the thermal aging of copolymers of ethylene and tetrafluoroethylene at 200°, 240°, and 290°. The infrared spectra of these copolymers indicate the presence of side-branches with terminal methyl groups. It was established that the rate of aging depended on the number of branches. It is suggested [109] that aging takes place chiefly at the tertiary carbon atom, without influencing the number of methyl groups, since the intensity of the bands

due to the $CH_3$ groups remains unchanged on aging. Thus to obtain products with a high stability towards aging it is necessary to prepare copolymers having a predominantly linear structure.

(c) Copolymerisation with Vinyl Acetate and Other Vinyl Esters

The copolymerisation of ethylene with vinyl esters opens up extensive possibilities for the preparation of a variety of polymers, since in this case, in addition to the products formed directly during copolymerisation, it is possible to bring about conversion to a number of different macromolecular compounds by polymer-analogue reactions involving the ester group.

Vinyl acetate is one of the most readily available vinyl esters, and the copolymerisation of ethylene with this compound has been studied in greatest detail. Copolymers of ethylene with vinyl acetate can be obtained in block, solution, and emulsion; organic peroxides, alkylborons, and ionising radiation are used to initiate the reaction.

The composition of an ethylene–vinyl acetate copolymer determines its properties, and the possibilities of further modification and application. A number of patents [110–117] deal with the preparation of copolymers of low vinyl acetate content, up to 20 mole %. These copolymers can be obtained by polymerisation at 800–1500 bars and 50–150° under the influence of peroxide initiators in aqueous medium [110,111] or in emulsion [112].

A continuous process operating under the same conditions but in a propane, benzene, or cyclohexane medium has been described [113]. Continuous emulsion copolymerisation has been carried out in the presence of redox initiators at 30°. [114]

Ethylene copolymers of low vinyl acetate content can also be prepared at a pressure of 400–600 bars. [115–117] The use of low temperatures (60–70°) and solvents having low chain-transfer constants makes it possible to obtain copolymers with a fairly high molecular mass; in this case a satisfactory reaction rate is ensured by using initiators which exhibit a high activity at these temperatures, such as lauryl peroxide, peroxodicarbonates, and azoisobutyronitrile.

Although the preparation of copolymers of low vinyl acetate content requires the use of high pressure, this is not the case for the copolymerisation of ethylene with a large quantity of vinyl acetate [118,119]. Thus even at a pressure of 50–60 bars, under the influence of free-radical initiators, it is possible to prepare copolymers of fairly high molecular mass, containing more than 50% of vinyl acetate [118]. Liquid copolymers of low molecular mass containing 60–75% of vinyl acetate are obtained either by carrying out the copolymerisation in chain-terminating solvents such as ethyl methyl ketone, ethyl acetate, and acetone, or by adding to the reaction mixture a small quantity of a chain-terminating agent, such as an aldehyde or a thiol [120].

The present reviewers, together with Rysakov [50], have studied the copolymerisation of ethylene with vinyl acetate throughout the whole range of compositions of the original mixture. The copolymerisation was carried out at 400 bars in benzene medium at 70° in the presence of azoisobutyronitrile, and at 130° under the influence of t-butyl peroxide. The observed values of the relative activities (Table 3) show that the relative activity of ethylene increases with increase in the temperature of the process, whereas that of vinyl acetate remains constant. Thus at 130° both relative activities are close to unity. Data obtained for the relative activities at 90° and 1000 bars (Table 3) [48] indicate that, as with temperature, a marked increase in pressure leads to an increase in the relative activity of ethylene.

The temperature dependence of the relative activity is given by the equation [59]

$$r_1 = \exp\left(\frac{\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger}}{RT}\right),$$

where $\Delta S_{11}^{\ddagger}$, $\Delta S_{12}^{\ddagger}$, $\Delta H_{11}^{\ddagger}$, and $\Delta H_{12}^{\ddagger}$ are the activation entropies and enthalpies in reactions of the radical $M_1$ with molecules of the monomers $M_1$ and $M_2$.

Since the relative activity of vinyl acetate remains unchanged with increase in the temperature of the process, the differences in the heats and entropies of activation of the reactions of growth of the vinyl acetate radical are zero. For the ethylene radical

$$\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger} = 4530 \text{ J mole}^{-1},$$

$$\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger} = 10.9 \text{ J mole}^{-1} \text{ deg}^{-1},$$

The rate of copolymerisation of ethylene with vinyl acetate, throughout the range of monomer ratios at 70° and 130°, increases monotonically with increase in the vinyl acetate content of the original mixture. The intrinsic viscosity of the copolymers, determined in *p*-xylene solution at 85°, has a minimum value at a vinyl acetate content of 40–60 mole %. [50]

Analogous relationships are observed for the block process carried out at a pressure of 500 bars and temperatures of 60°, 100°, and 150° in the presence of various initiators of the peroxide type: dicyclohexyl peroxodicarbonate, benzoyl peroxide, and t-butyl peroxide. The fact that the nature of the dependence of the copolymer composition on the original monomer ratio is the same in each case indicates that the ethylene–vinyl acetate system is homogeneous under the conditions studied [122].

Interesting results have been obtained in a study of the influence of the benzene concentration on the rate and degree of copolymerisation at vinyl acetate contents in the original mixture of 10 and 50 mole % and temperatures of 70° and 130°. For both these monomer ratios at 70° and for the equimolar ratio at 130°, a decrease in the rate and degree of copolymerisation with increase in the benzene concentration is observed, as a result of the homogeneity of the monomer–solvent–initiator system, in which increase in the relative quantity of solvent leads to a decrease in the total molar concentration of the monomers. A quite different pattern is observed in the copolymerisation of ethylene with 10 mole % of vinyl acetate at 130°: the rate and the degree of copolymerisation increase considerably with the addition of benzene to the system, the optimum molar ratio of benzene to monomers being 0.2–0.25. This phenomenon can be explained as follows. Under these conditions the reaction mixture apparently consists of molten copolymer saturated with all the components, and a gas phase consisting of monomers and initiator. In this case the addition of benzene and increase of its concentration to a definite limit will facilitate the diffusion of monomers into the molten copolymer, accelerating the growth of the macroradicals. The decrease in the rate and degree of copoly-

merisation with further increase in the benzene concentration is due to the decrease in the total molar concentration of monomers in the homogeneous system [119].

The dependence of the rate of copolymerisation in block and in solution on the ratio of the monomers is almost linear throughout the concentration range, indicating that the probability of chain-termination reactions is the same between radicals of different types and between radicals of the same type [119].

The properties of copolymers of ethylene and vinyl acetate show the following changes with increasing content of the latter [50]: copolymers containing up to 10–12 mole % of vinyl acetate are strong plastics, similar to high-pressure polyethylene, but differing from the latter in their higher elasticity and transparency and lower melting point. At vinyl acetate contents of 13–25% the products are rubberlike, and at 30–80% they are resins which are soft and sticky at room temperature. Copolymers containing more than 80% of vinyl acetate are again rigid and strong. The solubility of the copolymers in solvents such as benzene, xylene, carbon tetrachloride, alcohol, and acetone increases with increase in the vinyl acetate content, the copolymers becoming soluble in alcohol and acetone at vinyl acetate contents greater than 40%. [50,121]

X-Ray structural analysis of copolymers of ethylene with vinyl acetate has shown that their crystallinity decreases with increase in the vinyl acetate content [36,122] (Fig. 1). The density of the copolymer at first decreases, and then increases, approaching the value 1.2 characteristic of poly(vinyl acetate) [122]. The dependence of the tensile strength and the relative elongation of the copolymer on the vinyl acetate content is shown in Fig. 2. [122]

Data have been published [36,37,123] on the glass points of copolymers of ethylene with vinyl acetate and vinyl propionate.

The frost-resistance of copolymers of ethylene with low vinyl acetate content is almost independent of the monomer ratio. All specimens, irrespective of composition, withstand a temperature of -70° (bending test method) [121].

According to published data [36,121], the melting point of ethylene–vinyl acetate copolymers falls with increase in the content of the latter in the range 0–20 mole %, in accordance with Flory's formula [30]. The similarity in the curves giving the dependence of the melting point on the number of

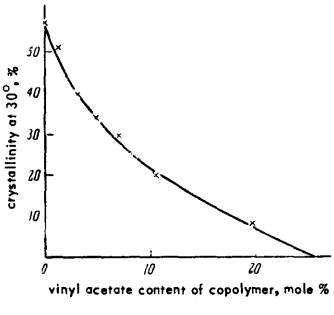



Fig. 1. Dependence of the crystallinity of copolymers of ethylene and vinyl acetate on composition (from Nielsen's data [36]).

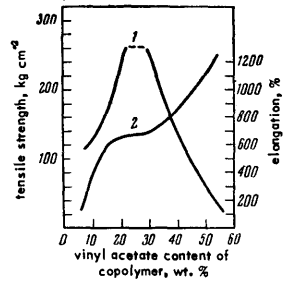



Fig. 2. Dependence of the tensile strength and relative elongation of copolymers of ethylene and vinyl acetate on composition [122]: 1) tensile strength; 2) relative elongation.

carbon atoms in normal paraffins and in polyethylene units of average length in the copolymers shows that the melting point of the copolymers is determined by [the melting point of crystals containing polyethylene sequences whose lengths are near] the average [sequence] length of the polyethylene units in the copolymers [36].

Copolymers of ethylene and vinyl acetate show strong adhesion to various synthetic materials (e.g. to polyethylene and to polyester films), wood, metal, and paper [124,125], and can be used as components in a variety of adhesives [126–128]. These copolymers mix readily with many resins, rosin, paraffin wax, and other waxes [124,129–132], poly(vinyl chloride) [133], and mineral oils containing more than 40% of aromatic hydrocarbons [134]. They can be used as elastomers in mixtures with fillers [134–136].

When ethylene–vinyl acetate copolymers are heated to 280–320°, acetic acid is split off with the formation of double bonds between neighbouring carbon atoms; no breakdown of the polymer chain was observed [137]. When the copolymers are heated above 350°, acetic acid and methane are split off; with further rise in temperature to 490°, the quantity of methane increases but the acetic acid remains constant [138]. This indicates that at 350° the removal of acetic acid from the copolymer is almost complete. This made it possible to develop a method for determining the composition of copolymers of ethylene and vinyl acetate by gas-chromatographic analysis of the pyrolysis products, from the quantity of acetic acid removed [138]. Good agreement is observed between the results obtained by this method and data obtained by high-resolution nuclear magnetic resonance and neutron activation analysis [139]. When combined with differential thermal analysis, this method can be used to establish the nature of the distribution of the monomer units in the copolymer [140].

The properties of copolymers of ethylene with vinyl acetate are altered appreciably when the copolymer molecules are cross-linked; this may be brought about by the action of peroxides [122,141–143], polycarboxylic acids [141,144], or ionising radiation [121,145]. The cross-linking of these copolymers by means of peroxo-compounds, and the properties of the products obtained in admixture with various fillers, have been described in detail by Bartl and Peter [122]. The degree of cross-linking increases with increase in the vinyl acetate content of the copolymer; it is suggested that cross-linking of the macromolecules takes place at the tertiary carbon atoms of the main chain and also at the primary

carbon atoms of the acetate groups. Vulcanised ethylene–vinyl acetate copolymers exhibit a number of valuable properties, such as high resistance to heat, aging, the action of light and ultraviolet rays, ozone, oxygen, and atmospheric conditions, together with excellent mechanical properties. It is suggested that these products are of particular interest to the rubber industry, since their addition to certain types of rubber produces a marked improvement in the properties of the latter [122]. Vulcanised elastomers based on a copolymer of ethylene and vinyl acetate can also be obtained by pyrolytic elimination of acetic acid followed by vulcanisation of the product at the double bonds [137].

According to data obtained by the reviewers [121], the action of $^{60}Co$ $\gamma$-radiation leads to a considerable increase in strength and melting point, with a comparatively small decrease in the relative elongation and frost-resistance, of the ethylene–vinyl acetate copolymer.

There are reports [128,146,147] that copolymers of ethylene and vinyl acetate are produced on the industrial scale and are used as elastomers, plastics, coatings, adhesives, etc.

Copolymers of ethylene and vinyl acetate are readily hydrolysed with the formation of copolymers of ethylene and vinyl alcohol or, in the case of partial hydrolysis, three-component ethylene–vinyl acetate–vinyl alcohol copolymers [148-151]. The hydrolysed copolymers are of considerable practical interest, since they exhibit valuable properties such as strength, rigidity, and resistance to common solvents; a significant advantage over poly(vinyl alcohol) is their insolubility in water [148-154]. The range of application of hydrolysed copolymers of ethylene with vinyl acetate can be extended considerably by chemical modification of these products [155-167].

Ethylene copolymerises with other vinyl esters besides vinyl acetate. Almost all the patents cited above mention, in addition to vinyl acetate, esters such as vinyl propionate, vinyl butyrate, and vinyl benzoate. Ethylene can be copolymerised also with vinyl esters of branched carboxylic acids (vinyl $\alpha\alpha$-dimethylpropionate, vinyl $\beta\beta$-dimethylbutyrate, etc.) [168], vinyl esters of thio-acids [169], methyl vinyl ether and ethyl vinyl ether [170,171], divinyl ether [172], 2,2′-vinyloxyethoxyethanol [173], 2-vinyloxyethanol [174], and divinyl and diallyl oxalate and sebacate [175]. The copolymerisation of ethylene with all these vinyl esters and ethers is generally carried out at high pressures (1000-2000 bars) under the influence of oxygen or peroxide initiators. Calculation (Table 5) shows that the relative activities of the monomers in the copolymerisation of ethylene with vinyl esters of aliphatic acids are close to one another.

Kurian and Muthana [176] showed that copolymerisation of ethylene with vinyl $\gamma$-methylvalerate is possible at 50–200 bars and 80° under the influence of benzoyl peroxide. According to their results, vinyl $\gamma$-methylvalerate under these conditions shows a higher relative activity than ethylene.

Copolymers of ethylene with vinyl and allyl salicylate are of considerable interest because of their ability to form chelate compounds [177].

Three-component copolymerisation involving ethylene and vinyl acetate has been described in a number of patents [174,177-181]. Vinyloxyalkanols [174,179], vinyl and allyl salicylates [177], alkyl acrylates [178], and carbon monoxide [180,181] have been used as third component. The copolymerisation of ethylene, vinyl acetate, and ethyl acrylate [178] is of particular interest. The process was carried out at 800–1500 bars in benzene medium under the influence of azoisobutyronitrile or a peroxide. The copolymerisation products were hydrolysed to give copolymers consisting of 25–60 mole % of ethylene, 10–30% of vinyl alcohol, and 25–60% of acrylic acid; the tensile strength of these copolymers reached 300–400 kg $cm^{-2}$.

(d) Copolymerisation with Vinylene Compounds

Known copolymers of ethylene with monomers of the vinylene type include compounds with maleic acid derivatives, diethyl fumarate, and vinylene carbonate. Copolymerisation of ethylene with maleic anhydride is carried out at comparatively low pressure under the influence of free-radical initiators in various organic solvents [182,183]. Copolymers of high maleic anhydride content and low molecular weight are formed at 20–30 bars under the influence of peroxide initiators in the presence of a chain-terminating agent such as cumene or an aldehyde [184-188]. The relative activities of this pair of monomers are apparently less than unity (Table 5). Copolymers of ethylene and maleic anhydride are soluble in water [189]. They are now produced on the industrial scale as the anhydride, acid, or ammonium maleamate, and are used in the production of transparent films, adhesives, fungicides, paint thickeners, etc. [147,189-197]. Ethylene copolymerises also with monoesters of maleic acid [198].

Hopff and Stark [199,200] have shown that the emulsion copolymerisation of ethylene with diethyl fumarate is possible, with the formation of products whose softening temperatures are lower than room temperature. The molecular mass (determined by the osmotic method) of the fraction with highest molecular mass was 41 000. According to our calculations (Table 5), diethyl fumarate should have a much greater relative activity than ethylene.

An interesting feature of the copolymerisation of ethylene with vinylene carbonate is the apparently much greater relative activity of ethylene compared with vinylene carbonate (Table 5). Their copolymerisation under high pressure in the presence of free-radical initiators gives products which are at least as valuable as polyethylene and have a number of advantages, such as high strength, stability during processing, satisfactory flow properties, absence of cross-linked molecules, transparency, and gloss [201]. Copolymers containing up to 30 wt. % of vinylene carbonate can be used as additives to poly(vinylidene chloride fluoride) [202], polyvinylformal [203], and styrene–acrylonitrile copolymers [204], to improve their quality. The addition of small quantities (up to 10%) of a copolymer of ethylene and vinylene carbonate during the polymerisation of styrene gives a polymer with an increased tensile strength [205].

The hydrolysis of copolymers of ethylene with vinylene carbonate gives compounds of the ethylene–vinyl alcohol copolymer type, in which the hydroxy-groups are present on neighbouring carbon atoms [201]. Copolymers of ethylene with hydroxy-groups in the side-chains can also be prepared directly by the copolymerisation of ethylene with allyl or methallyl alcohol at high pressure, but in this case the products are waxlike, with low molecular mass of $\sim 1500$. [206]

(e) Copolymerisation with Acrylic Monomers

Ethylene copolymerises readily with acrylic compounds such as acrylic acid, acrylonitrile, and acrylic and meth-

acrylic esters [3-7,9]. The reaction can be initiated by oxygen, organic peroxides [5-7], $^{60}Co$ $\gamma$-radiation [12-14], and alkylborons [15,16]. Copolymers with perfluoroacrylonitrile have also been prepared [207].

Table 5 gives the calculated values of the relative activities for the copolymerisation of ethylene with various acrylic and methacrylic monomers. On the basis of these data it may be assumed that compounds of this type have a much greater relative activity than ethylene, the relative activity of the latter being close to zero. Thus copolymers with acrylic monomers will always be enriched in the second component. These conclusions agree with the experimental relative activities for acrylonitrile and n-butyl acrylate (Table 3).

The copolymerisation of ethylene with acrylonitrile has been studied in greatest detail. The radiation copolymerisation of these monomers has been investigated by Gromov et al. [51] The process is carried out in toluene solution at an ethylene pressure of 10–44 bars, an absorbed dose rate of 1080 J $kg^{-1}$ $h^{-1}$, and a temperature of 20°. The yield of copolymer for acrylonitrile concentrations in the monomer mixture of 10 and 50 mole % depends linearly on the duration of polymerisation up to 40% conversion; at an acrylonitrile concentration of 70%, the rate increases with time (up to 25% conversion), and this is attributed to the heterogeneous character of the process. This is indicated also by the fact that the intrinsic viscosity of the copolymer increases with increase in the degree of conversion. The rate of copolymerisation and the intrinsic viscosity of the products increase with increase in the acrylonitrile content in the original monomer mixture.

$\gamma$-Irradiation of a mixture of acrylonitrile and liquid ethylene at -78° leads to formation of only the acrylonitrile homopolymer; and when the acrylonitrile content of the mixture is low, polymerisation takes place exclusively at the $-C\equiv N$ bond. In solutions with a moderate concentration of acrylonitrile in ethylene, polymerisation takes place both at the $-C\equiv N$ bond and at the $\rangle C=C\langle$ bond [208,209].

Kolesnikov et al. [16] studied the copolymerisation of ethylene with acrylonitrile under the influence of triisobutylboron at an ethylene pressure of 98 bars in solvent naphtha medium. As in the case of radiation copolymerisation, increase in the concentration of acrylonitrile in the original monomer mixture leads to an increased yield of copolymer; at the same time, however, a decrease in its intrinsic viscosity is observed. With increase in the triisobutylboron concentration from 1 to 2 wt.%, the yield of copolymer increases from 10 to 25%; further increase in catalyst concentration, however, leads not to an increase in the yield but to a slight decrease. Lowering the initial temperature of polymerisation from 18° to -70° results in an increased content of ethylene units in the copolymer; this effect is observed for the most part at considerable concentrations of ethylene in the original mixture. In all cases decrease in the initial temperature leads to an increase in the yield of copolymer.

Good agreement is observed between the values of the relative activities calculated by Gromov et al. [51] from published data [16] and those established in radiation copolymerisation (Table 3). This may indicate that the copolymerisation process initiated by alkylborons takes place by a radical mechanism.

An interesting feature is that copolymerisation of ethylene with acrylonitrile does not take place on organometallic complexes [210].

There is almost no published information on the properties of copolymers with acrylonitrile. It is known [16] merely that the copolymers are soluble only in dimethylformamide and that X-ray structural analysis indicates a high degree of order inside the chain bundles; their vitrification temperature is almost independent of the monomer ratio and the reaction temperature, and lies in the range 60–70°.

Copolymers of ethylene with alkyl acrylates (e.g. ethyl acrylate and n-butyl acrylate) can be obtained by a continuous process in a tubular reaction vessel at 1500–2000 bars and 100–200° in the presence of oxygen or organic peroxides [211,212]. The copolymerisation was carried out at very low concentrations of the comonomers in the original mixture (0.2–1.5 mole %), apparently because of their extremely high relative activity (see Tables 3 and 5).

The composition of copolymers of ethylene with ethyl acrylate can be determined by gas chromatography of the pyrolysis products [138], high-resolution nuclear magnetic resonance [139], neutron activation analysis [139], infrared spectrophotometry, and hydrolysis [213]. In the last case, to obtain satisfactory results, the analytical reaction must be carried out in a homogeneous medium. The distribution of the monomer units in the copolymer can be established by a combination of gas chromatography of the pyrolysis products and differential thermal analysis [140,214].

Liquid copolymers of ethylene with a content of ~ 30 mole % of an alkyl acrylate or alkyl methacrylate are formed by copolymerisation under the influence of peroxide initiators at about 300 bars in hexane, cumene, etc. medium [215]. Other known compounds include copolymers of ethylene with esters of hydroxybenzophenones and acrylic or methacrylic acid [216] and with $\omega$-methacrylamidoundecanoic acid [217], and three-component copolymers of ethylene, ethyl acrylate, and vinyl acetate [178] and of ethylene, an alkyl acrylate, and a monoester of maleic or fumaric acid [218], prepared under approximately analogous conditions.

The alkyl acrylate most widely used as comonomer with ethylene is ethyl acrylate; copolymerisation with this compound is now carried out on the industrial scale [73,219]. Published data [73,219-233] show that these copolymers exhibit properties such as flexibility over a wide temperature range, high resistance to cracking under stress, high strength at low temperatures, and excellent engineering properties. An extremely important advantage of these copolymers over polyethylene is their low embrittlement temperature, which in some specimens reaches -100°. The copolymers exhibit high adhesion and mix well with paraffin wax [224] and polyethylene [218], whose mechanical properties are improved by the addition of small quantities of copolymers of ethylene and ethyl acrylate containing up to 8 mole % of the latter.

The dependence on composition of the glass point of copolymers of ethylene with ethyl acrylate and n-butyl acrylate is shown in Fig. 3. [37] A characteristic feature of these copolymers, which distinguishes them from those of ethylene with vinyl chloride or vinyl acetate, is the decrease in their glass point (particularly in the case of the copolymers with n-butyl acrylate) with increase in the content of the comonomer.

### (f) Copolymerisation with Heterocyclic Compounds

According to data given in patents, ethylene copolymerises with *N*-vinyl compounds such as *N*-vinylphthalimide, *N*-vinylsuccinimide [225], and *N*-vinylcarbazole [226] at

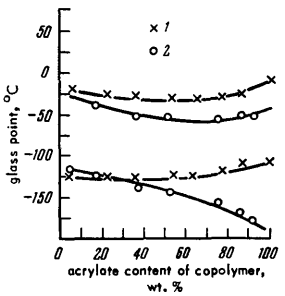



Fig. 3. Dependence on composition of the vitrification temperature of copolymers of ethylene with: 1) ethyl acrylate; 2) n-butyl acrylate. (Upper curves constructed from measurements on Instron tester; lower curves from data obtained with a torsion balance.)[37]

1000–2000 bars and 50–150° under the influence of organic peroxides or azo compounds, in water or a hydrocarbon solvent. The radiation copolymerisation of ethylene with *N*-vinylpyrrolidone has been carried out[12].

On the basis of the calculated values of the relative activities for the radical copolymerisation of ethylene with *N*-vinylcarbazole, *N*-vinylpyrrolidone, and *N*-vinylsuccinimide (Table 5) it may be assumed that these compounds have a much higher relative activity than ethylene.

The rigidity of copolymers of ethylene with small amounts of *N*-vinylsuccinimide and *N*-vinylpyrrolidone decreases with increase in the content of these compounds[31]. Copolymers containing 5–30 wt.% of *N*-vinylcarbazole have a much higher strength, elasticity, resistance to solvents, and better adhesion properties than high-pressure polyethylene[226].

According to data given in patents, copolymers of ethylene can be obtained with alkylene 1,2-oxides (e.g. ethylene oxide)[227,228], β-propiolactone[229], but-3-eno-3-lactone[230], and vinyloxoisochromans[231]. The copolymerisation is carried out at high pressures (500–1500 bars) and 50–200° under the influence of peroxide initiators. In the first two cases, however, the mechanism of the process is not clear.

(g) Copolymerisation with Compounds Incapable of Homopolymerisation

Compounds which are unable to undergo homopolymerisation but which form copolymers with ethylene include carbon monoxide, carbon dioxide, and sulphur dioxide.

1. Copolymerisation with carbon monoxide. Copolymers of ethylene with carbon monoxide were first prepared by one of the reviewers and his coworkers[232,233]. Copolymerisation of the monomers at 2000–2500 bars and 300° gave macromolecular products, consisting of viscous liquids or solids depending on the conditions of the experiment and the proportions of the original components. Copolymerisation was apparently initiated by molecular oxygen. Subsequently, methods have been described for the copolymerisation of ethylene and carbon monoxide under the influence of molecular oxygen[180], orthosilicates[234], complex nickel cyanides[235–237], alkali metals, their hydrides, and organic derivatives[238], Friedel–Crafts catalysts, carbonyl-forming heavy metals and their derivatives[239] (in the last two works cited, the process was initiated by traces of oxygen[240]), and $^{60}Co$ γ-radiation[11–14,34,52,53,241]. The greatest amount of work has been done on copolymerisation initiated by organic peroxides[54,180,234,242–259].

In the case of radiation copolymerisation in the gas phase at 70° and 160–180 bars, the rate of the process is proportional to the absorbed dose rate (rate of initiation) to the power 1.3. The fact that the rate of radical polymerisation is not proportional to the square root of the rate of initiation has been attributed to the heterogeneous character of the process[53].

The copolymerisation of ethylene with carbon monoxide takes place in the range 75–275° and also at room temperature in the case of initiation by γ-radiation. At high temperatures the process is complicated by side-reactions[260]. In the initiation of copolymerisation by peroxides at a pressure of 600 bars, increase in temperature from 200° to 260° led to a decrease in the molecular mass of the products of the reaction by a factor of about 3.[54] The maximum rate of radiation copolymerisation at 120–300 bars was observed at 70–120°.[53]

The copolymerisation pressure was varied over a wide range, from 14 to 2500 bars. At pressures below 100 bars, only products of low molecular weight are formed[180,257,258]. Copolymerisation under the influence of peroxide initiators was carried out in most cases at 600–1000 bars, and radiation copolymerisation at 120–300 bars and at 650–700 bars[12–14].

Copolymerisation initiated by peroxides has been carried out in the gas phase[54,180,246,248] and also in different reaction media, such as isooctane, benzene, cyclohexane, dioxan, water, etc.[54,180,243–258] In the presence of chlorinated hydrocarbons, isopropanol, thiols, ketones, esters, and chlorine, telomers of low molecular weight are formed[258,261–263]. Telomerisation was carried out at 30–8000 bars and 75–130° under the influence of peroxides or nitriles of azo-acids; under these conditions hydrogen sulphide inhibits copolymerisation[263]. The radiation copolymerisation of ethylene and carbon monoxide has generally been carried out in the gas phase.

The copolymerisation of ethylene and carbon monoxide is carried out both by batch and by continuous methods[32,54,234]. To prevent the formation of iron carbonyl during the reaction, it is recommended that the reaction vessel be lined with aluminium[53], silver, or other inert material[180].

The values of the relative activities of this pair of monomers (Table 3) show that the relative activity of carbon monoxide is in all cases zero¶. This means that, in the course of chain growth, the carbon monoxide molecules add only to radicals terminating in methylene groups. Thus the resulting copolymer contains no α-dicarbonyl groups, and the carbon monoxide content cannot exceed 50% (mole and weight percentages identical). This pair of monomers exhibit a high tendency to alternate, so that the composition of the copolymer depends little on the original monomer ratio over a wide range of original monomer concentrations.

¶ The values of the relative activities calculated by Gromov et al.[51] from the data of Brubaker et al.[257] — $r_{C_2H_4} = 0.57$ and $r_{CO} = 0.25$ — are incorrect, since no allowance was made for soluble monomers. An analogous error has been made by Steinberg and Colombo[13,52].

The composition of copolymers of ethylene and carbon monoxide shows a marked temperature dependence: the carbon monoxide content of the copolymer decreases with increase in the reaction temperature. The temperature dependence of the relative activity of ethylene corresponds to the equation given above [Section IV (c)] in the range 70–150°.[53] The parameters of this equation are

$$\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger} = 19300 \pm 1700 \text{ J mole}^{-1},$$

$$\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger} = 41.9 \pm 3.8 \text{ J mole}^{-1} \text{ deg}^{-1}.$$

According to the data of Coffman et al.[54], in the temperature range 200–260°,

$$\Delta H_{11}^{\ddagger} - \Delta H_{12}^{\ddagger} = 36000 \text{ J mole}^{-1},$$

$$\Delta S_{11}^{\ddagger} - \Delta S_{12}^{\ddagger} = 67 \text{ J mole}^{-1} \text{ deg}^{-1}.$$

As noted above, side-reactions take place at these high temperatures, and this possibly explains the marked discrepancy in the above data.

A noteworthy feature is the unusually large differences in the activation entropies and enthalpies of addition of ethylene and carbon monoxide to a radical terminating in a methylene group (see, for example, the data given by Alfrey et al.[264]).

An interesting feature of the copolymerisation of ethylene and carbon monoxide is the pressure dependence of the copolymer composition. Data have been published[257] indicating that, with increase in pressure in the reaction system from 14 to 1000 bars, the carbon monoxide content of the copolymer increases from 13 to 45% (the copolymerisation was carried out in cyclohexane solution in the presence of t-butyl peroxide at 135° with a carbon monoxide content in the original mixture of 42%). An explanation for this fact was put forward by Barb[265,266]†, who considered that carbon monoxide takes part in the copolymerisation not directly but in the form of an unstable equimolecular complex with ethylene, by a process similar to that occurring in the copolymerisation of alkenes with sulphur dioxide[237].

A consequence of this assumption is that the following relationship should be observed between the ratio $n$ of the numbers of molecules of ethylene and carbon monoxide in the copolymer and the carbon monoxide concentration [CO] in the reaction system

$$n = 1 + \frac{\text{const}}{[CO]}.$$

As shown by Walling[268–270], this relationship can also be obtained on the assumption that one of the elementary reactions of chain growth is reversible

$$RCH_2CH_2 + CO \rightleftarrows CH_2CH_2CO^{\cdot}, \qquad (1)$$

Using the experimental data of Brubaker and his coworkers, Barb showed that the above relationship is in fact observed at pressures up to 300 bars. Barb, however, assumed without justification that the solubility coefficients for ethylene and carbon monoxide in cyclohexane are constant up to partial pressures of 200 bars, and that the ideal gas laws are applicable to the ethylene–carbon monoxide system at partial pressures of ethylene greater than the critical pressure. It is possible that the change in the composition of the copolymer with change in the total pressure in the system is due to a change in the relative solubilities of ethylene and carbon monoxide in cyclohexane‡. Evidence in support of this suggestion is provided, in particular, by the fact that in the case of copolymerisation in the gas phase at 70°, no change was observed in the relative activity of ethylene with change in the total pressure from 120 to 270 bars, or with change in the concentration of carbon monoxide in the reaction system from 0.2 to 6.3 mole dm$^{-3}$.[53]

It is nevertheless possible that at higher temperatures the composition of the copolymer does depend on pressure because of the reversibility of reaction (1). This may explain the following facts — (1) the considerable decrease in the carbon monoxide content of the copolymer with increase in the temperature of copolymerisation, (2) the decrease in the yield and molecular weight of the copolymers with increase in temperature, and (3) the increase, unusual for radical copolymerisation, in the tendency of the monomers to alternate in the polymer with increase in pressure (at 120° and 220–230 bars, $r_{C_2H_4} = 0.33$;[53] at 120–130° and 850–1000 bars, $r_{C_2H_4} = 0.15$[54]). Further studies are required to clarify this question.

The rate of radiation copolymerisation increases with increase in the concentration of carbon monoxide in the original mixture[53].

Copolymers of ethylene and carbon monoxide have the structure of linear polyketones. This has been proved by infrared spectrophotometry[12,257,260] and also by the chemical reactions of the copolymers[257]. The composition of the copolymer can be determined by elementary analysis or by infrared spectrophotometry (from the intensity of absorption of the carbonyl group[272] or from the ratio of the intensities of absorption of the methylene groups attached and unattached to carbonyl[260]).

Copolymers of ethylene and carbon monoxide of sufficiently high molecular mass are crystalline[32,180]. X-Ray structural analysis indicates a high degree of order in copolymers obtained by radiation copolymerisation in the gas phase at 25–70°.[34,35,53] As noted above, these products retain the crystal structure of polyethylene. The structure of the orthorhombic cell of polyethylene and of two copolymers with different carbon monoxide contents is shown in Fig. 4.[35]

Natta et al.[26] point out that the absorption bands in the infrared spectra of homopolymers, usually related to the crystallinity of the specimen, disappear rapidly even on isomorphous replacement of the units in the polymer chains. This phenomenon is observed, in particular, in the spectra of copolymers of ethylene and carbon monoxide. Thus the spectrum of a copolymer containing 21% of carbon monoxide still shows the 730 cm$^{-1}$ band associated with the crystalline structure of polyethylene. This band disappears with increase in the carbon monoxide content to 43%; at the same time the appearance of a band at 1338 cm$^{-1}$ and splitting of the band due to stretching vibrations of the carbonyl group are observed. These phenomena are related to the crystal structure of the polyketone[260].

The melting points of ethylene–carbon monoxide copolymers of high molecular weight lie in the range 90–200°. With increase in the carbon monoxide content, the melting point falls slightly, possibly owing to a decrease in the molecular mass[53] or the heat of fusion of the copolymer[32].

† Speculations regarding the mechanism of the process have also been put forward by Curphy[259] and by Vatsulik[267].

‡ Gonikberg[271] considers that increase in pressure produces an extremely marked increase in the rate of attachment of –CO– groups to the growing polymer chain.

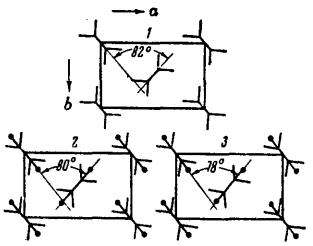



Fig. 4. Crystal structure of polyethylene and of copolymers of ethylene with carbon monoxide[35]: 1) polyethylene; 2) copolymer containing 31% of carbon monoxide; 3) copolymer containing ~50% of carbon monoxide.

With further increase in the carbon monoxide content, the melting point of the copolymer increases. A copolymer containing 10–20% of carbon monoxide has a vitrification temperature in the range between -25° and -125°.[37]

Copolymers of ethylene and carbon monoxide, obtained in the gas phase at 25–120° under the influence of $^{60}Co$ $\gamma$-radiation, are almost insoluble in paraffinic and naphthenic hydrocarbons, *m*-cresol, and pyridine[13,14,53]. The density of these copolymers lies in the range 1.1–1.2 (these are close to the calculated values)[13,14,34,35,53]. The density of copolymers obtained at 200–250° and 700–1100 bars increases from 0.92 to 1.02 with increase in the carbon monoxide content from 3 to 23%.[32] Copolymers of ethylene and carbon monoxide blend well with paraffin wax and other waxes[252], polyurethane elastomers[258], and chlorine-containing polymers[261]; the compatibility of the latter with the copolymers increases with increase in the carbon monoxide content of the copolymers. A disadvantage of copolymers of ethylene and carbon monoxide, which restricts their possible applications, is their brittleness. The optimum combination of mechanical properties is apparently shown by copolymers with a very low carbon monoxide content[180].

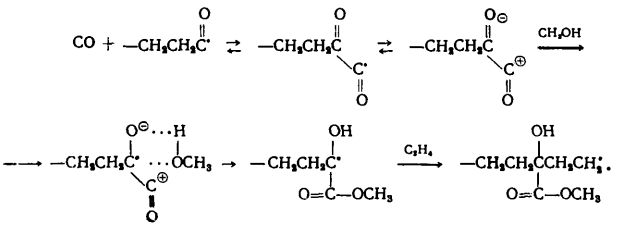
A characteristic property of copolymers of ethylene and carbon monoxide is their thermal reactivity[180,234,259,260]. When these products are heated above their melting points in air or *in vacuo*, they are rapidly converted into hard, brittle, infusible, insoluble substances, which soften when heated. This casts doubt on the accuracy of conclusions[32,257] based on the viscosity of the molten copolymers. The changes in the copolymers are accompanied by the liberation of water. The reaction rate increases sharply with temperature. It has been suggested[259,260] that this process involves the thermal initiation of crotonic condensation. The possibility of reaction is determined to a considerable extent by the mobility of the molecular chains, so that the rate of the process increases sharply on fusion of the copolymer. The process apparently takes place by an intermolecular mechanism, as indicated by the autoretardation of the reaction and the infusibility and insolubility of the products[260]. The polyketones can undergo condensation also under the influence of alkali[180,243,247,250,259,273,274].

The cross-linking of copolymers of ethylene and carbon monoxide by peroxides[180,275], chloramine[275], and nitrogen-containing bases[180,248] leads to an increase in their strength, a rise in their softening temperature, and a decrease in their solubility.

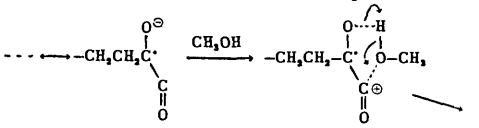
The high reactivity of the polyketones opens up extensive possibilities of chemical modification of these products and their utilisation for the preparation of macromolecular compounds of different classes — polyoximes[180,257], hetero-chain polyamides and polytetrazoles[160,276,277], poly-$\alpha$-ketone oximes and dioximes[278] and chelate compounds based on them[279], allyl derivatives[181], phosphorus-containing polymers[256], polyketo-nitriles and polyketo-acids[180,242,260], polycyanhydrins[251,257], polyhydantoins[255], polyalcohols[180,245,253,257,281-284], polyurethanes[245,253,282-287], polythiols and polysulphides[254], and polyamines and their derivatives[249,259,285-296]. The oxidation of copolymers of ethylene and carbon monoxide with nitric acid gives a mixture of dicarboxylic acids, whose composition yields information on the distribution of carbonyl groups in the copolymer chain[180,246,257].

In addition to copolymers of ethylene and carbon monoxide, patents describe the preparation of three-component copolymers of ethylene and carbon monoxide with propene[180,181,240,245,248,253,261,262], methylpropene[180,181,240,261], butadiene[180,181], vinyl acetate[180,181], diethyl maleate[180,181,247], diallyl phthalate[180], and sulphur dioxide[297]; and also the four-component copolymer of ethylene, carbon monoxide, vinyl acetate, and diethyl maleate[180]. The conditions of copolymerisation do not differ in principle from those for the copolymerisation of ethylene and carbon monoxide. The three-component copolymers can be subjected to the same chemical changes as those of ethylene and carbon monoxide.

If the copolymerisation of ethylene with carbon monoxide at high pressures is carried out in the presence of alcohols or alkyl formates, the molecules of these substances combine chemically with the copolymer and modify its structure (the copolymerisation was carried out at 130° in the presence of t-butyl peroxide)[298,299]. The quantity of chemically combined alcohol increases with increase in pressure; thus the copolymer obtained in the presence of methanol at 1000 bars contains 7% of methoxy-groups, whereas that obtained at 8000 bars contains 27%. Increase in the concentration of carbon monoxide in the original mixture decreases the yield and increases the concentration of alkoxy-groups in the copolymer. Chemical and spectroscopic data indicate that these copolymers contain the groups $-CH_2-CH_2-$, $-CO-$, and $-C(OH)(COOR)-$.[289,299] Special experiments showed that copolymers of ethylene and carbon monoxide do not react with carbon monoxide and methanol under the conditions of this reaction, so that the molecules of the alcohol combine with the copolymer directly during copolymerisation. Cairns et al.[299] suggested the following reaction mechanism§




§ Cairns et al. write the third and fourth species as




(Ed. of Translation).

This reaction mechanism is difficult to reconcile with the fact that $\alpha$-dicarbonyl groups are not formed in the copolymerisation of ethylene and carbon monoxide.

Products obtained by chemical transformation of the copolymers (hydrolysis, oxidation, hydrogenation, and treatment with formaldehyde and peroxides [298-300]) have also been described.

The catalytic hydrocondensation of ethylene and carbon monoxide is an unusual free-radical process: hydrogenation of the carbon monoxide gives methylene radicals, which copolymerise with the ethylene [301].

2. Copolymerisation with carbon dioxide. According to data given in patents [302], ethylene copolymerises with carbon dioxide under the influence of peroxide initiators at elevated temperatures and pressures up to 1000 bars. Vatsulik [267] suggests the following reaction mechanism

$$CH_2{=}CH_2 + CO_2 \rightarrow \dot{C}H_2{-}CH_2{-}O{-}CO{-}CH_2{-}\dot{C}H_2 \rightarrow$$
$$\rightarrow CH_3{-}CH_2{-}O{-}CO{-}(CH_2{-}CH_2{-}O{-}CO)_n{-}CH_2{-}CH_2{-}O{-}CO{-}CH_2{-}CH_3,$$

but gives no arguments in support of this scheme.

3. Copolymerisation with sulphur dioxide. The copolymerisation of alkenes with sulphur dioxide is of considerable theoretical and practical interest, and much work has been done on this reaction. In these studies, ethylene has been assigned a modest role. Since a number of fairly detailed reviews have been published [303-310], we shall merely discuss a few papers on the copolymerisation of ethylene, and shall not deal with general problems of the copolymerisation of alkenes with sulphur dioxide.

Ethylene copolymerises readily with sulphur dioxide under the influence of peroxides [311-313], azo-compounds [314-316], sunlight [317], ultraviolet rays [317,318], and $^{60}Co$ $\gamma$-radiation [319-321].

The substances used as copolymerisation initiators include, in particular, the peroxide products of the autoxidation of diethyl ether and ethylbenzene [311-313]. In the latter case, liquid sulphur dioxide copolymerises at temperatures from -20° to -30° and atmospheric pressure with pure ethylene and also with the technical product containing only 50% of ethylene [312,313].

A characteristic feature of the copolymerisation of alkenes with sulphur dioxide is the existence of a limiting temperature, specific for each alkenes, above which the reaction does not take place. This temperature is independent of the nature of the initiator, but depends on the monomer concentration [310]. It has not been determined for ethylene but is much higher than for other alkenes [318,322].

The kinetics of the radiation copolymerisation of ethylene and sulphur dioxide at 0° was studied by Bray et al. [321] on the basis of the following scheme for the copolymerisation process —

initiation

$$C_2H_4 \rightarrow R_1,$$
$$SO_2 \rightarrow R_2,$$

chain growth

$$RCH_2\dot{C}H_2 + SO_2 \rightarrow RCH_2CH_2SO_2^{\cdot},$$
$$RSO_2^{\cdot} + C_2H_4 \rightarrow RSO_2CH_2\dot{C}H_2,$$

chain termination

$$R_2CH_2\dot{C}H_2 + R_2CH_2\dot{C}H_2 \rightarrow P,$$
$$R_1CH_2\dot{C}H_2 + R_2SO_2^{\cdot} \rightarrow P,$$
$$R_1SO_2^{\cdot} + R_2SO_2^{\cdot} \rightarrow P.$$

It can be seen from the above scheme that Bray et al. considered that the two values of the relative activities for the copolymerisation of ethylene and sulphur dioxide are zero (the monomers do not add on to "their own" radicals). This assumption is not strictly justified, since the studies were carried out only with an equimolar mixture of monomers (the ratio of the original molar concentrations of ethylene and sulphur dioxide lay in the range 0.9–1.4); moreover, the sulphur content of the reaction products was slightly lower than that corresponding to an equimolar monomer ratio. According to the experimental data, almost no depolymerisation of the growing radicals takes place in the copolymerisation process.

In the copolymerisation of ethylene with sulphur dioxide, linear copolymers having a polysulphone structure are formed [311]. In most cases copolymers with an equimolar monomer ratio were obtained. The structure of these copolymers can be represented by the formula

$$\left[-CH_2-CH_2-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\right]_n.$$

Products of this type have a crystalline structure [323] and unusually high melting points. Thus the copolymers obtained at 0° under the influence of $^{60}Co$ $\gamma$-radiation melted over the range 312–341°, fusion being accompanied by decomposition of the copolymer [321]. The melting points of the copolymers generally lie above the temperatures of their thermal decomposition. Such high melting points are apparently due to the marked polarity of the sulphonyl groups (Table 1) and the regular structure of the copolymer.

Equimolecular copolymers of ethylene and sulphur dioxide do not dissolve in any known solvents, including concentrated sulphuric and nitric acids [311,324] (according to Bray et al. [321] these copolymers are very sparingly soluble in aliphatic ketones). They are stable towards powerful oxidising agents but decompose under the influence of dilute alkalis, forming salts of sulphinic acids and a small quantity of neutral products [311]. The equimolecular copolymers have high thermal stability. Staudinger and Ritzenhalter [311] noted that these copolymers broke down into the original components above 300°. According to Naylor and Anderson [315] the decomposition of copolymers of monoalkenes with sulphur dioxide takes place in conformity with a unimolecular mechanism.

Of all the equimolecular copolymers of alkenes with sulphur dioxide, those of ethylene have the highest melting point, lowest solubility, and highest thermal stability. The infusibility and the insolubility of these products make their processing extremely difficult, so that they have not found practical application. According to data given in patents, considerably improved properties are shown by polysulphones containing less than 50 mole % of sulphur dioxide [316,325]. These copolymers, which have a high tensile strength, can be processed by casting under pressure or by extrusion at 200°. The copolymers can be used as additives to drying oils [326].

Naylor and Anderson [315] describe the preparation, and give data on the rate of thermal degradation, of the three-component copolymer of ethylene, propene, and sulphur dioxide. They point out that this type of three-component copolymerisation can be carried out at temperatures lower than the limiting temperature of each alkene with sulphur dioxide. A continuous process for the ternary copolymerisation of ethylene, but-1-ene, and sulphur dioxide has also been described [327]. The ratio of the reactivities of cyclohexene and ethylene under the conditions of three-compo-

nent copolymerisation with sulphur dioxide has been determined by Hazell and Ivin [328]. The three-component copolymer of ethylene, carbon monoxide, and sulphur dioxide was mentioned above [297].


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# SALTING-OUT AND SALTING-IN OF NON-ELECTROLYTES

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The problem of the effect of electrolytes on the solubility of non-electrolytes is of great theoretical and practical importance. A great deal of work[1-57] has shown that electrolytes can either decrease or increase the solubility of neutral substances in water, the phenomenon being termed *salting-out* or *salting-in* respectively.

Processes associated with salting-out are widely used in the production of dyes, amines, soaps, etc. At the present time the employment of salting-out agents in extraction is becoming especially important[58-74]. On the other hand, substances which increase the solubility of non-electrolytes in water (hydrotropic substances) are beginning to find application in industry.

McKee[75] reported the employment of alkanesulphonates of the alkali and alkaline earth metals in papermaking, and referred to the possibility of replacing organic solvents by solutions of hydrotropic salts in the electrolysis of organic substances. The presence of a second phase in the system is known to diminish the rate of many organic reactions. By the use of hydrotropic salts the system can be made homogeneous, and the rate of the process thereby increased. In addition, salts influence the course of a reaction[76-79].

The behaviour of salts in aqueous solutions of non-electrolytes is a complicated phenomenon owing to the occurrence in the water–electrolyte–non-electrolyte system of various types of interaction: water–electrolyte, water–non-electrolyte, and electrolyte–non-electrolyte.

Systematic study of the effect of salts on the solubility of neutral substances in water has revealed several regularities, which have subsequently formed a basis for theories of salting-out and salting-in. The influences of some substances on the solubility of others has been investigated by various methods — by direct measurement of solubilities, determination of partition coefficients, determination of

freezing-point depression, and measurement of partial vapour pressures. The results obtained can be summarised briefly as follows:

1. In the overwhelming majority of cases, electrolytes diminish the solubility of non-electrolytes in water.

2. The smaller an ion having a given charge, the greater its salting-out action.

3. The sequence of salts remains the same for their action on many but not all non-electrolytes.

4. Increase in ionic radius (of cation or anion) results in a decrease in the salting-out effect and a change to salting-in.

5. The salting-out constant can be calculated from Sechenov's equation

$$\log\frac{S_0}{S} = K_S C_S, \qquad (1)$$

where $S_0$ and $S$ are the solubilities of the non-electrolyte in water and in the aqueous salt solution, $C_S$ is the concentration of the salt, and $K_S$ is the salting-out constant.

6. The change in the logarithm of the activity coefficient of the non-electrolyte is found to be proportional to the salt concentration expressed in moles or equivalents per litre.

Sechenov's equation has been tested many times[80-84], and, although the constant varies with the electrolyte concentration, especially at high values of the concentration, the equation has so far found wide application for assessing the effects of different salts.

Rendall and Failey[5-7] proposed as measure of the salt effect the ratio of the logarithm of the activity coefficient of the non-electrolyte $f_S$ to the ionic strength of the solution $\mu_{soln}$. In their view this quantity $(1/\mu_{soln})\log f_S$ has the advantage that it does not involve the valencies of the ions, and it remains constant in solutions of different ionic strength. Rendall and Failey's results for benzoic acid in solutions of sodium chloride at 25° may serve as illustration (Table 1).

Rendall and Failey give the following sequence for the action of the ions

$$OH^- > SO_4^{2-} > CO_3^{2-} > ClO_3^- > BrO_3^- > Cl^- > CH_3COO^- > IO_3^- > ClO_4^- > Br^-,$$
$$I^- > NO_3^- > Na^+ > K^+ > Li^+ > Ba^{2+} > Ca^{2+} > Ni^{2+} > Co^{2+} > Mg^{2+} > Fe^{2+} >$$
$$> Zn^{2+} > Mn^{2+} > Al^{3+} > NH_4^+ > H^+$$

This sequence is approximately maintained for many non-electrolytes, but investigations of the effect of 0.5 M NaCl solution on the solubility of various substances in water at 30° showed that the salting-out effect depends also on the nature of the non-electrolyte (Table 2).

TABLE 1. Activity coefficient and values of $(1/\mu_{soln})\log f_S$ in solutions of different ionic strengths[5].

| $\mu_{soln}$ | $f_s$ | $(1/\mu_{soln})\log f_s$ |
|---|---|---|
| 0.01982 | 1.007 | 0.153 |
| 0.02502 | 1.010 | 0.173 |
| 0.03320 | 1.014 | 0.182 |
| 0.05010 | 1.023 | 0.197 |
| 0.1002 | 1.045 | 0.191 |
| 0.2009 | 1.092 | 0.190 |
| 0.3356 | 1.154 | 0.185 |
| 0.5022 | 1.231 | 0.180 |

It is difficult from the data in Table 2 to establish a relation between the polarity of the non-electrolyte and the salting-out effect of the given electrolyte. Although the percentage salting-out is greatest for substances which possess no dipole moment $\mu$, it is also high with ethyl iodide ($\mu$ = 1.7) and low with chlorobenzene (1.56).

We can also examine Long and McDevit's data[4] in Table 3, in which the dipole moments and the salting-out constants of organic compounds are compared (with potassium chloride as electrolyte).

No very clear parallelism is observed on comparing the variation in salting-out constant with dipole moment. Thus nitrobenzene and benzene, which differ greatly in their polar properties, have the same salting-out constants, but if nitrobenzene and *p*-phenylenediamine are excluded, an increase in dipole moment entails a decrease in salting-out constant. Where the tables give no indication of salt concentration, the values of $K_S$ relate to infinite dilution, and have been calculated from the slope of the linear dependence of $\log f_S$ on salt concentration.

Interesting observations were made by Linderstrøm-Lang[86] on the effect of substituted ammonium chlorides on the solubility of benzoquinone and quinol in water. That of quinol increases and the salting-in constant changes with change in size of the cation, whereas benzoquinone is salted-out by all these salts, and the salting-out constant is small and unchanged.

Long and McDevit[87] examined the difference in the action of salts on acidic and basic non-electrolytes. If the non-electrolyte is basic in character, sensitivity to the charge on the anion is observed, and lithium salts cause salting-in. The salting-out of weak acids increases with the charge on the cation, and cations show the normal sequence in their action: i.e. salting-out is more intense with lithium than with sodium salts. In the view of these workers the difference in the action of salts on non-electrolytes of acidic and basic character is associated with the orientation of water

TABLE 2. Effect of 0.5 M NaCl solution on the solubility of various substances in water at 30°.[85]

| Compound | Salting out, % | $10^{18}\mu$ | Compound | Salting out, % | $10^{18}\mu$ |
|---|---|---|---|---|---|
| *p*-Nitroaniline | 3.0 | 7.1 | Methylene diiodide | 11.6 | 1.1 |
| *m*-Dinitrobenzene | 3.0 | 3.8 | Propyl bromide | 11.9 | 1.9 |
| Nitrobenzene | 3.1 | 4.0 | n-Butyl bromide | 12.3 | 1.9 |
| Bromobenzene | 4.1 | 1.50 | Propyl iodide | 13.2 | 1.7 |
| Chlorobenzene | 5.6 | 1.56 | Ethyl iodide | 13.5 | 1.7 |
| Bromoform | 8.2 | 1.0 | Ethylene dibromide | 13.7 | 1.0 |
| Methylene dibromide | 9.1 | 1.4 | Carbon tetrachloride | 16.7 | 0 |
| Chloroform | 9.7 | 1.2 | Benzene | 19.1 | 0 |
| Ethylene dichloride | 11.3 | 1.8 | Toluene | 24.3 | 0 |

TABLE 3. Dipole moment and salting-out constant[4].

| Compound | $\mu$ | $K_s$ | Compound | $\mu$ | $K_s$ |
|---|---|---|---|---|---|
| *p*-Nitroaniline | 6.5 | 0.049 | Benzoic acid | 1.7 | 0.144 |
| *p*-Nitrophenol | 5.0 | 0.050 | Phenol | 1.6 | 0.133 |
| *m*-Nitroaniline | 4.7 | 0.077 | Aniline | 1.5 | 0.130 |
| Nitrobenzene | 4.0 | 0.166 | *p*-Phenylenediamine | 1.5 | 0.018 |
| Salicylic acid | 2.6 | 0.126 | Benzene | 0 | 0.166 |

molecules in the hydration sphere of the ion. Water molecules hydrating a cation are oriented with the protons on the outside, non-electrolyte molecules of basic character being attracted to them, while those of acidic character are repelled. In studying the phenomenon of salting-out, many workers have noted that the effect diminishes with increase in size of the ions, and a change to salting-in is observed [88-94].

Neuberg [95] established that aqueous solutions of many salts, such as benzoates, benzenesulphonates, and their homologues, are able to bring into solution substances of various classes which are insoluble in water (hydrocarbons, alkaloids, aldehydes, ketones, nitro-compounds, proteins, fats, etc.). Numerous experiments have shown the widespread occurrence of this phenomenon, which is termed hydrotropism.

Hydrotropic substances are usually saltlike in character, containing COOM, $SO_3M$, $SO_2M$, or $OSO_3M$ groups. They can have either a chain or a ring structure, and may also contain halogeno-, amino-, nitro-, or hydroxy-groups.

Neuberg [95] noted that hydrotropic salts are specific in their action: sulphonates bring proteins and alkaloids into solution, but not essential oils, higher alcohols, or ketones. Table 4 shows the change from salting-out to salting-in with increase in size of the ions in the electrolyte.

Interesting results were obtained by Bockris et al. in a study of the effect of the radius of the cation on the solubility of benzoic acid in water [97]. Table 5 shows that the salting-in action increases with increase in radius of the cation.

Licht and Wiener [98] studied phase equilibria in the water–benzoic acid system containing sodium salts of benzene-, toluene-, and xylene-sulphonic acids. They noted that all the salts increase the solubility of benzoic acid in water, and that the hydrotropic effect increases as the alkyl group becomes longer, i.e. with increase in molecular weight of the salt. Introduction of a bromine atom (sodium *p*-bromobenzenesulphonate) gives the same result as increasing the size of the alkyl group. It is curious that introduction of a second sulpho-group (sodium benzene-*m*-disulphonate) destroys the salting-in property of the salt for benzoic acid, and a slight salting-out is observed. These workers remarked that the phase diagrams which they obtained give no indication of the formation of chemical compounds.

Booth and Everson [99] studied the effect of sodium *o*-, *m*-, and *p*-xylenesulphonates on the aqueous solubility of acetophenone, aniline, benzaldehyde, *o*-cresol, cyclohexanone, and diethyl ether, and found that all three salts increase the solubility of these substances to the same extent. Another paper by these workers [100] describes the action of the

TABLE 4. Constants for the salting-in of non-electrolytes by large ions at 25°. [96]

| Salt | Benzene | Benzoic acid | Aniline |
|---|---|---|---|
| LiCl | 0.148 | 0.189 | 0.070 |
| NaCl | 0.195 | 0.182 | 0.136 |
| $C_6H_5COONa$ | —0.052 | —0.218 | —0.043 |
| $C_6H_5SO_3Na$ | —0.090 | —0.170 | —0.062 |
| $p$-$CH_3C_6H_4SO_3Na$ | —0.070 | —0.355 | —0.093 |
| $(CH_3)_4NBr$ | —0.149 | —0.140 | —0.185 |
| $(C_2H_5)_4NI$ | —0.248 | —0.360 | —0.308 |

TABLE 5. Effect of quaternary ammonium salts on the solubility of benzoic acid in water at 25°. [97]

| Salt | $K_s$ |
|---|---|
| $NH_4I$ | +0.021 |
| $N(CH_3)_4I$ | —0.256 |
| $N(C_2H_5)_4I$ | —0.633 |
| $N(C_3H_7)_4I$ | —0.970 |
| $N(C_4H_9)_4I$ | —1.32 |

sodium salts of benzene-, toluene-, xylene-, and cymene--sulphonic acids on the solubility of various kinds of substances in water. They found that hydrotropic salts, which increase the solubility of benzoic acid, behave altogether differently towards some non-electrolytes. Thus the solubility of benzene, carbon tetrachloride, cottonseed oil, and n-hexane is not increased in solutions of these salts, whereas that of *o*-cresol and cyclohexane is greatly increased.

Larsson [101-104] and Kolthoff and Bosch [105] studied the effect of sodium and potassium benzoates on the solubility of benzoic acid in water. It would appear from the law of mass action that salts containing the same ion as the acid should diminish the solubility of benzoic acid, but the opposite results were obtained: the presence of salts of benzoic acid in water led to an increase in the solubility of the acid. Similar effects were found by Ross et al. [106] in a study of the influence of salts of mandelic acid on the solubility of this acid, and by Osol and Kilpatrick [107,108] with *o*-chlorobenzoic acid and the corresponding sodium salt.

Kolthoff and Bosch [105] attribute this action of salts on the solubility of weak acids to interaction between the ion of the salt and a molecule of the acid according to the equation

$$HB + B^- \rightleftarrows HB_2^-.$$

Observations of salting-in effects were accompanied by attempts to explain this phenomenon. Some authors assumed it to result from chemical interaction between electrolyte and non-electrolyte [18,106,109], but Neuberg [95] did not regard this as the sole cause, since in many cases the observed increase in solubility is not the result of a chemical process.

Gross [85] suggested that cations and anions have opposite effects, the former salting-out and the latter salting-in, and the overall action of a salt being the net effect of cationic and anionic components.

Gross [85] and Larsson [101-104] suggested that the constant of the salt effect is an additive function of two constants characteristic of the anion and the cation:

$$\log f_s = K_s C_s = (K_K + K_A) C_s.$$

Larsson assumed that $K_{K^+} = K_{Cl^-}$, and since $K_{KCl} = 0.14$, it follows that $K_{K^+} = K_{Cl^-} = 0.07$. This hypothesis was used as a basis for calculating salting-out constants for other ions.

It is seen from the data for benzoic acid in Table 6 that the ionic salting-out constants for many large anions are negative, showing that these ions have a salting-in action. Further investigation established that not only bulky anions but also large cations (quaternary ammonium halides) exert a salting-in effect [97,108].

TABLE 6. Ionic salting-out constants for benzoic acid[85].

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $H^+$ | 0.02 | $Cs^+$ | −0.08 | $Cl^-$ | 0.07 | $OCOCH_3Cl^-$ | −0.14 |
| $Li^+$ | 0.12 | $Mg^{2+}$ | 0.10 | $Br^-$ | 0.00 | $OCOCCl_3^-$ | −0.12 |
| $Na^+$ | 0.11 | $Ca^{2+}$ | 0.10 | $I^-$ | −0.02 | $OCOC_6H_5^-$ | −0.32 |
| $K^+$ | 0.07 | $Sr^{2+}$ | 0.09 | $NO_3^-$ | 0.03 | $OSO_3C_6H_5^-$ | −0.23 |
| $Rb^+$ | 0.02 | $Ba^{2+}$ | 0.08 | $ClO_4^-$ | 0.06 | $OSO_3C_{10}H_7^-$ | −0.86 |

All these investigations led to the development of theories to explain the action of salts on the solubility of non-electrolytes. The earliest of these was the hydration theory. During the 1890's a study of the solubility of carbon dioxide in water and salt solutions led Sechenov[1] to the conclusion that the gas was always less soluble in the presence of salts than in pure water. He put forward the hypothesis that "Salt solutions are compounds of the salt and water. On this basis we could regard the solution as if only the solvent, water, were the absorbing medium for the gas, while the salt combines with water, and weakens its absorbing power". Thus Sechenov was the first to express the opinion that the decrease in solubility of the non-electrolyte is due to hydration of the salt.

Rothmund[2], Philip[110-112], and later Glasstone[113-116] as well as Eucken and Herzberg[117] have assumed that the salting-out action of electrolytes is due to ions binding water molecules and diminishing the quantity of free solvent, so that the solubility of neutral molecules decreases. But this apparently extremely plausible view cannot explain the dependence of the hydration numbers of the ions during salting-out on the nature of the non-electrolyte. Moreover, the hydration theory cannot explain the increase in solubility of a non-electrolyte caused by the addition of certain electrolytes.

Another attempt to provide a theoretical basis for salting-out phenomena is due to Debye and McAulay[118,119], who take into account only the effect of one type of forces, the coulombic forces. Ions are regarded as spheres having a definite radius. The work done in discharging ions is calculated for the pure solvent of dielectric constant $D_0$ and for a medium of dielectric constant $D$, which medium may be the solution containing both electrolyte and non-electrolyte. This leads to the appearance of an additional component of the chemical potential, and thus the activity coefficient of the neutral molecules was found to be given by the equation

$$\log f_s = \log \frac{S_0}{S} = \frac{\beta}{2KTD_0} \sum \frac{n_j l_j^2}{r_j}, \qquad (2)$$

where $K$ is Boltzmann's constant, $T$ the absolute temperature, $n_j$ the number of ions of a given kind, $l_j$ the ionic charge, $r_j$ the ionic radius, $D_0$ the dielectric constant of water, $D$ that of the solution, and $n$ the number of moles of the non-electrolyte.

The constant $\beta$, characterising the non-electrolyte, can be found from the equation

$$D = D_0(1 + \beta n). \qquad (3)$$

This equation shows that, if the dielectric constant is smaller than that of the pure solvent, $\beta$ will be positive, indicating salting-out. If, however, the value of $D$ for the solution is greater than that for water, $\beta$ will be negative, and salting-in will occur. A single example satisfying this condition has been reported in the literature: the experiments of Gross[120] on the distribution of hydrogen cyanide and acetone between benzene and aqueous solutions of salts show that acetone is salted-out, since it decreases the dielectric constant of water, whereas hydrogen cyanide is salted-in, because hydrocyanic acid possesses a higher dielectric constant than water, and its addition to the latter increases the value of $D$ for the solution.

According to the equation of Debye and McAulay, $\log f_s$ should vary linearly with electrolyte concentration, as is also observed in most cases. Figs. 1 and 2 show as example the effect of various electrolytes on the solubility of hydrogen and benzoic acid[4]. It is noteworthy that this equation is similar in form to the empirical equation of Sechenov. Furthermore, the equation of Debye and McAulay gives the dependence of the salting-out action of an electrolyte on the radius of its ions: the smaller the radius of the cation, the greater the diminution in solubility of the non-electrolyte produced by a given electrolyte. Later Debye developed a more exact theory of salting-out, which was further developed in papers by Gross[121-124], Butler[125], Kirkwood[126], and others[127-132].

Long and McDevit[44] compare the effect of salts on the solubility of benzene in water with values calculated from the equations of Debye and of Kirkwood. It is seen from Table 7 that values calculated by means of the two equations differ little between themselves. They predict the general order of change on passing from one salt to another, but give an inadequate idea of the specific action of salts observed experimentally. This is understandable, since the

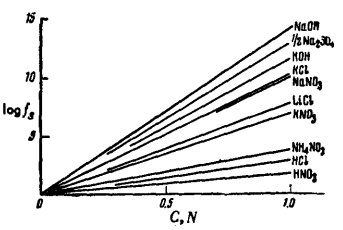



Fig. 1. Action of salts on the solubility of $H_2$.[4]

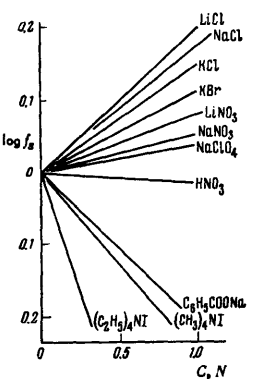



Fig. 2. Effect of salts on the solubility of benzoic acid in water at 25°.[4]

TABLE 7. Comparison of calculated and experimental salting-out constants for benzene[44].

| Salt | $K_{obs}$ | $K_{Debye}$ | $K_{Kirkwood}$ |
|---|---|---|---|
| NaF | 0.254 | 0.130 | 0.133 |
| NaCl | 0.195 | 0.126 | 0.125 |
| $NH_4Cl$ | 0.103 | 0.124 | 0.109 |
| LiCl | 0.141 | 0.127 | 0.143 |
| NaI | 0.095 | 0.122 | 0.120 |
| CsCl | 0.088 | 0.121 | 0.105 |
| $(CH_3)_4NBr$ | —0.24 | 0.110 | 0.093 |

whole specific action of an electrolyte is contained, in these equations, in the ionic radii, which differ little among themselves, so that the salting-out constants calculated from these equations vary insignificantly, and differ appreciably from the observed values. It is noteworthy that neither equation provides for salting-in.

Mikhailov[133] has attempted to refine the Debye equation by introducing the concept of a salting-out sphere of finite radius. A new term appears in the equation, which takes into account both the actual volume of the ion and the change in the salting-out sphere with increase in electrolyte concentration. Agreement between calculated and observed values is unsatisfactory. Thus for the water–benzene–sodium chloride system the calculated coefficient is 0.114, while the actual value is 0.260. The discrepancy between calculated and experimental values is attributed by the author to disregard of non-electrostatic interactions in the solution.

The defects of the Debye theory are not removed by refinements of a different type. As before, experimental activity coefficients differ substantially from the calculated values, and the Debye–McAulay equation gives no transition from salting-out to salting-in. It was mentioned above that several authors found an increase in solubility of a non-electrolyte to be produced by electrolytes having large ions, and it was therefore suggested that salting-in by large ions is due to the action of van der Waals forces. On this basis Bockris[97,132] put forward a theory which took into account the action of both coulombic and dispersion forces. If the latter predominate, salting-in is observed; if coulombic forces are predominant, salting-out occurs. Bockris has shown that, with ions of high polarising power, ion–non-electrolyte dispersion interaction may predominate over ion–water coulombic interaction. Large ions, of high polarisability, interact more strongly with non-electrolyte molecules than with the small water molecules, and therefore salting-in is observed.

The proposed equation is[97,132]

$$\frac{\Delta S}{S_0} = m_i\left(P_C - P_B\frac{v_C}{v_B}\right)\frac{2\pi l_0^2 N_A}{1000\epsilon_s^2 KT}\left(\frac{1}{a_+}-\frac{1}{a_-}\right)+\left(\frac{\alpha_C\nu_C}{\nu_{A\pm}+\nu_c}-\frac{\alpha_B\nu_B}{\nu_{A\pm}+\nu_B}\,\frac{v_C}{v_B}\right)\times$$
$$\times\frac{2\pi\times N_A h}{1000\epsilon_0^2 KT}\left(\frac{\alpha_{A+}\nu_{A+}}{a_+^2}+\frac{\alpha_{A-}\nu_{A-}}{a_-^2}\right), \qquad (4)$$

where $A$ represents the electrolyte, $B$ the solvent, $C$ the non-electrolyte, $a$ ionic radii, $P$ total molecular polarisations, $\gamma$ characteristic frequencies, $\alpha$ electron polarisabilities, $v$ molecular volumes, $\epsilon$ dielectric constants, $m_i$ the electrolyte concentration in g-ions litre$^{-1}$, $l_0$ the ionic charge, $h$ Planck's constant, and $N_A$ Avogadro's number. The first term in this equation represents coulombic interaction, and the second term dispersion interaction. Only these two types of forces are considered in this theoretical approach, other components of the van der Waals forces being ignored, since calculations by Bockris and his co-workers showed them to constitute, e.g. for the tetraethylammonium ion, less than 1% of the total dispersion energy.

Results calculated from Eqn. (4) are compared with experimental data in Table 8. Bockris et al.[97] comment on the table that, in view of the approximate character of the equation, it shows a certain agreement, giving the correct sign and sequence of change. In contrast to the Debye–McAulay equation, the possibility of two effects — salting-in and salting-out — is predicted by the present equation. Thus according to the views of Bockris[97] the increase in solubility of a non-electrolyte in the presence of a salt containing large ions results from the predominance of dispersion interaction between the non-electrolyte molecule and the large ion of the salt. Similar views had been expressed earlier by Kruyt and Robinson[86], Gross[85], etc. Thus Gross writes: "The reason for aggregation about the anion is more difficult to see, at least for the simple spherical ions such as the halogens. For the complex ions it is not so difficult. An ion like the benzoate ion consists of a large non-polar phenyl group and a small polar carboxy-group. The field around such an ion is highly unsymmetrical, and water molecules can accumulate around the carboxy-group, with non-electrolyte molecules at the other end. The size of the ion, the distribution of polar portions, and the possibility of orientation inherent in the non-electrolyte molecule should result in a highly specific character in the solubility effect".

Albright and Williams[134] concluded, from a comparison of experimental results for the action of various salts on the solubility of ethyl acetate in water with values calculated by means of various equations, that salt constants calculated on the basis of electrostatic theories disagree most with experimental data, and therefore dispersion interactions must be taken into account.

Work on other lines links the action of salting-in and salting-out agents with structural changes in the solvent (water) itself. At the end of the past century Tammann[135–140] pointed out that, if a substance which dissociates into ions is dissolved in water, the water behaves as if it were under an additional pressure, and the volume of the solution decreases owing to compression of the water itself.

Using this hypothesis, Gibson[141–143] suggested an extrapolation equation representing the property of water as a function of pressure and taking into account the change in volume of pure water when a salt is dissolved in it.

TABLE 8. Comparison of experimental salting-out with values calculated from Eqn. (4).[97]

| System | $\frac{\Delta S}{S_0 m}$ coulombic | $\frac{\Delta S}{S_0 m}$ dispersion | $\frac{\Delta S}{S_0 m}$ total | $\frac{\Delta S}{S_0 m}$ expt. |
|---|---|---|---|---|
| $N(C_2H_5)_4I$–ethylene glycol–benzoic acid | —0.480 | +0.536 | +0.06 | +0.26 |
| $N(CH_3)_4Br$–water–benzene | —0.283 | +0.864 | +0.58 | +0.72 |
| $N(CH_3)_4I$–water–benzoic acid | —0.279 | +1.224 | +0.95 | +0.80 |
| $N(C_2H_5)_4I$–water–benzoic acid | —0.257 | +1.224 | +0.97 | +0.22 |
| $N(C_3H_7)_4I$–water–benzoic acid | —0.242 | +1.224 | +0.98 | +8.3 |
| $N(C_4H_9)_4N$–water–benzoic acid | —0.231 | +1.224 | +0.99 | +2.0 |

Euler [144-146] was the first to point out the link between the decrease in solubility of a neutral substance and the magnitude of the compression produced by the added electrolyte. He states that a certain parallelism exists between the compression of the solvent and the diminution in solubility, but no quantitative relations have yet been found. Euler then compares the surface tension of the solution with the solvent power of the salt solutions, and shows that only a qualitative relation exists between decrease in surface tension and change in solubility.

Geffcken [147] also concluded, from determinations of the solubility of $H_2$, $O_2$, $N_2O$, and $CO_2$ in aqueous acids and bases, that the cause of the decrease in solubility of the gases must be sought in compression of the water itself.

Long and McDevit [44] measured the activity coefficients of benzene in aqueous salt solutions. This non-electrolyte was chosen as having a non-polar molecule, which almost completely excludes any type of interaction between the solution components and simplifies explanation of the results. These workers obtained for univalent anions the following salting-out sequence

$$OH^- > Cl^- > Br^- > NO_3^- > ClO_4^- > I^-,$$

and for alkali-metal cations

$$Na^+ > K^+ > Li^+ > Rb^+ > Cs^+.$$

Compounds containing large ions, such as $(CH_3)_4NBr$ and $C_6H_5COOK$, increase the solubility of benzene in water. These results were explained on the basis of Tammann's views: compression of the solvent under the influence of the ions impedes entry of neutral molecules into the solution, as a result of which the solubility diminishes; and conversely, large ions loosen the structure of water and thereby facilitate dissolution of neutral molecules.

In order to assess quantitatively the action of electrolytes on the solubility of non-electrolytes, Long and McDevit [44] proposed an equation of the form

$$K_s = \lim \frac{d \ln f_s}{dC_s} = \lim \frac{v_i^0 dP_e}{RTdC_s} = \frac{v_i^0 (v_s - v_s^0)}{RT\beta_0}, \qquad (5)$$

where $v_S^0$ is the partial molar volume of the salt at infinite dilution, $C_S$ the molar concentration of the salt, $\beta_0$ the compressibility of water, $v_S$ the molar volume of the liquid salt, $v_i$ the partial molar volume of the non-electrolyte, and $P_e$ the effective pressure. The quantity $v_S$ cannot be found directly, and therefore data on compression are mostly used and the quantity $dP_e/dC_S$ is employed.

Table 9 gives a comparison of salting-out constants for benzene, hydrogen, and oxygen from aqueous solutions of various salts as calculated by means of Eqn. (5) and found experimentally. With oxygen and hydrogen satisfactory agreement is observed between calculated and experimental values of the salting-out constants, but in the case of benzene the calculated value exceeds the experimental value by factors of 2–3. It was supposed [44] that, if a correction is introduced into Eqn. (5) to allow for the closest distance of approach of an ion and a non-electrolyte molecule, the equation would become

$$\lim \frac{d \ln f_s}{dC_s} = \frac{v_i^0 (v_s - v_s^0)}{RT\beta_0} \cdot \frac{a}{a+b}, \qquad (6)$$

where $a$ and $b$ are the radii of the ion and the neutral molecule. With this correction better agreement is obtained between experiment and calculation for benzene molecules.

TABLE 9. Comparison of calculated and experimental salting-out constants [44].

| Salt | Hydrogen | | Oxygen | | Benzene | |
|---|---|---|---|---|---|---|
| | $K_{obs}$ | $K_{calc}$ | $K_{obs}$ | $K_{calc}$ | $K_{obs}$ | $K_{calc}$ |
| $Na_2SO_4$ | 0.278 | 0.46 | — | — | 0.548 | 1.33 |
| NaOH | 0.140 | 0.25 | 0.179 | 0.29 | 0.256 | 0.85 |
| NaCl | 0.114 | 0.12 | 0.141 | 0.15 | 0.198 | 0.42 |
| NaBr | — | — | 0.110 | 0.12 | 0.155 | 0.34 |
| LiCl | 0.076 | 0.09 | 0.100 | 0.11 | 0.141 | 0.31 |
| KCl | 0.102 | 0.10 | — | — | 0.166 | 0.34 |
| RbCl | — | — | — | — | 0.140 | 0.31 |
| $NaNO_3$ | 0.100 | 0.09 | — | — | 0.119 | 0.31 |
| $KNO_3$ | 0.070 | 0.07 | 0.100 | 0.08 | 0.095 | 0.27 |
| $NaClO_4$ | — | — | — | — | 0.106 | 0.26 |
| CsCl | — | — | — | — | 0.088 | 0.26 |
| $NH_4Cl$ | — | — | — | — | 0.103 | 0.15 |
| HCl | 0.030 | 0.03 | 0.031 | 0.03 | 0.048 | 0.09 |
| $HClO_4$ | — | — | — | — | —0.041 | —0.05 |
| $(CH_3)_4NI$ | — | — | — | — | —0.24 | —0.54 |

A characteristic feature of Eqn. (5) is its prediction of salting-in by such substances as tetramethylammonium bromide and perchloric acid. According to the equation a linear dependence of $\log f_S$ on salt concentration corresponds to a linear dependence of $P_e$ on $C_S$ (Fig. 3), and the sequence of salting-out effects of the salts is approximately the same as that of the effective pressure.

This theory is in essence the same as the view expressed earlier by Bernal and Fowler [148] that in liquid water the molecules tend to form a tetrahedral structure, with the oxygen atoms at the corners. When a substance which dissociates into ions is introduced, the water molecules begin to orient themselves around these ions. The number of water molecules surrounding an ion depends on the relative size of ion and water molecule, the charge on the ion, and hence on the force field at the surface of this ion. These factors will determine the degree of hydration of ions in aqueous solution and the extent to which the water structure is compacted or loosened.

Small ions carrying a high charge will make the water structure more rigid, produce compression of the solvent or increase its internal pressure, and thereby impede penetration of non-electrolyte molecules into the solution:

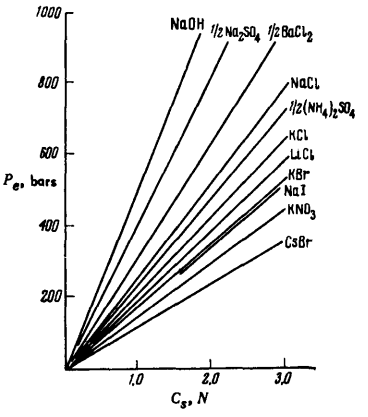



Fig. 3. Dependence of effective pressure $P_e$ on salt concentration [142,143].

they will diminish the solubility of the non-electrolyte, i.e. salt it out. Large ions having the same charge, on the other hand, will loosen the structure of water, diminish its internal pressure, and thereby favour the passage of molecules of non-electrolyte into the solution: they will salt it in.

The effect of ions on the structure of water is shown in many papers [149-159]. Gurikov [160], for example, links the salting-out action of ions with changes in the structure of water itself. The passage of water into a condensed state is accompanied by the formation of hydrogen bonds. This leads to a redistribution of electron density in the molecule and in the hydrogen bond, resulting in the appearance of a dipole possessing its own moment. In estimating the salting-out effect of electrolytes, therefore, we must take into account the structural correction produced by the action of "hydrogen dipoles" on the structure of water in the electrostatic field of the ions. The complete salting-out coefficient is made up of two terms: $K = K_S + \Delta K_S$, where $K$ is the salting-out constant calculated from Eqn. (5) and $\Delta K_S$ a structural correction which can be calculated from an equation suggested by Gurikov. Calculations made for singly charged ions give satisfactory agreement with experimental values of the salting-out constants of benzene at 20° (Table 10).

Samoilov and his coworkers [161-164] have examined the influence of the nature of the salting-out agent on the extraction of certain mineral salts from aqueous solution. The process of extraction involves complete or partial replacement of water molecules by molecules of the organic solvent. The role of the salting-out agent is in effect to facilitate this process. Regarding the thermal motion of the solvent molecules as consisting of vibrations and rotational oscillations about temporary equilibrium positions, together with intermittent displacements from one state of equilibrium to another, Samoilov considers that a molecule must have a certain activation energy in order to accomplish such a jump. This activation energy is affected by the salting-out agent, and may either decrease, which results in salting-out, or increase, which leads to salting-in.

In a study of the influence of various substances on the solubility of benzoic acid in water, alcohols, and water–alcohol mixtures [165-168] the reviewer and her collaborators have observed both salting-in and salting-out. If alkali-metal halides and perchlorates, biphenyl, phenanthrene, resorcinol, and diphenylamine are used as additives, the solubility of benzoic acid is diminished; whereas methylpyridinium, ethylpyridinium, and tetraalkylammonium iodides and urea increase the solubility of benzoic acid in water.

On the basis of these results we have put forward a hypothesis which enables the salting-in and the salting-out of non-electrolytes to be considered from a unified viewpoint. The essence of this hypothesis is that salting-in will be observed if the added solid dissolves the salted-in substance better than does the solvent (water, alcohol, or a mixture thereof) in which the solubility is determined; and conversely, if the added substance dissolves the non-electrolyte less well than does the solvent, salting-out will be observed. Similar views were put forward, but in a more general form, by Bancroft [169].

In order to test our hypothesis experimentally, we have made direct determinations of the solubility of benzoic acid in the substances added as electrolyte. Sodium and lithium chlorides, sodium iodide, lithium perchlorate, etc. do not lower the melting point of benzoic acid: i.e. they do not dissolve in it, and salt it out from any solvent (water or alcohol). Such salts as methylpyridinium and ethylpyridinium iodides and quaternary ammonium salts, which dissolve benzoic acid many times better than water, increase its solubility in water. For example, the solubility of benzoic acid in water at 100° is 0.108 mole fraction, whereas in tetraethylammonium iodide under the same conditions it is 0.680. On the other hand, these same substances salt out benzoic acid from ethanol, which, as is evident from Fig. 4, dissolves benzoic acid better than do the above electrolytes.

These results led us to study the effect of methylpyridinium, ethylpyridinium, and tetraethylammonium iodides on the solubility of benzoic acid in water–alcohol mixtures, since it should then be possible to observe the interesting phenomenon of a gradual transition from salting-out to salting-in. The experiments confirmed the correctness of this suggestion (Fig. 5). In aqueous–alcoholic solutions a change from salting-out to salting-in is observed, and in a mixture containing ~ 50% of alcohol the salt effect is zero [170-172]. Nevertheless, lithium perchlorate salts-out benzoic acid from water, alcohol, and water–alcohol mixtures (Fig. 5).

A study of the effect of electrolytes and non-electrolytes on the solubility of naphthalene in methanol has yielded similar results [173,174]. Substances which do not dissolve naphthalene (sodium iodide and bromide, lithium chloride and perchlorate, urea, etc.) salt it out from methanol. Biphenyl and phenanthrene form with naphthalene an ideal system obeying the Schröder–Le Châtelier equation, but nevertheless they salt naphthalene into methanol, since it is less soluble in this solvent than in phenanthrene and

TABLE 10. Comparison of calculated and experimental values for the salting-out of benzene [160].

| Salt | $K$ | $K_{calc}$ | $K_{exp}$ |
|---|---|---|---|
| NaCl | 0.42 | 0.245 | 0.195 |
| NaBr | 0.34 | 0.175 | 0.155 |
| NaI | 0.27 | 0.095 | 0.095 |

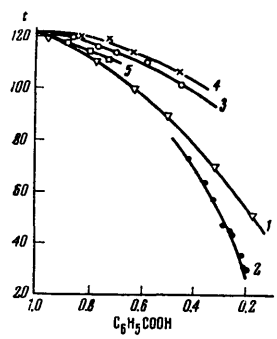



Fig. 4. Solubility of benzoic acid (mole fraction) in: 1) ideal solubility; 2) ethanol; 3) $C_5H_5NCH_3I$; 4) $(C_2H_5)_4NI$.

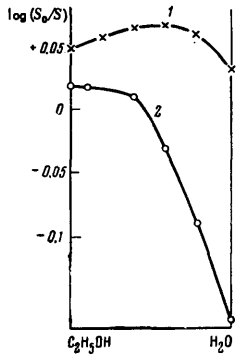



Fig. 5. Variation of logarithm of activity coefficient for benzoic acid with composition of binary solvent: 1) $LiClO_4$; 2) $C_5H_5NCH_3I$.

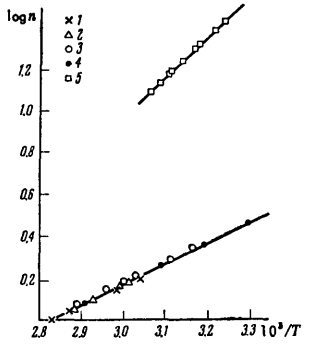



Fig. 6. Dependence of logarithm of mole fraction of benzoic acid ($\log n$) on reciprocal of absolute temperature for: 1) naphthalene–biphenyl; 2) naphthalene–phenanthrene; 3) naphthalene–diphenylamine; 4) ideal straight line; 5) naphthalene–methanol.

TABLE 11. Salting-out constants for naphthalene and benzoic acid in methanol.

| Compound | C, M | $C_{10}H_8$ $K_{35°}$ | $C_6H_5COOH$ $K_{35°}$ |
|---|---|---|---|
| LiCl | 0.1 | 0.185 | 0.245 |
| $LiClO_4$ | 0.1 | 0.073 | 0.123 |
| $(C_6H_5)_2$ | 0.1 | —0.512 | 0.630 |
| $(C_6H_5CH)_2$ | 0.1 | —0.512 | 1.34 |
| $(C_6H_5)_2NH$ | 0.1 | —0.403 | 0.033 |
| $(NH_2)_2CO$ | 1.0 | 0.051 | —0.056 |
| $C_6H_4(OH)_2$ | 2.0 | 0.006 | 0.049 |
| $C_5H_5NC_2H_5I$ | 0.1 | —0.155 | —0.512 |

biphenyl (Fig. 6). Benzoic acid is salted-out of methanol by these substances, because it is more soluble in methanol than in them.

Table 11 shows the effect of various substances on the solubility of naphthalene and of benzoic acid in methanol. The salting-out constant was calculated from Sechenov's equation. Experiments on the effect of biphenyl and phenanthrene on the solubility of naphthalene in methanol show that chemical interaction between these substances is not a necessary condition for a salting-in action.


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# STEPWISE REACTIONS IN ELECTROCHEMICAL KINETICS

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## I. INTRODUCTION

A cathodic process is usually divided into stages — (*a*) supply of the ion to the electrode surface, (*b*) reduction of the ion, and (*c*) desorption of the reaction product or its interaction with the electrode material — and an anodic process consists correspondingly of the reverse sequence of analogous stages. The departure of the electrode potential from the equilibrium value is governed by the rate of the slowest stage.

During 1930–1933 Erdey-Grůz and Volmer[1] and also Frumkin[2] linked the polarisation accompanying the discharge and ionisation of hydrogen with the stage actually involving reduction of the ion and oxidation of a neutral atom of hydrogen.

The concept of discharge–ionisation as the slow stage proved to be extremely fruitful, and led to a theory of so-called electrochemical kinetics which in several cases provided a quantitative account of experimental results. In this theory reduction or oxidation was usually regarded as a process occurring in a single act. In other words, it was assumed that an ion undergoing reduction added on at once all the electrons required to form the final product, and that in oxidation simultaneous removal of electrons at once yielded an ion of the required valency.

Recently, however, it has become clear that this simplest form of the theory is not always consistent with the experimental data. This has led to attempts to develop

fundamental ideas, both on the lines of refining the structure of the electrical double layer and on the lines of a detailed account of the actual act of discharge or ionisation.

Following the work of Kabanov et al.[3], the act of discharge or ionisation came to be regarded quite often as a series of consecutive electrochemical reactions, the slowest of which determined the overall rate of the process.

A kinetic equation for the dependence of current density on potential is then set up on the basis of the following general principles:

(*a*) If the electrochemical stages are preceded by a rapid chemical reaction, the concentrations of the reagents are determined by means of the equilibrium constant.

(*b*) Concentrations of intermediate products formed as a result of a rapid electrochemical reaction, i.e. under equilibrium conditions, are determined by means of the Nernst equation.

(*c*) The slow electrochemical stage is described by the usual kinetic equation with the concentrations determined from (*a*) and (*b*).

(*d*) Rapid stages following the slow stage are ignored.

The present paper examines the basic assumptions of the theory of stepwise reactions and surveys critically the most characteristic cases of processes of this type.

## II. FUNDAMENTALS OF THE THEORY OF THE STEPWISE OCCURRENCE OF ELECTRODE REACTIONS

Cathodic reduction, and correspondingly anodic oxidation, are inevitably accompanied by transfer of electric charges across the electrode–electrolyte boundary. There are two possibilities:

1. Charge transfer through the electrical double layer is effected by electrons. This process occurs in a pure form during electrolysis in redox systems, e.g. $NO_3^-/NO_2^-$, $Mn^{4+}/Mn^{2+}$, $Fe^{3+}/Fe^{2+}$, etc., in which only the valency of the reactants changes, without change in phase.

2. Charge transfer is effected by ions. This case is realised, for example, during electrolysis in metal–metal ion systems, in which the ions change phase between electrode and electrolyte.

The theory is based on the proposition that, in the discharge of multivalent ions, the transfer of $n$ electrons in a single elementary act is far less probable than the transfer of the same electrons in $n$ successive one-electron stages. This principle follows from views of the analogous course of redox processes at electrodes and of homogeneous oxidation–reduction reactions[4-8].

In the case of redox electrode processes, when charge is transferred through the phase boundary by electrons, the above hypothesis has a definite basis, although in Frumkin's opinion[4] "the possibility of simultaneous transfer of two electrons cannot be excluded". Bockris[7] also supposes that, in spite of the high probability of one-electron transitions in homogeneous redox reactions, it is not yet entirely clear whether spontaneous two-electron transfers are possible. A similar view is held by Basolo and Pearson[8], who regard bivalent transfers as possible when appropriate intermediate valencies are absent from the reactants.

Thus the basic assumption of one-electron transfers is not generally accepted even for the case of charge transfer by electrons. Nor is this assumption generally accepted for ionic transfers.

In the discharge–ionisation of metals, according to Grahame[6] "electrons do not leave the metallic phase, and therefore there is no theoretical necessity to postulate a one-electron transfer". Actually, the transport of charges through the phase boundary is effected in this case by charged metal ions, interaction with electrons ensuing already in the metallic phase, where, as Bockris remarks[7,9-11], the energetically most probable result is formation not of a neutral atom but of a complex of the adsorbed ion with $n$ electrons. Thus preferential interaction with any electron in such a complex is hardly possible.

If, however, the discharge of a multivalent, e.g. an $n$-valent, ion takes place in stages, the transfer of such an ion must be preceded by electrochemical redox reactions accompanied by the transfer of electrons. The last stage of discharge remains, as before, transfer of the ion. Either electron transfer or ion transfer may be the slow stage in the process.

Although transfer of a univalent ion does require a lower activation energy than that of a multivalent ion, and as a result the stepwise process would appear to be the more probable, nevertheless the formation of ions of lower valency may prove to be energetically unfavourable, and transfer of electrons will not be achieved. In this case direct transfer of the $n$-valent ion is possible. If, however, the ion of lower valency is relatively stable in solution, occurrence of the stepwise process becomes more probable†.

## III. CRITERIA OF THE STEPWISE OCCURRENCE OF ELECTRODE REACTIONS

At the present time three methods exist for establishing the stepwise occurrence of electrode reactions, and these have been termed "criteria for the stepwise occurrence of electrode reactions". One method is based on the theory of the transition state, which enables the heats of activation of all stages in the electrode reaction to be calculated; two methods involve an analysis of the fundamental equation of electrochemical kinetics.

### 1. Method Based on Determination of Heat of Activation of Intermediate and Final Stages in the Electrode Process

Conway and Bockris[7,9,10] have used the theory of the transition state to calculate potential-energy diagrams for the transfer of an ion from solution to the crystal lattice of the metal. By means of these diagrams it is possible to determine the free energies of the particle in each of the intermediate states, and hence to establish the stage which determines the rate of the electrode reaction.

The method has been employed by these workers to examine the conditions for the electrodeposition of $Ag^+$, $Cu^{2+}$, and $Ni^{2+}$. They showed that the transfer and formation of adsorbed neutral atoms requires a greater heat of

† It is interesting that the formation with anions of complexes adsorbed on the metal surface, especially of hydroxo-complexes, often facilitates the transfer of electrons and makes a stepwise occurrence of the process possible. This case will be examined in detail later.

activation than does the formation of adsorbed ions on the metal surface; in the discharge of $Ag^+$, $Cu^{2+}$, and $Ni^{2+}$, for example, ionic transfer is effected, with adsorption on the surface in the form of adsorbed ion + $n$ electrons.

For bivalent ions direct transfer to any part of the metal surface (i.e. a process which does not include successive dehydration or an intermediate redox stage) must be difficult because of the higher heat of activation for the discharge of bivalent ions compared with univalent ions; furthermore, the hydration of bivalent ions requires a greater consumption of heat than does that of univalent ions. If, therefore, stable intermediate ions exist, a stepwise process of discharge will be more probable than discharge involving simultaneously two or more electrons.

In the discharge of copper, for example, the direct process $Cu^{2+} + 2e \rightarrow Cu$ requires a greater heat of activation than does the stepwise process $Cu^{2+} + e \rightarrow Cu^+$ and $Cu^+ + e \rightarrow Cu$, and the latter is therefore the more probable. In the case of the discharge of nickel, the stage $Ni^{2+} + e \rightarrow Ni^+$, if it does occur, must involve a higher activation barrier than does the corresponding stage for copper, since in the opinion of the above authors a stable univalent nickel ion does not exist in aqueous solution. Consequently the non-stepwise transfer of $Ni^{2+}$ is possible, characterised by a high heat of activation and a low exchange current. In the opinion of Bockris low values of $i_0$ cannot be due to difficulties in building up the metal lattice, since $i_{0,Ni}$ is abnormally low even for deposition on liquid mercury (see also Ref. 12).

## 2. Method Based on Analysis of Polarisation Curves

The main theoretical regularities enabling the stepwise transfer of electrons to be established have been formulated by Parsons[13], Vetter[14-17], Losev[18-20], Mauser[21], and others. They are formally valid both for electronic and for ionic transfer of charge. Stepwise character is revealed sufficiently clearly only by the simultaneous study of cathodic and anodic polarisation.

Let us assume that the overall electrode reaction is represented by the equation

$$\text{cathodic:} \quad S_{ox} + ne \rightarrow S_{red}, \tag{1}$$

$$\text{anodic:} \quad S_{red} - ne \rightarrow S_{ox}, \tag{2}$$

where $S_{ox}$ represents a species (ion or neutral particle) in the extreme oxidised state, and $S_{red}$ in the extreme reduced state, the remaining subscripts denoting intermediate redox states (these symbols apply throughout the paper).

If this reaction occurs in one stage, the corresponding kinetic equations, for potentials sufficiently far from the equilibrium potential, are of the usual form

$$i_c = k_-[S_{ox}]e^{-\frac{\alpha nF\varphi}{RT}}, \tag{3}$$

$$i_a = k_+[S_{red}]e^{\frac{\beta nF\varphi}{RT}}. \tag{4}$$

If, however, reactions (1) and (2) involve $n$ one-electron stages —

cathodic

$$\begin{gathered} S_{ox} + e \rightarrow S_{ox-1}, \\ S_{ox-1} + e \rightarrow S_{ox-2}, \\ \cdots\cdots\cdots \\ S_{ox-(n-1)} + e \rightarrow S_{red}, \end{gathered}$$

anodic

$$\begin{gathered} S_{red} - e \rightarrow S_{ox-(n-1)}, \\ \cdots\cdots\cdots \\ S_{ox-2} - e \rightarrow S_{ox-1}, \\ S_{ox-1} - e \rightarrow S_{ox}, \end{gathered}$$

the character of the kinetic curves will depend on the nature and sequence of these stages. Let us consider the following most characteristic cases.

($a$) Slow stage is cathodic addition of first electron or anodic detachment of last electron. The equation will be for the cathodic process

$$i_c = k_-[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}}, \tag{5}$$

and for the anodic process

$$i_a = k_+[S_{ox-1}]e^{\frac{\beta_1 F\varphi}{RT}}, \tag{6}$$

where $\alpha_1$ and $\beta_1$ are the transfer coefficients for the slow stage. We determine $[S_{ox-1}]$ from the Nernst equation

$$[S_{ox-1}] = k'[S_{red}]e^{\frac{(n-1)F\varphi}{RT}}. \tag{7}$$

Substitution of Eqn. (7) in (6) yields

$$i_a = k'_+[S_{red}]e^{\frac{(n-1+\beta_1)F\varphi}{RT}}. \tag{8}$$

Thus if the transfer coefficient $\beta'$

$$\beta' = n - 1 + \beta_1, \tag{9}$$

determined experimentally from the slope of the Tafel plot for the anodic process exceeds unity, while the coefficient $\alpha'$ has its normal value close to 0.5, a consecutive reaction with a slow first stage must be assumed.

($b$) Slow stage is cathodic addition of last electron or anodic detachment of first electron. It is readily shown that in this case the relations will be the opposite of those in the previous case:

$$i_c = k_-[S_{ox}]e^{-\frac{(n-1+\alpha_n)F\varphi}{RT}}, \tag{10}$$

$$i_a = k_+[S_{red}]e^{\frac{\beta_n F\varphi}{RT}}, \tag{11}$$

and the transfer coefficient $\alpha$ determined from the slope of the Tafel straight line for the cathodic process will exceed unity.

($c$) Slow stage is addition or abstraction of some intermediate electron. In this case the slow stage in cathodic and anodic processes is preceded by equilibrium electrochemical stages, and both transfer coefficients exceed unity. If, for example, the reaction takes place in $n$ stages of which the $m$th stage is slow, we have

$$i_c = k_-[S_{ox}]e^{-\frac{(m-1+\alpha_m)F\varphi}{RT}}, \tag{12}$$

$$i_a = k_+[S_{red}]e^{\frac{(n-m+\beta_m)F\varphi}{RT}}. \tag{13}$$

It is seen from Eqns. (12) and (13) that if, for example, the reaction occurs in four stages of which the third is slow, then

$$\alpha' = 3 - 1 + \alpha_m = 2 + \alpha_m,$$

and

$$\beta' = 4 - 3 + \beta_m = 1 + \beta_m.$$

It is evident from these relationships that the experimental transfer coefficients $\alpha'$ and $\beta'$ differ appreciably from one

another. However, in the particular case in which the middle stage of three is slow, it is impossible to establish from the experimental values of the transfer coefficients any differences between the stepwise and the direct course of the three-electron reaction.

(*d*) A two-stage process comprises a slow first stage followed by disproportionation:

$$S_{ox} + e \rightarrow S_{ox-1},$$
$$2S_{ox-1} \rightleftarrows S_{ox} + S_{red}.$$

The kinetic equation for the cathodic process is

$$i_c = k_-[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}}, \quad (14)$$

and that for the anodic process

$$i_a = k_+[S_{ox-1}]e^{\frac{\beta_1 F\varphi}{RT}} = k'[S_{ox}]^{\frac{1}{2}}[S_{red}]^{\frac{1}{2}}e^{\frac{\beta_1 F\varphi}{RT}}. \quad (15)$$

In this case the kinetic equations for both cathodic and anodic processes are of the form characteristic of one-electron reactions.

(*e*) The separate stages have comparable rates. Let us consider for simplicity the two-stage reaction

$$S_{ox} + e \underset{k_2}{\overset{k_1}{\rightleftarrows}} S_{ox-1} \qquad S_{ox-1} + e \underset{k_4}{\overset{k_3}{\rightleftarrows}} S_{red}.$$

The sum of the current densities $i_1$ and $i_2$ for each reaction gives the total current $i$, and for steady-state conditions we must have

$$i = i_1 + i_2 = 2i_1 = 2i_2 \quad (16)$$

otherwise the concentration of the intermediate product will not remain constant with time. Apart from the constancy of $[S_{ox-1}]$ with time, we must also assume the concentration of the intermediate product to be so low that its diffusion from the electrode surface can be neglected.

Let us write the kinetic equations in the form

$$i_1 = k_2[S_{ox-1}]e^{\frac{\beta_1 F\varphi}{RT}} - k_1[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}}, \quad (17)$$

$$i_2 = k_4[S_{red}]e^{\frac{\beta_2 F\varphi}{RT}} - k_3[S_{ox-1}]e^{-\frac{\alpha_2 F\varphi}{RT}}. \quad (18)$$

We determine the concentration of the intermediate product by Bodenstein's method of quasi-stationary concentrations:

$$\frac{d[S_{ox-1}]}{dt} = k_1[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}} + k_4[S_{red}]e^{\frac{\beta_2 F\varphi}{RT}} -$$
$$- k_2[S_{ox-1}]e^{\frac{\beta_1 F\varphi}{RT}} - k_3[S_{ox-1}]e^{-\frac{\alpha_2 F\varphi}{RT}} = 0,$$

whence

$$[S_{ox-1}] = \frac{k_1[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}} + k_4[S_{red}]e^{\frac{\beta_2 F\varphi}{RT}}}{k_2 e^{\frac{\beta_1 F\varphi}{RT}} + k_3 e^{-\frac{\alpha_2 F\varphi}{RT}}}. \quad (19)$$

On substituting for $[S_{ox-1}]$ from Eqn. (19) in (17) and (18), we obtain

$$i = 2k_1[S_{ox}]e^{-\frac{\alpha_1 F\varphi}{RT}} \frac{1 - \frac{k_2 k_4}{k_1 k_3}\frac{[S_{red}]}{[S_{ox}]}e^{\frac{2F\varphi}{RT}}}{1 + \frac{k_2}{k_3}e^{\frac{(\beta_1+\alpha_2)F\varphi}{RT}}} \equiv 2k_4[S_{red}]e^{\frac{\beta_2 F\varphi}{RT}} \frac{1 - \frac{k_1 k_3}{k_2 k_4}\frac{[S_{ox}]}{[S_{red}]}e^{-\frac{2F\varphi}{RT}}}{1 + \frac{k_2}{k_3}e^{-\frac{(\beta_1+\alpha_2)F\varphi}{RT}}}. \quad (20)$$

At sufficiently high cathodic potentials Eqn. (20) becomes

$$i_c = 2k_1[S_{red}]e^{-\frac{\alpha_1 F\varphi}{RT}} = 2i_{0,1}e^{-\frac{\alpha_1 F\Delta\varphi}{RT}}, \quad (21)$$

and at sufficiently high anodic potentials it becomes

$$i_a = 2k_4[S_{red}]e^{\frac{\beta_2 F\varphi}{RT}} = 2i_{0,2}e^{\frac{\beta_1 F\Delta\varphi}{RT}}. \quad (22)$$

Thus when the rates of the two stages are comparable, the transfer coefficients determined from Tafel straight lines for cathodic and anodic processes are not linked by the equation $\alpha + \beta = 1$, since they relate to different reactions. Furthermore, it follows from these same equations that extrapolation of these Tafel straight lines to the equilibrium potential gives different values of the exchange current for cathodic and anodic processes, since these values of $i_0$ correspond to different stages of the process.

On the basis of the above, the following criteria can be formulated for the stepwise occurrence of an electrode process: (1) the transfer coefficients determined from the slopes of the Tafel straight lines for anodic and cathodic processes have anomalous values; and (2) exchange currents determined from these straight lines have different values (for cases in which the separate stages occur at comparable rates).

### 3. Methods Based on Concentration Relations

These methods [14-17,22-27] are closely linked with the preceding methods, since they derive essentially from the same fundamental equations of electrochemical kinetics. In fact, the equations of electrochemical kinetics contain the concentrations (activities) of the reactants. Consequently the potential, overpotential, or exchange current must depend on the concentration of species taking part in the electrode reaction. The values of the partial derivatives with respect to concentration will depend on the coefficient of potential in the equation, i.e. on the number and sequence of stages and the prior occurrence of a rapid chemical reaction. Concentration criteria supplement criteria obtained from an analysis of polarisation curves. From the above equations of electrochemical kinetics we can obtain the partial derivatives

$$\left(\frac{\partial\varphi}{\partial\log[S_{ox}]}\right)_i = -\frac{2.3RT}{\alpha' F} \text{ and } \left(\frac{\partial\varphi}{\partial\log[S_{red}]}\right)_i = \frac{2.3RT}{\beta' F}.$$

Moreover, the derivative of current density with respect to the concentrations of components of the solution gives the order of reaction $\nu_i$:

$$\left(\frac{\partial\log i}{\partial\log[S_i]}\right)_\varphi = \nu_i, \quad (23)$$

which enables us to determine which substances take part in the slow stage.

In cases in which reactions occur so rapidly that polarisation curves cannot be obtained, and only exchange currents can be measured, concentration criteria provide the sole criteria of the stepwise character of reactions, as follows from the relations

$$\left(\frac{\partial\varphi_{eq}}{\partial\log i_{ox}}\right)_{S_{ox}} = \frac{2.3RT}{\beta' F}, \quad (24)$$

$$\left(\frac{\partial\varphi_{eq}}{\partial\log i_{ox}}\right)_{S_{red}} = -\frac{2.3RT}{\alpha' F}. \quad (25)$$

## IV. SOME EXAMPLES OF THE STEPWISE OCCURRENCE OF ELECTRODE REACTIONS

### 1. Reactions Having One Slow Stage

(*a*) Zn(Hg)/$Zn^{2+}$ electrode. The anodic behaviour of zinc in sulphate solutions has been investigated by Losev and his coworkers [28-35]. Application of Eqns. (24) and (25)

to the concentration relations of $i_0$ gives the transfer coefficients $\beta' = 1.40$ and $\alpha' = 0.52$: i.e. $\beta' > 1$ and $\beta' > \alpha'$, which corresponds to a case of slow detachment of the last electron in the ionisation of zinc — see Eqns. (8) and (9).

The true transfer coefficients, corresponding to the slow stage of the process, are $\alpha_2 = \alpha' = 0.52$ and $\beta_2 = \beta' - 1 = 0.40$. The possibility of the existence of the singly charged ion $Zn^+$ in aqueous solution[36-38] confirms the correctness of the above mechanism. It is therefore hardly possible to justify Gerischer's view[39,40] that, although he obtained the same values of $\alpha'$ and $\beta'$, the process was a two-electron process with $\alpha$ and $\beta$ respectively 0.3 and 0.7.

It must be noted, however, that lack of symmetry of the potential barrier is not by itself a sufficient criterion of the stepwise occurrence of a process, since reactions of the singly charged silver ion, which occur in one stage, have values of $\alpha \simeq 0.3$ and $\beta \simeq 0.7$.[41]

(*b*) In(Hg)/$In^{3+}$ electrode. Losev and his coworkers have investigated the anodic behaviour of indium in perchlorate solutions[42-46]. They obtained values for the transfer coefficients of $\beta' = 2.2$ from polarisation curves and concentration relations of the exchange current (24), and $\alpha' = 0.9$ from the concentration relations of the exchange current (25). Here $\beta' > 2$ and $\beta' > \alpha'$ — see Eqns. (8) and (9) — and therefore the anodic process can be regarded as occurring in stages. These workers consider that three stages are involved: $In - e \rightleftharpoons In^+$, $In^+ - e \rightleftharpoons In^{2+}$, and $In^{2+} - e \rightarrow In^{3+}$, the last stage being slow. The transfer coefficients for this stage are then $\alpha_3 = \alpha' = 0.9$ and $\beta_3 = \beta' - 2 = 0.2$. In this case an extremely unsymmetrical energy barrier is already obtained for the one-electron transfer.

Similar results have been obtained by other workers[47] in sulphate electrolytes at current densities below 0.001 A $\times$ $\times$ $cm^{-2}$. A more acceptable scheme is probably one involving a two-electron slow stage: $In - e \rightleftharpoons In^+$ and $In^+ - 2e \rightarrow In^{3+}$. We then have $\alpha_2 = \frac{1}{2}\alpha' = 0.45$ and $\beta_2 = \frac{1}{2}(\beta' - 1) = 0.6$.

On the basis of the results for zinc and indium, Losev and his collaborators[20,42] suggested that, with all multivalent metals, electrode processes take place in stages. They give results for transfer coefficients in the cases of copper, cadmium, iron, nickel, and cobalt. Analysis of these data shows that this hypothesis can be applied to the discharge and ionisation of copper, for example[48,49]; with cadmium there are two groups of contradictory data[50-53]; and in the case of the iron-group metals, discharge of the simple hydrated ions in a non-complexing medium, and in the absence of specific adsorption of anions, is most probably a one-stage process involving bivalent ions[7,9,10,54-58].

(*c*) $Hg/Hg(CN)_4^{2-}$ electrode. Gerischer and Perez-Fernandes[59] have investigated the reaction $Hg(CN)_4^{2-} + 2e \rightleftharpoons Hg + 4CN^-$ under conditions such that the complex $[Hg(CN)_4]^{2-}$ predominated in the solution. The slopes of the Tafel curves gave values of $\alpha' = 0.30 \pm 0.03$ and $\beta' = 1.67 \pm 0.05$. From the dependence of $i_c$ and $i_0$ on the concentrations of $CN^-$ and $Hg(CN)_4^{2-}$ it was established that the complex $[Hg(CN)_3]^-$ participates in charge transfer. Consequently the transfer reaction $Hg(CN)_3^- + 2e \rightarrow Hg + 3CN^-$ is accompanied by the chemical equilibrium $Hg(CN)_4^{2-} \rightleftharpoons Hg(CN)_3^- + CN^-$.

If, however, transfer coefficients are calculated for a simultaneous two-electron transfer, values are obtained of $\alpha < 0.2$ and $\beta > 0.8$. The possibility was therefore considered that the reaction took place in stages according to the scheme

$$Hg(CN)_3^- + e \rightleftarrows HgCN_{ads} + 2CN^-,$$
$$HgCN_{ads} + e \rightleftarrows Hg + CN^-.$$

The experimental data indicate that the first of these stages is slow. Then $\beta' = 1.67 \pm 0.05 = 1 + \beta_1$, whence $\beta_1 = 0.67 \pm 0.05$ and correspondingly $\alpha_1 = 0.30 \pm 0.03$.

The hypothesis that the transfer reaction takes place in stages has been tested by measuring the capacitance by the charging method. If the reaction occurs in stages, and the first stage is slow, a charging pulse should not only charge the double layer but also cause the establishment of a new equilibirum concentration of $HgCN_{ads}$, which is shown in an apparent increase in capacitance. The experimental relation obtained supports the accepted mechanism for the electrode reaction.

(*d*) $Ni/Ni^{2+}$ electrode. In a study of the electrolysis of nickel in chloride electrolytes containing boric acid, Fedot'ev and Dmitreshova[60] found that at 80° discharge–ionisation takes place according to the simple scheme $Ni^{2+} + 2e \rightarrow Ni$ with transfer coefficients of $\alpha = 0.4$ and $\beta = 0.6$, whereas at 25° they found that $\alpha + \beta = 1$ only when $n = 1$. On this basis a stepwise scheme $Ni^{2+} + e \rightarrow Ni^+$ and $Ni^+ + e \rightarrow Ni$ was suggested, in which one of the stages was slow. Such a suggestion can apply if the first stage is slow in both anodic and cathodic processes. Values of $\alpha + \beta = 1$ satisfy also a one-electron transfer with subsequent disproportionation $Ni^{2+} + e \rightarrow Ni^+$ and $2Ni^+ \rightleftharpoons Ni + Ni^{2+}$.

A stepwise course for the electrode process involving the $Ni^+$ ion has been suggested by several workers[61-64] who have studied the polarographic behaviour of nickel. The existence of $Ni^+$ has been demonstrated by Khlopin[65]. Nevertheless, calculations by Conway and Bockris[7,9,10], as well as several experimental results[54-56,66], justify a simple two-electron scheme for the process. However, more detailed investigations are desirable.

A stepwise mechanism can be expected for electrode reactions with all other metals where ions of lower intermediate valencies can exist in the solution. The presence of univalent states has been detected, for example, with simple ions of the metals Mg,[37,67-69] Al,[37,67,71] Be,[37,67,71] Zn, La, Ce, Ti, U, Hg, Cu, In, and Ga,[37,67] as well as with complex ions of Cr, Mn, Co, etc.[72]

## 2. Reactions Having Two Slow Stages

(*a*) Quinhydrone electrode. For the quinhydrone electrode Vetter[73] has established that the electrode reaction has different mechanisms in acid and alkaline media. On the basis of experimental results he states that the two electrons of the overall reaction are transferred successively, the rates of the two stages of the reaction being comparable.

However, examination of the experimental data in Ref. 73 reveals insufficient grounds for such a conclusion in the case of results obtained in the acid region, since the anodic Tafel line has been drawn rather arbitrarily (see Fig. 1). Even with these straight lines, values of $\beta_2 = 0.46$ and $1 - \alpha_1 = 0.54$ were obtained, which are hardly sufficient for the conclusion reached by this worker.

In the alkaline region, anodic and cathodic polarisation curves have well-defined Tafel sections with different

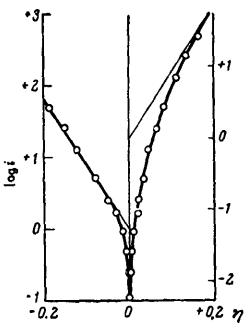



Fig. 1. Polarisation curves for the quinone–quinol system at high acidities (0.001 m quinone + 0.01 m quinol in 1 M HCl).

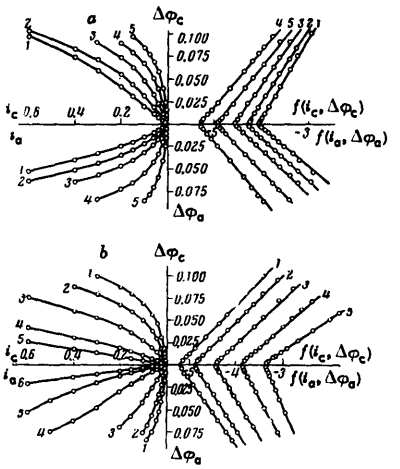



Fig. 2. Effect of pH on polarisation of cathodic and anodic processes in the quinone–quinol system in the region of:
*a*) high acidities (pH): 1) 0.48; 2) 1.07; 3) 1.52; 4) 2.01; 5) 3.01;
*b*) low acidities (pH): 1) 3.92; 2) 5.06; 3) 6.02; 4) 7.06; 5) 7.92; 6) 8.6.

slopes, of $1 - \alpha_1 = 0.37$ and $\beta_2 = 0.19$. Exchange currents determined by extrapolation of anodic and cathodic Tafel lines do not coincide. Thus the totality of experimental data not only support Vetter's theoretical conclusions, but also provide one of the very few examples of more than one slow electron transfer in the same overall reaction.

The electrochemical behaviour of the quinhydrone electrode has been investigated also by Loshkarev and his coworkers[74]. Their experimental results contradict Vetter's data, since exchange currents determined from anodic and cathodic Tafel lines coincide at all pH values (Fig. 2). According to Loshkarev and Tomilov, the slow stage is the complete electrode process involving two electrons.

Bagotskii et al.[75] have attempted to ascertain the reason for such a sharp discrepancy in the experimental data in these papers. They have shown that the results of Ref. 74 are due to the carrying out of experiments at low current densities and small polarisations, when the rate of the reverse reaction still cannot be neglected. These workers' own data are on the whole close to Vetter's results. In contrast to the latter, however, Bagotskii and his coworkers consider that the slow stage of the cathodic process in the quinone–quinol system is addition of the first electron, while that in the anodic process is abstraction of the first electron. It must be noted, however, that the experimental data obtained by Bagotskii et al. also fit a scheme in which the slow stage is addition of the first electron (and abstraction of the last) combined with rapid disproportionation. This system, too, requires further investigation.

(*b*) $Tl^{3+}/Tl^{+}$ redox electrode. Antropov and Mizgireva[76], probably the first to investigate this system, concluded that both concentration polarisation and chemical polarisation were present. In their opinion the chemical polarisation was associated not with a slow discharge–ionisation stage but with slow desorption of secondary (reduced) ions.

Vetter and Thiemke[77] have also shown that the overpotential is determined not only by a slow electrochemical reaction but also by diffusion, and therefore curves corresponding to the experimental points have no linear sections. Curves were plotted on the basis of Eqn. (20) after allowing for diffusion. Transfer coefficients were so chosen that the curves corresponded to the experimental points (Fig. 3). The values determined in this way were $\beta_2 = 0.67$ and $\alpha_1 = 0.36$. Their sum was taken as not equalling unity, although the difference was only 0.03. By means of Eqns. (21) and (22), with the values of $\beta_2$ and $\alpha_1$ substituted in them, straight lines were then plotted representing the relation between $\eta$ and $\log i$ in the absence of diffusion hindrances. Exchange currents found by extrapolation of such hypothetical straight lines were also found to be rather different (Fig. 3).

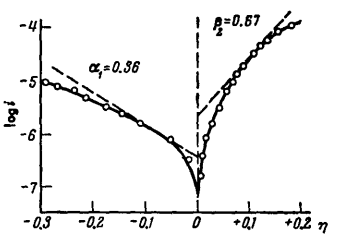



Fig. 3. Polarisation curves for the $Tl^{3+}/Tl^{+}$ system: points represent experimental data; full curves calculated from Eqn. (20) with correction for diffusion; broken lines from Eqns. (21) and (22).

It was concluded from these results that the kinetics of the process was determined by two stages

$$Tl^{+} \rightarrow Tl^{2+} + e \text{ and } Tl^{2+} \rightarrow Tl^{3+} + e.$$

It is noted in the paper that the data were processed on the hypothesis that two electrons were transferred simultaneously, and that this hypothesis is inconsistent with the experimental results.

There is an indication in the literature that the homogeneous exchange $Tl^{+}$–$Tl^{3+}$ may occur in stages with the formation of $Tl^{2+}$.[78] It has also been suggested that the reduction of $Tl^{3+}$ ions on the electrode by atomic hydrogen to $Tl^{+}$ takes place in two stages[79].

Thus the possibility of the stepwise occurrence of the electrode process is to some extent supported by hypotheses concerning the presence of $Tl^{2+}$ ions, but the experimental data reported in Ref. 77 cannot provide adequate evidence of a stepwise mechanism.

### 3. Participation of Hydroxide Ions in Electrode Processes

Anions play an important part in homogeneous redox reactions between multicharged cations in the bulk of the electrolyte, by facilitating the transfer of charge from one cation to another. Thus, for example, $Cl^{-}$ accelerates the exchange of charges between $Fe^{3+}$ and $Cr^{3+}$, an activated complex of the type $[Cr-Cl-Fe]^{4+}$ being formed in which $Cl^{-}$ acts as an "anionic bridge" for the transfer of charge[4].

Hydroxide ions have a similar effect. The participation of $OH^{-}$ ions in electrode processes in the discharge–ionisation of metals is revealed by the fact that the rate of the electrode reaction depends on the pH of the electrolyte. Here, too, hydroxide ions have an accelerating effect, the exchange of charges between the metal surface and ions in solution through the hydroxide "bridge" being made so easy that conditions are produced for the stepwise transfer of electrons in the discharge–ionisation even of such stable bivalent aquo-ions as those of the iron-group metals.

The exchange of charges is some thousandfold more rapid between $Fe(OH)^{2+}$ and $Fe^{2+}$ than between $Fe^{3+}$ and $Fe^{2+}$. Similar results are obtained in a study of the effect of pH on the rate of exchange between chromium, cerium, plutonium, and praseodymium ions of different degrees of oxidation, as well as on the rate of oxidation of $U^{4+}$ by $Tl^{3+}$ and $Fe^{3+}$ ions, and of $Cr^{2+}$ by $[CoH_2O(NH_3)_5]^{3+}$ ions[4,80].

The kinetics of the elementary electrochemical act depends in general on the potential difference at the electrode–solution interface, the reactant concentrations at the electrode surface, and the strength of the bonds which are ruptured or formed on participation of the reactant species in the electrode process. Therefore the catalytic action of $OH^{-}$ ions in the formation of active complexes of the reactant species with these ions can be explained by the fact that they produce changes both in the total charge on the reactant species and in its electronic structure[4].

Let us examine the effect of hydroxide ions on the electrode process with a few metal electrodes as examples.

(*a*) $Fe/Fe^{2+}$ electrode. Study of the part played by hydroxide ions in the anodic dissolution of iron in alkaline solutions, undertaken by Kabanov and others[3,81], established that the rate of anodic dissolution is far greater in alkaline than in acid solutions, $i_a$ being proportional to $[OH^{-}]^2$. An electrochemically active layer of adsorbed product is present on the electrode surface, and produces unusually high values for the capacitance of the double layer (of the order of 1500 $\mu F\ cm^{-2}$). The results were explained on the basis of the stepwise mechanism of the electrode process involving $OH^{-}$ ions

$$Fe + OH^{-} \rightleftarrows FeOH_{ads} + e,$$
$$FeOH_{ads} + OH^{-} \rightarrow FeO_{ads} + H_2O + e \text{ (slow stage)},$$
$$FeO_{ads} + OH^{-} \rightleftarrows HFeO_2^{-},$$
$$HFeO_2^{-} + H_2O \rightleftarrows Fe(OH)_2 + OH^{-}.$$

The corresponding kinetic equation is

$$i_a = k_1 [FeOH]_{ads} [OH^{-}] e^{\frac{\beta F\varphi}{RT}} = k_2 [OH^{-}]^2 e^{\frac{(1+\beta)F\varphi}{RT}}. \quad (26)$$

With $\beta = 0.5$, the slope of the Tafel straight line is $2RT/3F$, as has been obtained experimentally.

Bonhoeffer and Heusler[82,83] found that the rate of anodic dissolution of very pure iron in perchloric and sulphuric acids (under conditions of constant corrosion, when $\varphi_{eq}$ is independent of pH) depends on the pH, the relation being the same for acid and alkaline solutions when the process occurs under steady-state conditions. The high values obtained for the capacitance from galvanostatic charging curves could also be explained by the presence of an active layer of an intermediate product. These results indicate that hydroxide ions take part in the electrode process in acid solutions, and, because of the better adsorbability of hydroxide ions, displacement of the equilibrium $H_2O \rightleftharpoons H^{+} + OH^{-}$ in the catholyte can ensure an $OH^{-}$ concentration sufficient to have a catalytic effect. These workers determined the orders of reaction — see Eqn. (23) — from the $OH^{-}$ concentration for the non-stationary process ($\nu_{OH^-} = 1$) and the steady-state process ($\nu_{OH^-} = 2$, compared with an experimental value of 1.55) in the anodic dissolution of iron. Determination of the slopes of the Tafel lines gave $b_a$ (non-stationary) = 0.063 V and $b_a$ (stationary) = 0.030 V, which formed the basis for the following scheme for the process

$$Fe + OH^{-} \rightleftarrows FeOH_{ads} + e,$$
$$Fe + OH^{-} + FeOH_{ads} \rightarrow FeOH^{+} + FeOH_{ads} + 2e \text{ (slow stage)}.$$

The corresponding kinetic equation is written

$$i_{a,stat} = k_{+} [OH^{-}]^2 e^{\frac{(1+2\beta)F\varphi}{RT}}, \quad (27)$$

where $\beta = 0.46$ (determined from the non-stationary polarisation curve).

It was suggested that the cathodic deposition of iron takes place in a similar manner, formation of the surface catalyst being associated with the chemical equilibrium $Fe^{2+}.aq + OH^{-} \rightleftharpoons FeOH^{+} + aq$. This is followed by the discharge of $FeOH^{+}$ with formation of the catalyst: $FeOH^{+} + e \rightleftharpoons \rightleftharpoons FeOH_{ads}$. The slow stage is

$$FeOH^{+} + FeOH_{ads} + 2e \rightarrow Fe + OH^{-} + FeOH_{ads},$$

which corresponds to the kinetic equation

$$i_{c,stat} = k_{-} [OH^{-}]^2 [Fe^{2+}]^2 e^{-\frac{(2\alpha+1)F\varphi}{RT}}. \quad (27a)$$

With $\alpha = 1 - \beta = 0.54$, the slope of the Tafel straight line should be $\sim 0.028$ V.

Similar values, of 0.027–0.030 V, were found for the slopes $b_a$ and $b_c$ by Hurlen and Hoar[84–87] in a study of the kinetics of the discharge–ionisation of iron in sulphate and chloride solutions, using a slow galvanostatic method with determination of current efficiencies and construction of partial polarisation curves for iron and hydrogen.

However, according to these results, the rate of the cathodic deposition and anodic dissolution of iron is proportional to the hydroxide-ion concentration to the first power, not the second as required by Eqns. (26) and (27). The cathodic reaction is of the second order with respect to $[Fe^{2+}]$. The combined effect of the data is to give a scheme for the process involving two atoms (or ions) of iron and four electrons in the rate-determining stage

$$2\,Fe + OH^- \rightarrow 2\,Fe^{2+} + OH^- + 4e.$$

Hurlen[85,86] suggested that this process can occur in stages, but his proposed reactions correspond not to successive stages of one process but to two independent modes of oxidation of iron

$$Fe + OH^- \rightleftarrows \text{active complex A} \rightleftarrows Fe^{2+} + OH^- + 2e,$$
$$Fe + H_2O \rightleftarrows \text{active complex B} \rightleftarrows Fe^{2+} + H_2O + 2e.$$

Thus if the process does occur in stages, they comprise different reactions.

Ivanov and Iofa[58] have shown that at a dropping mercury electrode the rate of reduction of iron actually depends on the relative proportions of the complexes A′ and B′, which themselves depend on the pH of the solution.

$$\underset{B'}{[Fe(H_2O)_n]^{2+}} + H_2O \rightleftarrows \underset{A'}{[FeOH(H_2O)_{n-x}]^+} + H^+ + x\,H_2O.$$

At low pH values the kinetics of the process is determined by discharge of the ion B′, whereas with rise in pH the equilibrium shifts towards the formation of A′, and the rate of the process is determined by the stage

$$[FeOH(H_2O)_{n-x}]^+ + 2e \rightarrow Fe + OH^- + (n-x)\,H_2O.$$

Unfortunately, the paper does not give results for the determination of $b_c$ and $\alpha$.

Bockris et al.[88] have put forward the hypothesis that the difference in activation energy between the different paths for the electrode reaction is extraordinarily small in the case of iron, and therefore even a slight change in the conditions of electrolysis may change the mechanism of the electrode process.

(*b*) Ni/$Ni^{2+}$ electrode. The effect of hydroxide ions on the anodic dissolution of nickel has been studied by Hollnagel and Landsberg[89] using a non-stationary galvanostatic method at 60°. They find that the anodic potential decreases with increase in pH. These workers assume that the adsorption of hydroxide ions facilitates the escape of nickel ions through the intermediate formation of NiOH, in an analogous manner to Heusler's scheme[83] for iron.

Solov'eva and Abrarov[90] investigated the effect of solution pH on the electrodeposition of nickel and cobalt at constant current density. They noted a sharp decrease in cathodic potential within a definite narrow pH range, which was explained by the conversion of aquo-complexes of the metal ions into partly hydrolysed active complexes containing the $OH^-$ group.

The same workers reached a similar conclusion concerning the dependence of the kinetics of discharge on changes in the composition of the species undergoing discharge on studying the effect of boric acid on the discharge of cobalt and nickel[91], as did also Kovalenko and Nadezhdina[92] from an investigation of the effect of various complexing agents on the discharge of aquo-ions of nickel and cobalt at a dropping mercury cathode.

Matulis and Slizhys[93] concluded, from a study of the effect of catholyte pH on the cathodic process in a nickel sulphate electrolyte, that the sharp decrease in cathode potential at $pH_S \simeq 4$ is due to the discharge of $NiOH^+$ ions which are formed in the bulk of the solution at pH 4 as a result of hydrolysis

$$Ni^{2+} + OH^- \rightleftarrows NiOH^+.$$

At pH ⩾ 4 a stepwise process is assumed with formation of a neutral species

$$NiOH^+ + e \rightarrow NiOH_{ads}.$$

The following stage is desorption of hydrogen evolved simultaneously on the metal surface

$$NiH_{ads} + NiOH_{ads} \rightleftarrows Ni + H_2O.$$

In the more acid region the process of discharge corresponds to the simple scheme

$$Ni^{2+} + 2e \rightarrow Ni.$$

(*c*) $Co/Co^{2+}$ electrode. Kravtsov and his coworkers[94,95] have suggested a possible mechanism, involving hydroxide ions, for the discharge of cobalt ions at an electrode. An oscillographic method was used to obtain cathodic polarisation curves at pH 3.5 and 4.2 [95] in 1 *N* $CoSO_4 + H_3BO_3$ solutions at room temperature, as well as stationary and non-stationary anodic curves under these conditions.

The values obtained for $b_a$ of 0.064 and 0.040 V under non-stationary and stationary conditions respectively suggest that the mechanism of the anodic dissolution of cobalt resembles that proposed by Heusler for iron[83]. It was also suggested that the two electrons involved in the anodic reaction are split off successively, not in a single act, which is consistent with the large slopes of $b_c$ = 0.111–0.114 V obtained for the cathodic curves and the low values of $b_a$.

The rates of corrosion and of anodic dissolution of cobalt have been studied as a function of pH over a wide range of the latter by Iofa and Wei Pao-ming[96]. The values of $b_a$ = 0.026 V and $\nu_{OH^-} = 2$ obtained experimentally correspond to the mechanism of the anodic dissolution of iron described in Refs. 81–83.

Heusler has investigated[97,98] the effect of the acidity of the solution on the mechanism of anodic and cathodic processes in the discharge–ionisation of cobalt from perchlorate solutions. His experimental results corresponded to the scheme which he had suggested for iron[83].

The effect of pH on the cathodic deposition of cobalt from sulphate solutions at 55° has been investigated with simultaneous measurement of the pH of the catholyte[57]. The totality of experimental data[57] obtained for the partial polarisation curves of cobalt in the $pH_S$ range (in the catholyte) of 0.5–2.2 ($b_c$ = -0.085 V, $\nu_{OH^-} = 0$, and $\nu_{Co^{2+}} = 1$) shows that the discharge of cobalt takes place according to the simple two-electron scheme

$$Co^{2+} + 2e \rightarrow Co.$$

In the $pH_S$ range 2.5–4.0 an increase in $b_c$ from 0.085 to 0.150 V is observed on a negatively charged surface, which can be explained by partial hydrolysis of the aquo-ions of cobalt according to the equation

$$Co^{2+} + H_2O \rightleftarrows CoOH^+ + H^+,$$

with simultaneous participation of the ions $Co^{2+}$ and $CoOH^+$ in the electrode process. Increase in pH is accompanied

by displacement of the equilibrium towards formation of $CoOH^+$, and discharge takes place in the stages

$$CoOH^+ + e \rightarrow CoOH \text{ (slow stage)},$$
$$CoOH + e \rightleftarrows Co + OH^-,$$

which is consistent with Kravtsov's experimental results[95]. In this same pH range the discharge of cobalt occurs on a positively charged electrode surface (zero-charge potential about -0.45 V), where the experimental values of $b_c = -0.026$ V, $\nu_{Co^{2+}} = 2$, and $\nu_{OH^-} = 1$ correspond to an overall reaction involving four electrons, analogous to the scheme suggested by Hurlen and Hoar[84-87] for iron:

$$2Co^{3+} + OH^- + 4e \rightarrow 2Co + OH^-,$$

$$i_c = k[Co^{3+}]^2[OH^-]e^{-\frac{\alpha' F\varphi}{RT}}. \quad (28)$$

Such a process may be supposed to occur in one stage if the species transferring the charge is assumed to be the complex $[Co_2OH]^{3+}$. In this case the transfer coefficients $\alpha' = 2.5$ and $\beta' = 1.5$ [55,95] (value of $\beta'$ taken from Ref. 55 is 1.4 at 60°) are regarded as $\alpha' = 4\alpha$ ($\alpha = 0.62$) and $\beta' = 4\beta$ ($\beta = 0.38$). However, the high activation energy required for the transfer of a triply charged species, and also the possibility of the transfer of electrons from the cathode surface through a hydroxyl "bridge", suggest that the process takes place in stages, with the following possibilities:

I. $$Co^{3+} + H_2O \rightleftarrows CoOH^+ + H^+, \quad (a)$$

$$CoOH^+ + e \rightleftarrows CoOH \text{ rapid}, \quad (b)$$

$$\underbrace{CoOH + Co^{3+}}_{Co_2OH^{3+}} + 3e \rightarrow 2Co + OH^- \text{ slow}. \quad (c)$$

In this case $\alpha' = 1 + 3\alpha$ ($\alpha = 0.5$) and $\beta' = 3\beta$ ($\beta = 0.5$).

II. Stages ($a$) and ($b$) remain as before, but subsequent electrons are also added on successively:

$$CoOH + Co^{3+} + e \rightleftarrows Co_2OH^+ \text{ rapid},$$
$$Co_2OH^+ + e \rightarrow Co_2OH \text{ slow},$$
$$Co_2OH + e \rightleftarrows 2Co + OH^- \text{ rapid}.$$

The experimental values of $\alpha'$ and $\beta'$ correspond to slow addition of the third electron — see Eqn. (16). In fact, with $n = 4$ and $m = 3$, $\alpha' = \alpha_3 + 3 - 1 = \alpha_3 + 2$ ($\alpha_3 = 0.5$) and $\beta' = \beta_3 + 4 - 3 = \beta_3 + 1$ ($\beta_3 = 0.5$).

In order to choose between the possibilities suggested, it is necessary to obtain additional data on the intermediate products involved in the electrode process.

It must be noted that the reaction order with respect to hydroxide ions of $\nu_{OH^-} = 1$, which determines the mechanism of the electrode process (see, for example, Heusler's scheme[83,97], where $\nu_{OH^-} = 2$) is obtained only when the pH adjacent to the cathode is taken into account. Relations based on the pH in the bulk of the solution give values of $\nu_{OH^-} \simeq 2$. This illustrates the necessity of measuring pH in the layer adjacent to the electrode, and taking this quantity into account in investigating the mechanism of electrode reactions.

($d$) In(Hg)/$In^{3+}$ electrode. The pH dependence of the electrode process has been investigated by Losev and Molodov[44]. At $HClO_4$ concentrations below 0.1 M the rate of anodic dissolution of indium is proportional to the hydroxide-concentration to the first power, and the process is described by the equation

$$i_a = k[In][OH^-]e^{\frac{\beta' F\varphi}{RT}} \text{ (where } \beta' = 2.2).$$

The overall process is

$$In + 5H_2O + OH^- \rightleftarrows In(H_2O)_5OH^{2+} + 3e.$$

The possibility of stepwise occurrence of this process has been discussed above. Cathodic and anodic polarisation curves obtained at various pH values in this work are reproduced in Fig. 4. The unusually steep slope of the cathodic curves was explained as due to a prior chemical stage of hydrolysis, and the decrease in slope with increase in cathode potential as due to acceleration of this reaction.

However, curves of this type can be explained by a change in the charge on the cathode surface. In fact, the zero-charge potential for indium amalgam (~ 0.1 at. %) calculated by Antropov's method[99] gives a value of about -0.4 V (zero-charge potential for indium taken from Ref. 100), which corresponds to a potential region in which the polarisation curves slope steeply. Consequently the more gently sloping linear section at potentials between -0.6 and -0.8 V on the cathodic curves corresponds to the discharge of indium ions on a negatively charged surface. The slope of this section is ~ 0.14 V, which gives a transfer coefficient $\alpha'$ of around 0.4. Such kinetic parameters may correspond to a slow stage involving addition of an electron to the $In^{3+}$ ion, while determination of the order of reaction with respect to hydroxide ions may show whether indium ions exist in the form of aquo-complexes or partly hydrolysed complexes.

## 4. Reactions of the Oxygen Electrode

The great practical importance of electrode reactions involving oxygen has given rise to several investigations of their mechanism. The overall four-electron process undoubtedly comprises a series of stages. In this case the presence of at least one intermediate product — hydrogen peroxide — has been firmly established experimentally both in the cathodic reduction of oxygen molecules and in the anodic oxidation of water molecules or hydroxide ions[101].

Investigation of the electrochemical reactions of oxygen is complicated by oxidation of the electrode surface, not only in the course of anodic evolution but in several cases even during the cathodic reduction of $O_2$ molecules[102]. As a result, the mechanism may differ on different electrodes.

Krasil'shchikov[102] established that the cathodic reduction of oxygen on silver and gold electrodes in acid medium takes place according to the scheme

$$O_2 + e \rightarrow O_2^- \text{ (slow stage)},$$
$$O_2^- + H^+ \rightleftarrows HO_2,$$
$$HO_2 + e \rightleftarrows HO_2^-,$$
$$HO_2^- + H^+ \rightleftarrows H_2O_2.$$

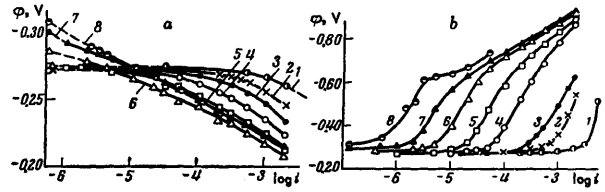



Fig. 4. Dependence of: $a$) anodic; $b$) cathodic polarisation curves for indium on acidity of electrolyte ($HClO_4$, M): 1) 0.002 ($a$) and 0.00095 ($b$); 2) 0.0077; 3) 0.016; 4) 0.05; 5) 0.1; 6) 0.5; 7) 1.3; 8) 3.3.

According to Krasil'shchikov's results, the slow stage is the same in alkaline medium as in acid solutions. Bagotskii and Yablokova [103] accept the above scheme for acid solutions, but suggest a different mechanism for alkaline solutions, at any rate on a mercury electrode, because in this case the reduction of oxygen takes place under nearly equilibrium conditions.

In the anodic evolution of oxygen all electrodes are oxidised, so that the process actually takes place on an oxidised surface. Depending on the electrode potential (current density), either chemisorbed layers can be formed in which the metal–oxygen bonding energy varies with time, or oxides of different compositions as separate phases. Their participation in the electrode process has been discussed many times in the literature (e.g. Ref. 104).

Krasil'shchikov [105] regards the following scheme

$$OH^- - e \rightleftarrows OH,$$
$$OH + OH^- \rightleftarrows H_2O + O^-,$$
$$O^- - e \rightarrow O \text{ (slow stage)},$$

as valid for oxygen evolution from alkaline solutions on nickel and cobalt. Kheifets and Rivlin [106] suggest for acid solutions a mechanism including two-electron stages. Other views have also been held on the mechanism of oxygen evolution [11]. It is significant that they all start from the assumption that the overall reaction consists of several stages.

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Examination of the above results undoubtedly shows that the concept of stepwise (consecutive) electrochemical reactions has in several cases opened up new possibilities in the theory of the slow discharge of ions and has permitted a deeper insight into the mechanism of electrode processes. However, the view that a many-electron reaction must necessarily involve a series of successive one-electron stages is not justified. Actually, non-stepwise reactions and reactions having two-electron intermediate stages are also observed.

Published data do not always provide convincing evidence of the stepwise character of processes. If we ignore papers in which the conclusions of the authors are supported neither by their own experimental results, nor by later publications, there still remain a large number of cases in which the experimental results are quite contradictory, and not always sufficient for a definite conclusion to be reached. Furthermore, the electrochemical criteria themselves are such that it is not always possible to use them to substantiate details of the mechanism of a process. However, this must not be regarded as a rejection of the whole idea of successive stages. In several cases the stepwise occurrence of electrochemical reactions has been demonstrated convincingly, as in the electrode reactions of oxygen (see above), the anodic production of peroxodisulphuric acid [101] and of the higher oxygen compounds of chlorine [107,108], a considerable number of processes involving the oxidation or reduction of organic compounds [109], the reduction of nitric acid [109], etc.


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# ADVANCES IN THE SYNTHESIS OF POLYPEPTIDES

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## I. INTRODUCTION

Among polyamides there is a large group of polymers which differ from other polyamides in their properties and methods of preparation. This group, called polypeptides or poly-α-amino-acids, is very close in its composition and structure to one of the most important classes of polymeric substances — proteins. In contrast to proteins in which there is a strictly defined alternation of amino-acids, synthetic polypeptides usually contain only one amino-acid or several amino-acids with a random distribution along the chain of the macromolecule.

By polycondensation of various low-molecular-weight derivatives of peptides, it proved possible to prepare block-polypeptides with a random distribution of the blocks but with a known alternation of the amino-acids within each block, and also polypeptides with a defined alternation of amino-acids, whose number however was small.

$$[-HNCHR_1COHNCHR_2CO-]_x[-HNCHR_3COHNCHR_4CO-]_y \text{ and}$$
$$[-HNCHR_1COHNCHR_2COHNCHR_3CO-]_n.$$

Starting with the work of Fischer [1], Bergmann [2], and Leuchs [3], studies of the synthesis and properties of peptides and polypeptides have proceeded on a wide front. The results of the investigations published up to 1957 were described in detail previously [4,5]. The further increase in the number of papers published, including reviews, on the individual problems of the chemistry of polypeptides [6-13] indicates the growing importance of synthetic polypeptides.

One of the main aims of protein chemistry in the last decade has been the elucidation of the correspondence between biological functions and the chemical structure of proteins [14]. Synthesis of polypeptides as model compounds is one of the possible ways of determining the effect of various amino-acids, their sequence, and steric configuration on biological properties.

Synthetic polypeptides are also of considerable interest for polymer chemistry, since the methods of their preparation permit nowadays the synthesis of polymers with various amino-acid compositions and different structures, and with molecular weights ranging from several hundred to a million and above, and also they provide a means of modelling natural peptides, and modifying their composition, structure, and properties. This makes it possible to obtain polymers whose properties vary within very wide limits, and thereby solve important problems in the chemistry of macromolecular compounds.

In view of the abundance of data available, we are obliged to restrict ourselves to a description of the principal results of studies of the synthesis of polypeptides, published between 1957 and 1963, including certain important sections such as the chemical reactions and conformational analysis of polypeptides and also the methods of investigating their structures. Furthermore, the review does not deal with the important field of stepwise syntheses of peptides and their application, which is of independent interest. The review considers in detail the synthetic methods which have been most extensively developed in the last six years.

## II. SYNTHESIS OF POLYPEPTIDES FROM α-AMINO--ACIDS, PEPTIDES, AND 2,5-DIOXOPIPERAZINE DERIVATIVES

### 1. Thermal Polycondensation of α-Amino-Acids and Peptides

It has been found that the usual method of polycondensation of amino-acids containing an amino-group at some distance from the carboxy-group [$H_2N(CH_2)_nCOOH$, $n \geq 5$] cannot be successfully used with α-amino-acids and peptides. At elevated temperatures the amino-acids and peptides undergo various side reactions (decarboxylation, deamination, cyclodehydration, etc.) resulting in the formation of low--molecular-weight products. Furthermore, the closeness of the amino- and carboxy-groups in α-amino-acids favours the formation at high temperatures of 2,5-dioxopiperazines, dimeric cyclic derivatives with high stability [15]. 2,5-Dioxopiperazines are also formed as a result of the degradation of polypeptides [16-18] on prolonged exposure to high temperatures. All these facts make it extremely difficult to obtain linear polypeptides directly from α-amino-acids. However, attempts to simplify to the greatest possible extent the synthesis of polypeptides are continued and to this day attract the attention of many investigators.

Among the various amino-acids studied, glycine undergoes polycondensation most readily. Meggy [19] suggested that, since glycine can be dehydrated at 140–180° in glycerol or ethylene glycol with the formation of 2,5-dioxopiperazine and the latter is thermodynamically less stable over a wide temperature range (60°–180°) than polyglycine, direct condensation of glycine to polyglycine is quite possible. Indeed, when glycine is heated with a small amount of hydrochloric acid in sealed tubes at temperatures in excess of 140°, it is converted into polyglycine, the yield of the polymer varying with the glycine : hydrochloric acid ratio.

Polyglycine is not obtained below 130° and when tubes which had been heated to 140° are kept a further 24 h at 130° the yield of the polymer falls appreciably. It appears that this reaction requires a temperature above 140° and the presence of a solid phase. Apart from hydrochloric acid, the reaction is catalysed by phosphoric acid, ammonium chloride, and sodium hydroxide. It can also be carried out in the presence of water alone, but hydrochloric acid ensures the highest yield and the best quality of the polymer.

Meggy believes that the polymerisation of glycine may be regarded as a heterogeneous stepwise reaction between glycine in solution and the solid polyglycine:

$$\text{glycine} + \text{X-mer} = (\text{X} + \text{I})\text{-mer} + H_2O. \qquad (1)$$

It would appear that this process could result in prolonged growth of the polymeric chain and hence in a prolonged increase of the average degree of polymerisation $n$. However, it is probably accompanied by internal hydrolysis of the peptide bonds (X + Y)-mer + $H_2O$ = X-mer + Y-mer, as a result of which equilibrium is established under the given conditions and $n$ remains constant. Having measured the partial pressure of water in the system, Meggy calculated that for this reaction $\Delta H$ = 3.3 kcal mole$^{-1}$ and $\Delta S$ = = 5.9 kcal mole$^{-1}$ deg$^{-1}$.

Attempts at polycondensation of other amino-acids were unsuccessful. α-Aminoisobutyric acid does not change on heating with a small amount of hydrochloric acid at 140° for 24 h. At 220–240° traces of a sublimate were observed, which Meggy believes to be 3,3,6,6-tetramethyl-2,5-dioxopiperazine. Prolonged heating at this temperature resulted in appreciable pyrolysis of the initial amino-acid. Under similar conditions DL-phenylalanine decomposes partially with the formation of resinous products; L- and DL-alanine is converted into dark viscous products which are completely soluble in water. Thus the majority of α-amino-acids do not form homopolypeptides on heating. The ease with which glycine undergoes polycondensation is probably due to the absence of a side-chain capable of causing steric hindrance.

Fox and Middlebrook [20-22] suggested that the conditions of the thermal polycondensation of amino-acids are very similar to the conditions obtaining in the formation of protein species on earth and showed that amino-acids which fail to yield peptides when heated in a pure form are partially converted into linear polypeptides when they are heat-treated in a mixture with other amino-acids. Further study led to a number of interesting findings and the observation of a number of interesting phenomena. Thus when equimolar mixtures of the DL-forms of aspartic acid, leucine, valine, and phenylalanine are heated at 200° for 0.5–3 h, in addition to appreciable quantities of acetone-soluble tarry products, polymers were obtained whose hydrolysate contained the initial amino-acids [23,24]. On the basis of the results obtained for the polycondensation of various pairs of amino--acid in different combinations, Fox and Harada concluded that copolymeric peptides are obtained by the thermal method only when the reaction mixture contains either glutamic or aspartic acid [25]. Table 1 presents the results of biuret tests of the products of the joint thermal condensation of glutamic acid with other α-amino-acids. Usually [25] L- or DL-glutamic acid was heated for 0.5–2 h with various amino-acids in equimolar proportions at 160–190°. The

TABLE 1.

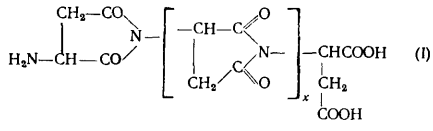
| Reactants | Results of biuret test | Reactants | Results of biuret test |
|---|---|---|---|
| Glutamic acid + glycine | + | Pyroglutamic acid + lysine hydrochloride | + (intense) |
| Glutamic acid + glycyl-glycine | + | Pyroglutamic acid + + leucine + glycine | + |
| Glutamic acid + 2,5-dioxo-piperazine | + | Pyroglutamic acid + + proline + glycine | + |
| Pyroglutamic acid + + glycine | + | Pyroglutamic acid + + aspartic acid + glycine | + |
| Pyroglutamic acid + 2,5--dioxopiperazine | 0 | Pyroglutamic acid + lysine hydrochloride + glycine | + |
| Pyroglutamic acid + 2,5--dioxopiperazine + water | + | Pyroglutamic acid + lysine hydrochloride + cystine | + |
| Glutamic acid + aspartic acid | + | Pyroglutamic acid + lysine hydrochloride + cystine + + glycine | + |
| Pyroglutamic acid + + aspartic acid | + | 2,5-Dioxopiperazine + + glycylglycine | 0 |
| Glutamic acid + asparagine | + | 2,5-Dioxopiperazine + + glycine + phenylalanine | 0 |
| Pyroglutamic acid + alanine | + | Glycine + aspartic acid | + (weak) |
| Pyroglutamic acid + valine | + | Glutamine + aspartic acid | + |
| Pyroglutamic acid + leucine | + | Glutamine + asparagine | + (weak) |
| Pyroglutamic acid + phenyl-alanine | + | | |
| Pyroglutamic acid + serine | at 160° the product darkens before the test | | |

molecular weight of the copolymers with glycine reached 10 000–20 000.

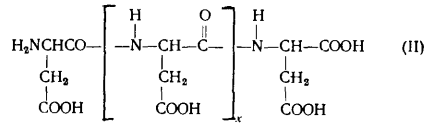
During thermal copolycondensation glutamic acid is converted into pyroglutamic acid[26] which melts in the presence of other substances at 170° and probably behaves as a solvent for the reaction mixture thus favouring a more rapid and complete reaction. Furthermore, a relative estimate of the yields of the products showed that pyroglutamic acid is more reactive than glutamic acid. It is also extremely probable that glutamic and pyroglutamic acids can behave as "acid" catalysts for amino-acid copolycondensation, since it is known that the formation of the amide bond is catalysed by protons, in particular in the presence of traces of water. However, the above workers did not present any evidence for this hypothesis.

Heating of aspartic acid does not result in the formation of any liquid products at temperatures below 200° but the acid is also capable of forming copolymers, which in contrast to the copolymers with glutamic acid, contain a smaller proportion of neutral and basic acids. A striking property of aspartic acid is that it is capable of homopolymerisation on heating above 100°. This interesting property attracted attention long ago and has been the subject of numerous studies.

It has been shown[27,28] that polyaspartic acid is a polyimide (I), which firmly retains water (approximately one molecule of water per imide bond); the latter can only be removed by thorough drying at 200° in a vacuum. The polyimide polyhydrate is converted into polyaspartic acid with the structure of a true polypeptide (II) on brief heating in dilute sodium hydroxide solution. The mean molecular weight of polyaspartic acid, which is approximately 110 000, was determined by end-group analysis and from the rate of sedimentation in the ultracentrifuge.

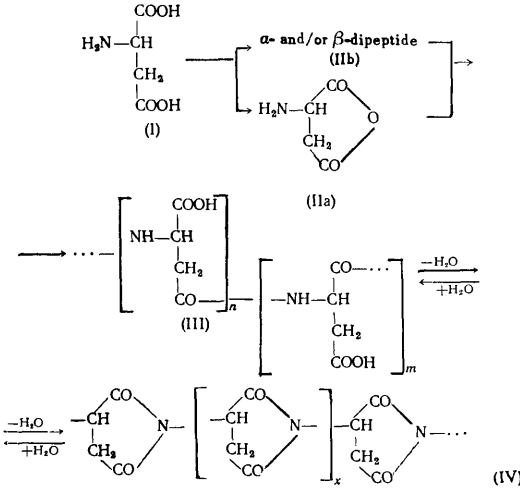


(I)



(II)

Earlier, Kovacs, Könyves, and coworkers[29-34], who studied the mechanism of the thermal polycondensation of aspartic acid and the structure of the resulting polymeric products, arrived at a similar conclusion. The polycondensation of aspartic acid was carried out either by heating in a vacuum (0.1 mmHg) at 200° or by boiling a suspension of aspartic acid in tetralin which made it possible to remove the water, evolved during the condensation, by azeotropic distillation. The authors found that thermal polycondensation of aspartic acid (I) yields the so-called "anhydropolyaspartic acid" (IV):



(IV)

Using the Hofmann degradation, the authors determined the ratio of the $\alpha$- and $\beta$-links in the intermediate $\alpha\beta$-polyaspartic acid (III), which proved to be 1 : 1.3. The molecular weights of different specimens of substance (III) calculated by Van Slyke's method were in the range 6000–12 000.

Anhydropolyaspartic acid, prepared by different methods, had identical properties: it did not dissolve in water or a dilute solution of sodium bicarbonate, and on partial hydrolysis (0.1 *N* NaOH) it was converted into $\alpha\beta$-polyaspartic acid. In addition, study of the mechanism of the initial stage of the condensation showed that heating of acetylaspartic acid (145–200°) also yields anhydropolyaspartic acid (IV) instead of the expected monomeric anhydride.

When mixtures of aspartic and glutamic acids in various proportions were heated at 170–180°, polymers of fairly high molecular weight, with a polyimide structure according to infrared spectroscopic data, were obtained[35]. As in the case of the homopolymer of aspartic acid, the imide form of the copolymer is converted into the polypeptide on treatment with a hot solution of sodium hydroxide or boiling water. If the polypeptide thus isolated is heated, it is reconverted into the imide form, identical with the initial polymer. The authors propose the following mechanism for the mutual interconversions of the various forms of polyaspartic acid and the products of the thermal copolycondensation of glutamic and aspartic acids.

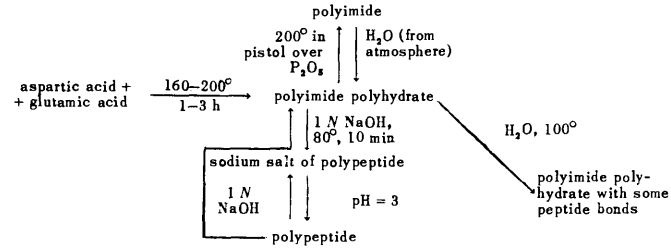


Table 2 presents data on the effect of temperature on the copolycondensation of L-aspartic and L-glutamic acids [35]. It is evident that the mean molecular weight and the yield appreciably increase with temperature. The dependence of the yield of the polymer on the proportions of the initial acid is given in Fig. 1, which shows that the optimum yield of the polypeptides is achieved when the aspartic : glutamic acid ratio is (3–4) : 1.

It was found that the glutamic acid content of the copolymer in the *N*-terminal position is 2–2.5 times greater than its total content in the polypeptide (Table 3).

On the basis of these data, Fox and Harada put forward the hypothesis [35-39] that on copolycondensation amino-acids "spontaneously" take up a specified ordered arrangement in the polymeric chain.

The results of the polycondensation of glutamic and aspartic acids with one another and with other α-amino-acids show that all 18 amino-acids which are present in natural proteins can take part in polycondensation simultaneously. As a result of such synthesis, Fox and Harada obtained a number of protein-like substances which they called "proteinoids"; the qualitative composition of their hydrolysates was the same as that of most natural proteins [36-38]. "Proteinoids" are fairly readily obtained only in the presence of a large excess of aspartic and glutamic acids. When they are present in equimolar proportions with other amino-acids, side-products are formed (for example 2,5-dioxopiperazines) in addition to peptides, and the isolation of the peptides becomes difficult.

The proteinoids were prepared by heating (2 h at 170–180°) two parts of glutamic acid, two parts of aspartic acid, and one part of an equimolar mixture of the remaining amino-acids. Apart from an excess of the acid amino-acids, the success of the reaction requires the removal of water from the reaction vessel, which is achieved by heating the reactants above 100°. Glutamic acid may be replaced by glutamine. The reaction is accelerated by orthophosphoric acid, whose effect on the copolycondensation of α-amino-acids was studied using as an example the copolycondensation of aspartic acid with glutamic acid and of aspartic acid with glycine, which takes place readily [39]. Phosphoric acid increases the yield but has almost no effect on the molecular weight of the polypeptides. On more prolonged heating, the amount of product which does not dialyse through the cellophane membrane increases, which is probably due to an increase in the yield of the high-molecular-weight fraction of the polymer. The formation of non-dialysable polymer after heating for 1 h begins at a temperature as low as 150°. In the absence of phosphoric acid comparable results are obtained only at 170°. Table 4 presents data on the effect of temperature on the copolycondensation.

In the presence of phosphoric acid the *N*-terminal composition of the copolymer changes little and the aspartic acid content of the copolymer rapidly increases with increase of the aspartic acid : glutamic acid ratio in the initial mixture. The difference between the aspartic acid : glutamic acid ratios calculated from the total and *N*-terminal compositions is in this case even greater. It follows from this that phosphoric acid favours the self-regulation of the disposition of the amino-acid residues in the polypeptide chain. The relative content of phosphoric acid in the initial reaction mixture has an appreciable effect on the rate of condensation (Fig. 2). The authors believe that phosphoric acid can behave in this reaction both as a solvent and as an acid catalyst and can also facilitate the removal of water from the reaction sphere and the formation of intermediate active compounds [40].

All the proteinoid fractions gave positive biuret, xanthoproteic, and other qualitative tests for protein. In the cold proteinoids do not react with ninhydrin. However, in hot solutions they give the colour characteristic of this test (clearly as a result of the partial removal of amino-acids)

TABLE 2. Copolycondensation of L-aspartic (0.01 M) and L-glutamic (0.01 M) acids.

| Temperature, °C | Yield of crude polymer, g | Yield of polymer after dialysis, g | Mean molecular weight of the copolymer |
|---|---|---|---|
| 160 | 0.64 | — | — |
| 170 | 0.19 | 0.16 | — |
| 180 | 0.49 | 0.40 | 5 100 |
| 190 | 0.88 | 0.71 | 13 000 |
| 200 | 0.98 | 0.83 | 18 000 |

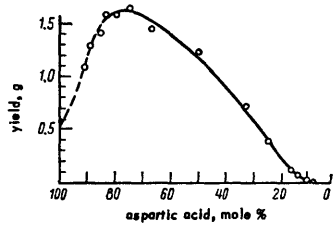



Fig. 1. Variation of the yield of the copolymers of aspartic and glutamic acids with the reactant ratio; the total amount of aspartic and glutamic acids in each determination was 0.025 mole; temperature 180°; duration of reaction 3.5 h; in the region corresponding to the continuous line the reaction mixture was present in a single phase.

TABLE 3.

| Moles of aspartic acid in reaction mixture | Moles of glutamic acid in reaction mixture | Content of glutamic acid in the polymer as a whole (A), % | Content of glutamic acid in the *N*-terminal position (B), % | B/A |
|---|---|---|---|---|
| 0.01 | 0.01 | 29 | 59 | 2.0 |
| 0.02 | 0.01 | 19 | 54 | 2.8 |
| 0.03 | 0.01 | 15 | 54 | 3.6 |

TABLE 4. Effect of temperature on the thermal copolycondensation of aspartic (0.02 M) and glutamic (0.01 M) acids in the presence of 0.8 ml of 85% orthophosphoric acid.

| Temperature, °C | Yield of polymer before dialysis, g | Yield of polymer after dialysis, g | Aspartic acid : glutamic acid ratio in copolymer | | Mean molecular weight | |
|---|---|---|---|---|---|---|
| 130 | 1.15 | 0 | | | | |
| 140 | 0.39 | traces | | | | |
| 150 | 0.62 | 0.44 | | | | |
| 160 | 2.00 | 1.61 | | | | |
| 170 | 1.99 | 1.76 | 17 | 2.1 | 6700 | 0.01 |
| 180 | 2.27 | 2.09 | 18 | 1.5 | 11 800 | 0.018 |
| 190 | 2.28 | 2.13 | 11 | 1.6 | 12 300 | 0.024 |
| 200 | 2.30 | 2.14 | 12 | 1.0 | 33 600 | 0.020 |
| 210 | 2.33 | 2.18 | 9 | 1.1 | 25 600 | 0.014 |

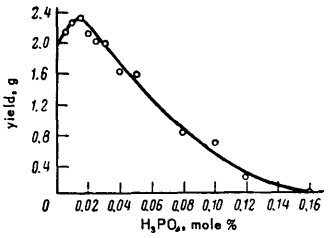



Fig. 2. Variation of the yield with the number of moles of 85% phosphoric acid in the copolymerisation of 0.02 mole of aspartic acid and 0.01 mole of glutamic acid.

but at a slower rate than natural proteins. The mean molecular weight of proteinoids is smaller than that of the copolymers of aspartic and glutamic acids obtained under the same conditions, amounting to about 4000–8000.

Infrared spectra show that proteinoids have a typical polypeptide structure. In addition, the spectra show absorption bands characteristic of imide bonds but the peaks characteristic of 2,5-dioxopiperazines are completely absent.

The solubility of proteinoids depends on the method of preparation. Copolymers synthesised in the usual way were nine-tenths insoluble in water but were soluble in salt solutions, for example in 0.1 *N* phosphate buffer at pH 7.9 or in 3.5% solution of sodium chloride. Like natural proteins, synthetic proteinoids can be salted out by the addition of a saturated solution of ammonium sulphate to the salt solution.

Proteinoids can replace the peptone in the broth culture of *Lactobacillus arabinosus*; although the growth rate of the bacteria in the broth based on the proteinoid is somewhat lower, the very fact of the growth of the microorganisms indicates that the links in the proteinoid are susceptible to attack by bacterial proteases.

Thus in many of their properties the products of the thermal copolycondensation of the mixture of 18 amino-acids closely resembles natural proteins. However, heating at 170–180° inevitably results in partial racemisation of the asymmetric centres in the amino-acids and, in contrast to the protein chain, the peptide chain of protenoids is built up of amino-acid residues of different configuration. As a result of this, it is impossible to obtain by this method polypeptides with the steric structure of protein molecules.

The available data are insufficient for a complete answer to the problem of the arrangement of the amino-acid residues in proteinoids — whether the arrangement is completely random or whether it is ordered in some specified way. The authors of the investigation believe that, since the *N*-terminal ratios of glutamic acid, aspartic acid, and neutral amino-acids appreciably differ from the ratios in the total composition and from the ratios of the components in the initial mixture (Tables 5 and 6) and since the *N*-terminal amino-acid composition varies with the temperature of the synthesis while the total composition remains constant, the thermal reaction of the mixture of amino-acids cannot be regarded as a completely disordered process.

Krampitz[41-43] obtained several proteinoids by heating a mixture of amino-acids in sealed tubes in an atmosphere of nitrogen (3 h at 170°). Proteinoid (I) was synthesised from two parts of aspartic acid, two parts of glutamic acid, and one part of an equimolar mixture of other amino-acids, namely: DL-alanine, DL-isoleucine, DL-thereonine, DL-valine, DL-methionine, DL-phenylalanine, DL-serine, DL-tryptophan, L-arginine, L-histidine, L-proline, L-leucine, L-tyrosine, glycine, and lysine monohydrochloride. Proteinoid (II) contained four parts of aspartic acid, four parts of glutamic acid, and one part of the above equimolar mixture of amino-acids. After purification the copolymers give the following positive reactions: biuret, xanthoproteic, Hopkins–Cole–Adamkewicz, Salkowski, and the reaction with Azocarmine B. The *N*-terminal positions in both proteinoids contain mainly aspartic and glutamic acid residues, the contents of neutral and basic acids being only slight. It was found that the hydrolysis of copolymers (I) and (II) by a number of proteolytic enzymes, such as pepsin, trypsin, erepsin, and papain proceeds to different extents. Similar results were obtained by Fox and Harada, who studied the effect of chymotrypsin and pepsin on two proteinoid specimens[37]. Fig. 3 presents the results of the proteolysis of the synthetic products and casein. It is evident that casein is hydrolysed more

TABLE 5. Effect of temperature on the amino-acid composition of proteinoids for two amino-acid ratios.

| Temperature, °C | Aspartic acid, % | Glutamic acid, % | Neutral amino-acid, % |
|---|---|---|---|
| 2:2:1 ratio | | | |
| 160 | 66 | 13 | 22 |
| 170 | 65 | 12 | 23 |
| 180 | 63 | 13 | 24 |
| 190 | 56 | 14 | 29 |
| 1:1:1 ratio | | | |
| 160 | 56 | 14 | 30 |
| 170 | 55 | 13 | 32 |
| 180 | 55 | 14 | 31 |
| 190 | 46 | 19 | 35 |

TABLE 6. Effect of temperature on the *N*-terminal amino-acid composition of proteinoids for two amino-acid ratios.

| Temperature, °C | Aspartic acid N : amino-acid ΣN, % | Glutamic acid N : amino-acid ΣN, % | Neutral acid N : amino-acid ΣN, % |
|---|---|---|---|
| 2:2:1 ratio | | | |
| 160 | 7 | 57 | 36 |
| 170 | 6 | 46 | 48 |
| 180 | 11 | 37 | 53 |
| 190 | 8 | 13 | 80 |
| 1:1:1 ratio | | | |
| 160 | 8 | 42 | 50 |
| 170 | 7 | 30 | 63 |
| 180 | 10 | 20 | 71 |
| 190 | 9 | 10 | 81 |

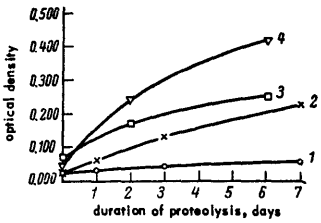



Fig. 3. Proteolysis of proteinoids with pepsin and chymotrypsin:
1) proteolysis of 2 : 2 : 1-proteinoid with chymotrypsin; 2) proteolysis of casein with chymotrypsin; 3) proteolysis of 1 : 1 : 1-proteinoid with pepsin; 4) proteolysis of casein with pepsin.

completely by the enzymes than the proteinoid, because proteases act only upon the links between L-amino-acid residues. Pepsin is particularly active in the presence of acid amino-acid residues and for this reason proteinoids are more susceptible to "attack" by pepsin than by other enzymes.

Like dicarboxylic amino-acids, free DL-lysine is converted at 150–170° into the liquid lactam and at 180–230° it undergoes homopolymerisation[44]. Lysine also readily condenses with glycine, alanine, and other neutral amino--acids, glutamic and aspartic acids, caprolactam, and succinic, terephthalic, and other acids. The infrared spectra of the lysine homopolymer and the copolymers of lysine with neutral amino-acids and with glutamic acid show that these are typical polypeptides. Lysine monohydrochloride is incapable of homopolycondensation but it readily undergoes copolycondensation with glutamic acid and other amino-acids in the presence of orthophosphoric acid.

The lysine homopolymer is soluble in water but does not dialyse through a cellophane membrane. The copolymers of lysine with glutamic acid and with glycine are gel-like substances while its copolymer with aspartic acid is a spongy solid mass. The amorphous copolymers of lysine with glutamic and with aspartic acids swell in alkalis and acids but do not dissolve in them. This is probably because the copolymers are highly branched and probably possess to some extent also a three-dimensional structure.

In 1961 Fox et al.[45] reported the thermal copolymerisation of all 18 α-amino-acids in the presence in the reaction mixture of acid or basic components. One of the copolymers was obtained on heating the mixture of amino-acids with an excess of aspartic acid and another, under similar conditions, with an excess of lysine. In many of their properties both copolymers closely resemble proteins. The first proteinoid readily dissolved in water, dilute sodium bicarbonate solution, and phosphate buffer, had a molecular weight of the order of 3000–9000, and an isoelectric point close to 2.8. The infrared spectrum shows that the copolymer contains a considerable number of imide links which disappear when the proteinoid is treated with alkali, its spectrum then becoming typical of a polypeptide structure. Copolymer (II) was an elastic rubberlike substance soluble in mineral acids and only partially soluble in water (10%). Its molecular weight exceeded 25 000, its isoelectric point was of the order of 8.4, and it had the additional interesting feature that it could form films.

Soon after the start of the investigation of the thermal synthesis of peptides, Fox et al.[23] observed by chromatography that the hydrolysis mixtures contain a greater number of amino-acids than were taken initially in the reaction. This is probably because under the conditions of the thermal polycondensation the initial reactants undergo various chemical changes with the formation of new amino-acids and other products. It was shown, for example, that aspartic acid is converted into α- and β-alanine, and on heating with urea into ureidosuccinic acid, an intermediate in the synthesis of many pyrimidine bases. It is also interesting that spots characteristic of alanine and aspartic acid were found on chromatograms of the hydrolysis products from polymers obtained on heating ammonium fumarate and maleate.

Meggy[46] described the synthesis of polymers on heating glycine in water at 140–180° in an autoclave. The yield of products varied with temperature and the reactant ratio. The reaction is catalysed by hydrochloric acid, nitric acid, sulphuric acid, phosphoric acid, ammonium hydroxide, sodium hydroxide, and potassium hydroxide.

Bahadur[47–49] studied the photosynthesis of α-amino-acids and peptides in aqueous media. The reaction of electric light on a sterilised mixture of paraformaldehyde, water, and colloidal molybdenum oxide resulted in the formation of alanine and glycine together with a small amount of valine, histidine, glutamic acid, and ornithine, the nitrogen required for the synthesis being "fixed" from the atmosphere. Illumination of aqueous solutions of glycine in the presence of sucrose leads to the formation of oligomeric peptides, in particular glycylalanine, glycylnorleucine, and glycylglycine. When sterilised solutions of glycine and aspartic acid were illuminated with a 1000 W electric lamp for 400 h in the presence of benzoyl peroxide as the photocatalyst and sucrose as an additional energy source, new amino-acids and peptides were formed. A control experiment in the dark gave a negative result.

Ellenbogen[50] published an interesting paper on the synthesis of polypeptides on illumination with a mercury or a hydrogen lamp of aqueous solutions of ammonium salts through which a mixture of hydrocarbons (from methane to pentane) was passed continuously. The catalysts were certain salts of sodium, potassium, calcium, and a number of heavy metal oxides. The amino-acid composition of the resulting polypeptides varied with the composition of the reaction mixture and the conditions of synthesis.

Apart from early work[51–54] in which it was shown that thermal polycondensation of glycylglycine and glycylalanine usually yields 2,5-dioxopiperazines, there is no information in the literature on the polycondensation of di- and tri--peptides, probably because no significant results were obtained in such attempts.

## 2. Synthesis of Polypeptides Using Condensing Agents

Synthetic polypeptides frequently have a relatively low molecular weight; it may be increased by means of condensing agents which are widely used in experiments on stepwise synthesis of peptides with a known amino-acid sequence. Such condensing agents are *NN'*-dicyclohexylcarbodiimide[55], tetraethyl pyrophosphite[56], phosphorus pentoxide[57], etc. Furuyama et al.[58] used the relatively readily available bis-*o*-phenylene pyrophosphite as a condensing agent. After polycondensation of L-leucylglycylglycine in dry pyridine (for 6 h at 100°), two polypeptide

TABLE 7.

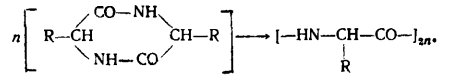
| Initial peptide | M | Final polypeptide | |
|---|---|---|---|
| | | solvent | M |
| Poly(γ-benzyl L-glutamate) | 200 000 | dioxan | 950 000 |
| Poly(γ-benzyl L-glutamate) | 225 000 | chloroform | 1 000 000 |
| Poly-ε-benzyloxycarbonyl-L-lysine | 350 000 | chloroform | 840 000 |
| Poly-L-proline | 10 000 | water | 32 000 |
| Poly(γ-benzyl L-glutamate) + poly-ε-benzyloxycarbonyl-L-lysine(1 : 1) | 200 000<br>300 000 | chloroform | 6 000 000 |

fractions with molecular weights ($M$) of 3220 and 1730 were isolated. The polypeptides dissolved in 80% aqueous phenol and 85% formic acid.

When $NN'$-dicyclohexylcarbodiimide is used for the polycondensation of oligomeric peptides with free carboxy- and amino-groups, polymers with high molecular weight are obtained (Table 7)[59]. The polycondensation was carried out at room temperature in different organic solvents. The authors of these studies believe that the condensation involves three terminal $NH_2$ and COOH groups. In those cases where the polypeptide has terminal amino- and carbamoyl groups, no increase in molecular weight is observed. The method can also be used to prepare high-molecular-weight polypeptides, including water-soluble peptides, whose synthesis by other methods presents considerable difficulties. In the presence of free carboxy- and amino-groups at the end of the peptide chain, this method can yield block copolymers and branched-chain polypeptides.

### 3. Polymerisation of 2,5-Dioxopiperazine Derivatives

It has been shown in a number of investigations[60-63] that 2,5-dioxopiperazine is thermodynamically less stable than polyglycine and is relatively readily converted into the polypeptide under various conditions. By analogy with glycolide and lactide, which polymerise into linear polyesters, it might have been expected that substituted 2,5-dioxopiperazine would also polymerise into polypeptides by the following reaction:

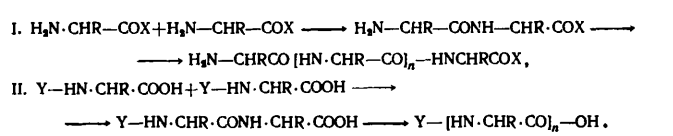


However, there have been only a few studies on the polymerisation of 3,6-substituted 2,5-dioxopiperazines. Goto[64] achieved the copolymerisation of 3,6-diisobutyl-2,5-dioxopiperazine with 2-oxopyrrolidine-5-carboxylic acid by heating an equimolar mixture of the starting materials (200°, 36 h) in glycerol. The copolymer thus isolated (yield 70%) gave a positive biuret reaction. The author believes that the product is the polypeptide, which he called a "protein analogue". Fox and Harada[25] mentioned the possibility of the copolymerisation of glutamic acid with 2,5-dioxopiperazine. However, they established that, when 2,5-dioxopiperazine and 2-oxopyrrolidine-5-carboxylic acid are heated together under anhydrous conditions, no polypeptide is formed and only after the addition of a certain amount of water to the mixture does the copolymer give a positive biuret test.

Attempts to prepare polypeptides by hydrolytic polymerisation of 1-ethyl-1,4-diphenyl- and 3,6-dimethyl-2,5-dioxopiperazines were unsuccessful. Hall[65] failed to obtain positive results in the anionic polymerisation of 1,4-dimethyl-2,5-dioxopiperazine in the presence of metallic sodium, sodium hydride, and acetylcaprolactam.

## III. SYNTHESIS OF POLYPEPTIDES FROM α-AMINO-ACID DERIVATIVES WITH MODIFIED AMINO- OR CARBOXY-GROUPS

The low tendency of free α-amino-acids and dipeptides towards polycondensation and their marked tendency to undergo cyclisation precludes their use for the synthesis of high-molecular-weight peptides under conditions excluding the possibility of racemisation of asymmetric centres. To facilitate the formation of the peptide bond, it is necessary to activate the carboxy- or the amino-group of the acid. An enhanced reactivity of amino-acids is usually achieved[4,5] by converting them into various $O$- or $N$-derivatives in which the link between the substituent and the amino-acid residue is readily susceptible to aminolysis in the case of $O$-derivatives or to acylation in the case of $N$-derivatives.



Usually such derivatives are esters and thioesters of amino-acids and peptides, amides, acid chlorides, azides, and also $N$-benzyloxycarbonyl-, $N$-phenylthiocarbonyl-, $N$-nitrophenoxycarbonyl-, and other derivatives of amino-acids.

### 1. Polycondensation of α-Amino-Acid Amides and Nitriles

Kovacs and Nagy[66] described the separation of polyaspartic acid by boiling a 5–10% aqueous solution of L-asparagine. Part of the asparagine hydrolyses to aspartic acid but most of it is converted into an amorphous mixture of oligo- and poly-peptides, among which, in particular, L-asparagylaspartic acid was identified. The mean molecular weight of the polymeric products isolated was about 500, the yield being 63%. If the reaction is carried out at 70–75°, the yield falls to 18%. Polymers of high molecular weight were obtained by dialysis. The mean molecular weight of various preparations after dialysis varied from 1700 to 3000. Like αβ-polyaspartic acid, these polypeptides readily dissolve in water and give a positive biuret reaction; their infrared spectra are identical with those of polyaspartic acid.

Guidry[67,68] studied the polycondensation of glycine amide in aqueous ammonia solution. The reaction was carried out by heating glycine amide (or its hydrochloride) with half its weight of ammonium hydroxide solution at 100° for several hours. The product was purified by dialysis and then lyophilised. Table 8 presents data on the yield and mean degree of polymerisation.

The authors quote preliminary kinetic data on the polycondensation of glycine amide, which are presented in Fig. 4. The graph shows that the initial rate of reaction is fairly high, so that polycondensation can successfully compete with hydrolytic and aminolytic side-reactions. The polycondensation products were white or slightly coloured powders, insoluble in water but soluble in concentrated lithium bromide solutions; they gave the biuret reaction

TABLE 8.

| Composition of reaction mixture | Mean degree of polymerisation | Molar yield of polyglycine, % |
|---|---|---|
| 2 g of glycine amide hydrochloride + + 1 ml 2 *N* $NH_4OH$ | 40 | 16.5 |
| 2 g glycine amide hydrochloride + + 1 ml 8 *N* $NH_4OH$ | 29 | 74.8 |
| Glycine amide (not recrystallised) | 33 | 27.4 |
| Glycine amide (recrystallised) | 34 | 75.0 |

Note. The specimens were heated in closed tubes at 100° for 20 h and more. The degree of polymerisation of the first two substances was determined by formol titration by the Sorensen method in lithium bromide solution, and that of the other two by the Van Slyke method.

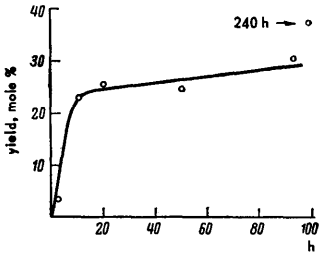



Fig. 4. The rate of formation of polyglycine from glycine amide on heating the latter in ammonium hydroxide solution at 100°.

and were completely hydrolysed to glycine in boiling acid. The infrared spectra of the polymers showed two broad absorption bands characteristic of the NH and CO bending vibrations (1534–1562 and 1634–1648 $cm^{-1}$ respectively), which means that the polymers contain predominantly bonds corresponding to the $\alpha$- and $\beta$-forms of polyglycine. This is also indicated by the presence of absorption bands in the region of 1015 $cm^{-1}$ ($\alpha$) and 1028 $cm^{-1}$ ($\beta$). At a lower reaction temperature (60°) the polyglycine was obtained in 20% yield.

Copolycondensation of glycine amide with the amides of other amino-acids does not give appreciable yields of polymeric products, but the residues of most of the amino-acids whose amides were used as starting materials were detected in the copolymers.

On heating aminoacetonitrile[67] in aqueous ammonia, a black polymer was obtained, which however could not be characterised. Heat treatment of methyleneaminoacetonitrile in the presence of ammonium sulphate leads to the formation of a non-dialysable product consisting mainly of glycine and probably cysteine residues. All the peptides were characterised by the usual analytical methods and had relatively low molecular weights of the order of 570–930.

Mach put forward the hypothesis[69] that the primary synthesis of amino-acids and proteins took place in three stages. Initially aminoacetonitrile was formed from the simple compounds HCN, HCOOH, and $NH_3$ and this then underwent polycondensation into polyglycine. The reaction of the polyglycine with aldehydes and unsaturated compounds in the third stage resulted in the synthesis of polypeptides. To confirm this hypothesis, the author heated one part of aminoacetonitrile with kaolin (20 parts) at 130° for 5 h. Chromatographic analysis revealed the presence in the reaction products of glycylglycine, diglycylglycine, and polyglycine. After treatment of the polyglycine with formaldehyde in the presence of basic catalysts, serine was detected in the hydrolysis mixture.

Losse and Anders[70] studied the polymerisation of $\alpha$-aminopropionitrile on mineral carriers. They regarded this reaction as one of the possible ways in which protein is synthesised in nature. One part of $\alpha$-aminopropionitrile was heated with two parts of a mineral adsorbent (Fuller's earth) for 50 h at 80° and 5 h at 130°. The initial nitrile was then converted to the extent of 60% into polyamidine, the hydrolysis of which yielded polyalanine with a number-average molecular weight of the order of 20 000.

$$n\,H_2N{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}C{\equiv}N \longrightarrow (-HN{-}CH(CH_3){-}\underset{\displaystyle NH}{\underset{\|}{C}}{-})_n \xrightarrow[-n NH_3]{+n H_2O} (-HN{-}CH(CH_3)\,CO{-})_n.$$

The polypeptide was isolated, characterised by the usual analytical methods, and compared with the polymer obtained by the synthesis from *N*-carboxyalanine anhydride. The properties of both polypeptides proved to be identical. It is interesting that, when $\alpha$-aminopropionitrile is heated in the absence of a mineral carrier, there is virtually no polymerisation, $\alpha\alpha'$-iminodipropionitrile $HN[CH(CH_3)CN]_2$ being formed.

## 2. Polycondensation of $\alpha$-Amino-Acid Esters

The alkoxy-group in amino-esters is fairly active and readily undergoes aminolysis, particularly in the presence of acid catalysts[71]:

$$H_2NCHRCOOR' + H_2NCHRCOOR' \xrightarrow{H^+} H_2NCHRCOHNCHRCOOR'.$$

Thus polycondensation of amino-acid esters would appear to be a convenient way of synthesising linear polypeptides; however, the main reaction in the polycondensation is frequently the cyclisation of the ester of the dipeptide formed into 3,6-disubstituted 2,5-dioxopiperazines[72,73]. Thus the methyl esters of glycine and DL-alanine gave 53 and 96% respectively of 2,5-dioxopiperazines on their polycondensation in the presence of 2% $CO_2$ [74] and $SiO_2$.[75]

The characteristic features of the polycondensation of glycine and DL-alanine esters in the presence of carbon dioxide and ester carbamates have been investigated[76,77]. According to the authors, the first stage in the reaction is rapid formation of the carbamate of the amino-acid ester:

$$CO_2 + 2H_2NCHRCOOR' \longrightarrow R'OOCCHR\overset{+}{N}H_3\cdot\overset{-}{O}OCNHCHRCOOR'.$$

The reaction is strongly exothermic and in the case of the ethyl ester of glycine terminates after 2–3 s with absorption of one mole of carbon dioxide for two moles of the ester[78]. The resulting carbamate is fairly stable, decomposing into the initial compound at about 60°.

In the symmetric carbamate one ester group is in the activated state and readily undergoes aminolysis. Thus in the polycondensation of amino-esters the growth of peptide chains proceeds as a result of the reaction of the symmetric carbamate with the amino-groups of the peptides or (in the

case of the initiation of a new chain) with the amino-group of the amino-acid ester with the formation of an asymmetric carbamate[77,79]:

$$R'OOCCHR\overset{+}{N}H_3\cdot\overset{-}{O}OCNHCHRCOOR'+H-[HNCHRCO]_x-OR'\xrightarrow{-R'OH}$$

$$\longrightarrow R'OOCCHR\overset{+}{N}H_3-\overset{-}{O}OCNHCHRCO-[HNCHRCO]_x-OR'\longrightarrow$$

$$\longrightarrow R'OOCCHRNH_2+CO_2+H-[HNCHRCO]_{x+1}-OR'.$$

Because of its instability[80], the asymmetric carbamate breaks down with the regeneration of carbon dioxide and the formation of a peptide containing one amino-acid residue more than the initial peptide or, what is more probable, the carbamate reacts with a new molecule of the monomer with the formation of the symmetric carbamate and the free peptide[81]:

$$R'OOCCHR\overset{+}{N}H_3\cdot\overset{-}{O}OCHNCHRCO[HNCHRCO]_xOR'+H_2NCHRCOOR'\longrightarrow$$

$$\longrightarrow R'OOCCHR\overset{+}{N}H_3\,\overset{-}{O}OCHNCHRCOOR'+H[HNCHRCO]_{x+1}OR'.$$

The increase of the reactivity of the ester group in the symmetric carbamate of the amino-acid ester, as a result of the influence of the carbamate group, was confirmed by the study of the polycondensation of the ethyl ester of glycylglycine. In this case the increased distance between the carbamate and ester groups results in a sharp decrease of their mutual influence, which is reflected in an almost complete absence of the catalytic effect of carbon dioxide on the polycondensation of the glycylglycine ester[82].

The polycondensation process probably proceeds in steps, its rate increasing with the concentration of the initiator (Fig. 5).

The slowest stage in the polycondensation of ethyl glycinate is the formation of the ester of the dipeptide, which is relatively rapidly converted into the tripeptide and 2,5-dioxopiperazine. Figs. 6 and 7 show the variation of the products of the polycondensation of ethyl glycinate with the duration of the reaction. At the beginning of the process almost half the solid products consist of 2,5-dioxopiperazine, whose relative amount diminishes as the process approaches completion. The amount of tripeptide reaches a maximum and then gradually falls as a result of its rapid conversion into the polymer. The process is autocatalytic and, as the peptides accumulate and their length increases, there is an increase of the relative rate of consumption of the monomer by virtue of the polypeptide chain growth.

Determination of the rate of aminolysis of *p*-nitrophenyl esters of benzyloxycarbonyl derivatives of glycine and its

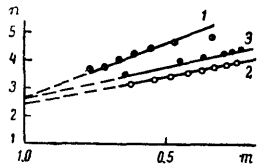



Fig. 5. Variation of the mean degree of polymerisation $n$ of the initial fraction with the consumption of the monomer $m$ for different initial molar ratios $\xi_0$ of carbon dioxide and the monomer:
1) $\xi_0 = 0.02$; 2) $\xi_0 = 0.04$; 3) $\xi_0 = 0.08$.

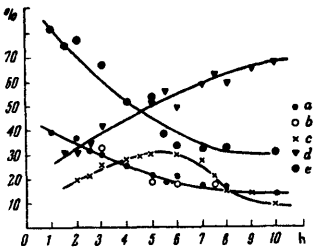



Fig. 6. Composition of the polycondensation products of ethyl glycinate (%):
*a*) 2,5-dioxopiperazine, determined from the increase in amino-nitrogen; *b*) 2,5-dioxopiperazine, determined by the "copper" method; *c*) ethyl ester of diglycylglycine; *d*) tetrapeptide fraction; *e*) free ethyl glycinate.

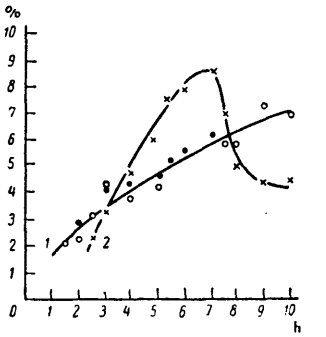



Fig. 7. The content of 2,5-dioxopiperazine and the ethyl ester of diglycylglycine (as a percentage of the initial monomer sample):
1) 2,5-dioxopiperazine; 2) ethyl ester of diglycylglycine.

di- and tri-peptides by ethyl glycinate and also the esters of the di- and tri-peptides indicates an increase in the rate of reaction of the amino- and ester groups with increase in chain length, particularly on going from the monomer to the dipeptides, which is consistent with the idea that polycondensation of amino-acid esters is autocatalytic[86].

In the absence of carbon dioxide the polycondensation of ethyl glycinate is very slow and takes place in two stages. The rate of the first stage is very low, but subsequently it increases (Fig. 8). In the second stage the monomer is used up much more rapidly. Addition of the polycondensation mixture accelerates the reaction, which still takes place in two stages, but the first stage is much shorter. An even greater shortening of the first stage occurs on addition of 20 mole % of the methyl ester of alanylglycylglycine, the rate of the second stage remaining almost unchanged, as in the case where the polycondensation mixture was added[87]. It was found that the addition of ethanol has a similar accelerating effect[88] on the polycondensation, which the authors explained by the catalytic action of the alcohol on the aminolysis reaction.

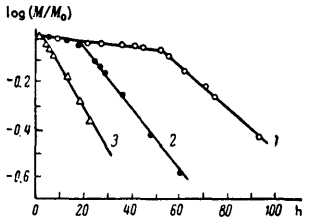



Fig. 8. Polycondensation of ethyl glycinate: 1) without additives; 2) in the presence of the polycondensate; 3) in the presence of the tripeptide ester.

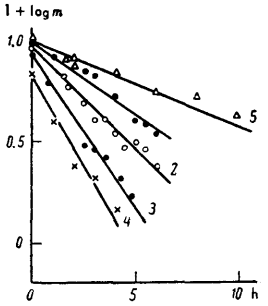



Fig. 9. Kinetics of the monomer consumption ($m$) in the polycondensation of ethyl glycinate; initial concentration of the initiator ($\xi_0$): 1) 0.02; 2) 0.04; 3) 0.08; 4) 0.16; 5) 0.01; the values of $m_0 - 1 - 2\xi_0$ are plotted along the ordinate.

Extrapolation of the data obtained in the polycondensation of ethyl glycinate with carbon dioxide (Fig. 9) shows that the true relative concentration of the monomer $(M_2 - \Delta M_0)/M_0 = m$, where $\Delta M_0$ is the amount of monomer combined with carbon dioxide, is less than unity at zero time and decreases with increase in the concentration of the initiator. This confirms that, at the beginning of the reaction, part of the monomer $(1 - m_0)$ is rapidly combined and only then does the second stage of the reaction, characterised by first-order consumption of the monomer, begin.

Study of the kinetics of the polycondensation of ethyl glycinate in the presence of its carbamate [89,90] and carbon dioxide [87] showed that the nature of the process does not change when the method of initiation of the polycondensation is modified and confirmed that the carbamate of the amino-acid ester indeed catalyses the polycondensation. At all the catalyst concentrations investigated, the monomer is consumed by a first-order reaction. Comparison of the rate constants for the consumption of the monomer when the polycondensation of ethyl glycinate is initiated with the carbamate and carbon dioxide shows that the reaction kinetics in the two cases are the same (Fig. 10).

The nature of the polycondensation of the amino-esters does not change in the presence of the anhydrides of the $N$-carboxy-derivatives of the acids [91-93]. As in the polycondensation initiated with carbon dioxide, the reaction proceeds in two stages. In the polycondensation of ethyl

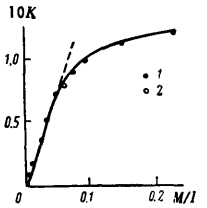
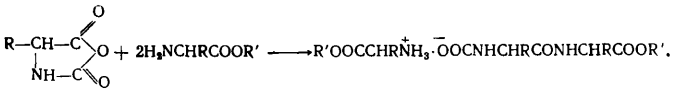



Fig. 10. Dependence of the rate constant for the consumption of the monomer ($K$, $s^{-1}$ $mole^{-1}$) on the initial concentration of the initiator (weight fraction): 1) initiation with carbon dioxide; 2) initiation with carbamate.

glycinate and the anhydride of $N$-carboxyglycine it was found that in the first stage the ester is consumed very rapidly, which in the authors' view is due to the formation of the asymmetric carbamate:




The second stage, which is slower, proceeds by the carbamate mechanism with the formation of similar polycondensation products as in the case where the process is initiated with carbon dioxide or the carbamate of the amino-acid ester [93,94].

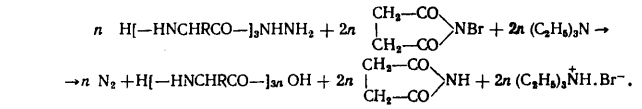
Metallic sodium and triphenylmethylsodium have also been described as catalysts for the polycondensation of amino-acid and peptide esters. Brenner and Rickenbacher [95] carried out the polycondensation of the methyl esters of DL-lysine and L-leucine (3–4 h at 5°) with a suspension of sodium (without additional solvent) and obtained in 60–70% yield polypeptides with a mean degree of polymerisation of 7 and 10 respectively. Polycondensation under these conditions of a mixture of the esters of L-leucine, DL-lysine, and DL-aspartic acid gave only a mixed polypeptide with a molecular weight of about 4000, which is difficultly soluble in water. The authors indicate that in the polycondensation of the methyl ester of L-leucine almost complete racemisation takes place. The authors explain the decrease of the yield of 2,5-dioxopiperazines when esters are subjected to polycondensation with metallic sodium by the adsorption of the amino-acid esters and the formation of polypeptides on the surface of the catalyst, while 2,5-dioxopiperazines form mainly in solution. In the polycondensation of esters in the presence of triphenylmethylsodium in ethereal solution the mean degree of polymerisation reaches 10–13. [96]

The polycondensation of the esters of oligopeptides has been considered in a relatively small number of studies. Thus Poroshin et al. state that when the methyl ester of L-prolyl-glycyl-L-proline is heated (15 h at 110° and $3 \times 10^{-3}$ mmHg), a complex mixture of polypeptides is formed, which the authors did not analyse in detail [97]. De-Tar et al. [98] treated the hydrobromide of the $p$-nitrophenyl ester of $\beta$-methoxy-L-asparagylglycylglycine with the exact calculated amount of triethylamine in dimethylformamide or dimethylsulphoxide at room temperature and obtained a polypeptide with a molecular weight of about 12 000. It was shown that whether a linear polypeptide or cyclic compounds are formed is to a large extent determined by the concentration of the initial tripeptide ester. Thus treatment of a 15% solution of the

tripeptide ester resulted in a very small yield of polypeptides because of the formation of a cyclic hexapeptide. The authors used this method to prepare a number of polypeptides containing aspartic acid, phenylalanine, and glycine, or histidine and glycine, or phenylalanine and glycine. The synthesis of the last polypeptide from the hydrobromide of the *p*-nitrophenyl ester of phenylalanylglycine is particularly interesting, because it shows that linear polypeptides and not cyclic compounds are formed from the nitrophenyl esters of dipeptides.

Polypeptides of high molecular weight were prepared by the polycondensation of the thiophenyl $\alpha\gamma$-dimethyl ester of $\gamma$-L-glutamyl-L-glutamic acid, the mixture being slightly heated[99]. After purification the resulting polypeptide gave positive biuret and ninhydrin reactions. The authors demonstrated by paper chromatography that the polypeptide is polydisperse and contains high-molecular-weight fractions which remain at the starting point of the paper chromatogram after a 36 h run.

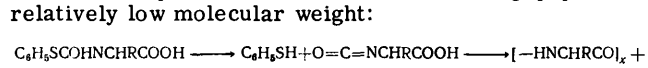
Among other work on the synthesis of polypeptides from tripeptide derivatives, that of Wolman et al.[100] is interesting. They oxidised the hydrazide of prolylglycylglycine with bromosuccinimide in dimethylformamide in the presence of triethylamine and obtained a polypeptide with a molecular weight of 1400. They suggested the following mechanism for the reaction:



The method is fairly simple and may be used when the initial tripeptide does not contain side-groups susceptible to oxidation by *N*-bromosuccinimide.

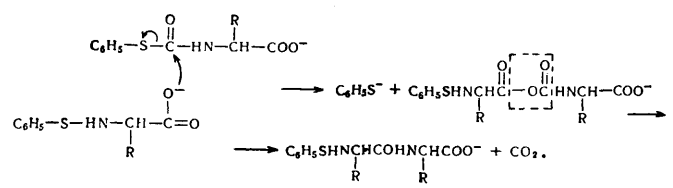
### 3. Polycondensation of *N*-Phenylthiocarbonyl Derivatives of $\alpha$-Amino-Acids and Oligopeptides

Noguchi[101,102] showed that on heating *N*-phenylthiocarbonyl amino-acids to 150–160° thiophenol and carbon dioxide are split off with the formation of oligopeptides of relatively low molecular weight:



Apart from the polypeptides, the reaction products include 2,5-dioxopiperazine and other side-products. When the polycondensation is carried out in solution (frequently in the presence of pyridine), high-molecular-weight polypeptides with molecular weights up to more than 100 000 are formed.

Thermal polycondensation of *N*-phenylthiocarbonyl amino-acids can yield both homogeneous and mixed polypeptides of almost all nautral and basic amino-acids. The authors assumed the possibility that thiophenol may be split off as a result of the intermolecular reaction with subsequent removal of carbon dioxide from the anhydride and formation of the polypeptide chain:



Tables 9 and 10 list the polypeptides prepared by this method and some properties of the initial *N*-phenylthiocarbonyl amino-acids and polypeptides. The data in Tables 8 and 9 indicate the possibility of wide application of the method involving the polycondensation of *N*-phenylthiocarbonyl derivatives of amino-acids for the preparation of DL-polypeptides. When derivatives of dipeptides are used, the formation of polypeptides with a known sequence of amino-acid residues may be expected.

However, Weymouth[122] showed that this method has a number of disadvantages. When polyglycine is synthesised under the above conditions, considerable amounts of 2,5-dioxopiperazines (in excess of 20% of the total weight of products) are deposited on the walls of the vessel. Usually about 50% of the residue is soluble in water, and comparison of the viscosity of the solutions of these polymers with the viscosity of similar specimens of polyglycine, for which the end-groups have been determined, yields the molecular weight in the range 1000–2500. Noguchi and coworkers[104] found the molecular weight of polyglycine of similar viscosity to be 135 000.

Having checked Noguchi's data using the polycondensation of phenylthiocarbonylalanine and sarcosine, the author concludes that the polycondensation of *N*-phenylthiocarbonyl amino-acids involves the formation of polypeptides of relatively low molecular weight. Furthermore there is no proof that these polymers are purely linear polypeptides.

The polycondensation of other *N*-substituted amino-acids has been described, i.e. the polycondensation of *N*-benzyloxycarbonyl[123] and phenoxycarbonyl[124] derivatives, including those with different substituents in the phenyl ring. Ishizuka and Saito[125] established that the most suitable medium for the polycondensation of phenoxycarbonyl amino-acid derivatives is nitrobenzene. In this case the time of polycondensation is greatly reduced and the polypeptide has a higher molecular weight (Table 11).

Ishizuka[126–128] carried out the polycondensation of *N*-*o*-nitrophenoxycarbonyl derivatives of amino-acids and dipeptides by this method and obtained polyleucine ($M$ = 14 000), poly-DL-phenylalanine ($M$ = 12 000), polyglycine ($M$ = 14 000), polyalanylglycine ($M$ = 28 500), polyglycylalanine [a previous line is repeated at this point in the Russian text instead of the conclusion of the sentence (Ed. of Translation)].

The polycondensation of *N*-*p*-methylphenoxycarbonyl amino-acids, in solution in a mixture of benzene and toluene, in a sealed tube at 60° for 1200 h yielded polyglycine ($M$ = 10 500), poly-DL-phenylalanine ($M$ = 17 600), poly-L-leucine ($M$ = 11 000), and poly-$\alpha$-aminobutyric acid ($M$ = 18 300). The molecular weights were determined osmometrically in dichloroacetic acid[129]. Polyleucine with an intrinsic viscosity of 0.28 was prepared by the polycondensation of *N*-phenoxycarbonyl-L-leucine in nitrobenzene at 125° for 20 h.[130]

Bruckner et al.[99] prepared a high-molecular-weight polypeptide from the $\alpha\gamma$-dimethyl ester of benzyloxycarbonyl-$\gamma$-L-glutamyl-L-glutamic acid. The initial dipeptide was treated with ethyl chloroformate in the presence of triethylamine. After the hydrogenolysis of the benzyloxycarbonyl group over a palladium catalyst, the catalyst was filtered off and the solution of the mixed anhydride of the dipeptide was divided into two parts. The first part was allowed to stand for 24 h at room temperature, after which the solvent was distilled off in a vacuum and the residue was further heated for 1 h also in a vacuum. The

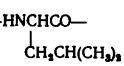
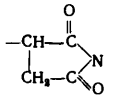
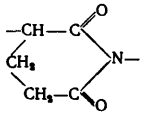
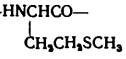
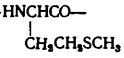
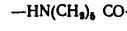
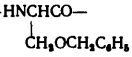
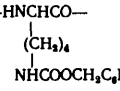
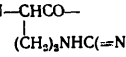
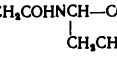
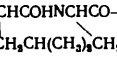
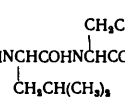
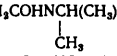
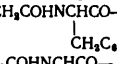
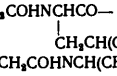
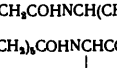
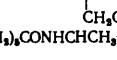
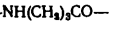
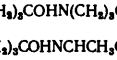
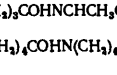
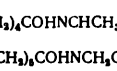
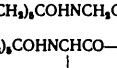
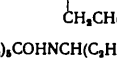
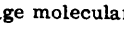
TABLE 9. Properties of *N*-phenylthiocarbonylamino-acids and their esters ($C_6H_5S-\overset{\overset{O}{\|}}{C}-HN-\underset{\underset{R}{|}}{CH}-COOH$ and $C_6H_5S-\overset{\overset{O}{\|}}{C}-HN-\underset{\underset{R}{|}}{CH}-COOR'$).

| *N*-Phenylthiocarbonylamino-acids | | | Esters of *N*-phenylthiocarbonylamino-acids | | |
|---|---|---|---|---|---|
| initial amino-acid | R | properties | R′ | properties | references |
| β-Alanine | H | m.p. 104° | $C_2H_5$ | m.p. 52° | 101 |
| DL-Phenylalanine | $C_6H_5CH_2$ | m.p. 56° | $C_2H_5$ | m.p. 63–65° | 101 |
| L-Phenylalanine | $C_6H_5CH_2$ | m.p. 66°, $[\alpha]_D^{17}$ 12.5° | $C_2H_5$ | m.p. 55–56°, $[\alpha]_D^{18}$ 14.3° ($C_2H_5OH$) | 121 |
| DL-Valine | $(CH_3)_2CH$ | m.p. 121° | $C_2H_5$ | m.p. 54° | 121 |
| L-Valine | $(CH_3)_2CH$ | m.p. 115°, $[\alpha]_D^{17}$ 6.0° ($C_2H_5OH$) | $C_2H_5$ | m.p. 60°, $[\alpha]_D^{18}$ 42.9° ($C_2H_5OH$) | 121 |
| L-Leucine | $(CH_3)_2CHCH_2$ | | $C_2H_5$ | oil | 101 |
| DL-Methionine | $CH_3SCH_2CH_2$ | m.p. 99° | $C_2H_5$ | oil | 121 |
| L-Methionine | $CH_3SCH_2CH_2$ | m.p. 65°, $[\alpha]_D^{18}$ 8.9° ($C_2H_5OH$) | $C_2H_5$ | m.p. 53°, $[\alpha]_D^{18}$ 38.1° ($C_2H_5OH$) | 121 |
| *O*-Benzyl-DL-serine | $C_6H_5CH_2OCH_2$ | – | $CH_3$ | m.p. 73–74° | 116 |
| ξ-*N*-Benzyloxycarbonyl--DL-lysine | $C_6H_5CH_2OCOHN(CH_2)_4$ | m.p. 116–118° | $C_2H_5$ | m.p. 174–175° | 110 |
| L-Nitroarginine | – | m.p. 134–136° | $C_2H_5$ | m.p. 59–60°, $[\alpha]_D^{15}$ 9.4° | 118 |
| L-Aspartic acid | $HOOCCH_2$ | m.p. 100–102° | | – | 119 |
| γ-Aminobutyric acid | – | m.p. 110–111° | $C_2H_5$ | oil | 113 |
| δ-Aminovaleric acid | – | m.p. 125° | $C_2H_5$ | | 114 |
| ξ-Aminohexanoic acid | – | m.p. 95° | | | 111 |
| Ditto | – | m.p. 97–98° | $C_2H_5$ | oil | 109 |
| DL-Alanylglycine | $CH_3$ | m.p. 136–137° | $C_2H_5$ | m.p. 119–120° | 121 |
| Glycyl-DL-alanine | $CH_3$ | m.p. 156° | $CH_3$ | m.p. 122–123° | 107 |
| Ditto | | – | $C_2H_5$ | m.p. 109–110° | 107 |
| L-Leucyl-L-alanine | $(CH_3)_2CHCH_2$ and $CH_3$ | m.p. 147–148° $[\alpha]_D^{27}$ 30.8° ($C_2H_5OH$ 1.95 g/100 ml) | | m.p. 105–106° $[\alpha]_D^{27}$ 39.8° ($C_2H_5OH$ 2.23 g/100 ml) | 111 |
| Glycyl-DL-phenyl-alanine | $C_6H_5CH_2$ | m.p. 178–179° | $C_2H_5$ | m.p. 107–108° | 107 |
| Glycyl-L-leucine | $(CH_3)_2CHCH_2$ | m.p. 155°, $[\alpha]_D^{26}$ 15.0° ($C_2H_5OH$) | $C_2H_5$ | oil | 107 |
| β-Alanyl-DL-alanine | $CH_3$ | m.p. 146.5° | $CH_3$ | m.p. 112–113° | 108 |
| γ-Aminobutyryl-DL--alanine | $CH_3$ | m.p. 113° | $CH_3$ | m.p. 95° | 113 |
| ε-Aminohexanoyl-L--phenylalanine | $C_6H_5CH_2$ | m.p. 130–131°, $[\alpha]_D^{27}$ 24.1° ($C_2H_5OH$) | $C_2H_5$ | oil | 109 |
| ε-Aminohexanoyl-DL--alanine | $CH_3$ | m.p. 133–134° | $CH_3$ | m.p. 80–82° | 110 |
| γ-Aminobutyryl-γ--aminobutyric acid | | m.p. 146° | $C_2H_5$ | m.p. 127° | 113 |
| δ-Aminovaleryl-δ--aminovaleric acid | | m.p. 152–153° | $C_2H_5$ | m.p. 97–98° | 114 |
| δ-Aminovaleryl-DL--alanine | $CH_3$ | m.p. 155° | $CH_3$ | m.p. 115° | 114 |
| ε-Aminohexanoyl-glycine | | m.p. 151° | $C_2H_5$ | m.p. 105° | 115 |
| ε-Aminohexanoyl-L--leucine | $(CH_3)_2CHCH_2$ | oil, $[\alpha]_D^{18}$ 20.4° ($CH_3COOH$) | $C_2H_5$ | oil | 115 |
| ε-Aminohexanoyl-α--aminobutyric acid | $C_2H_5$ | m.p. 137° | $C_2H_5$ | m.p. 89° | 115 |

TABLE 10. Properties of polypeptides prepared by the thermal polycondensation of *N*-phenylthiocarbonylamino--acids [$C_6H_5SCOHNCH(R)COOH$].

| Initial amino-acid | Formula of the structural unit of polypeptide | Conditions of preparation of polypeptide | Properties of polypeptide | References |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| Glycine | $-HNCH_2CO-$ | in benzene with pyridine, 150 h at 80° | $M_W$* = 135 200, yield 91% | 104 |
| DL-Alanine | $-HNCH(CH_3)CO-$ | in benzene with pyridine, 1000 h at 60° | $M_W$ = 22 400, yield 69.6% | 105 |
| β-Alanine | $-HNCH_2CH_2CO-$ | in benzene with pyridine, 1000 h at 60° | $M_W$ = 37 300, yield 38.2% | 108 |
| » | $-HNCH_2CH_2CO-$ | 20 h in the melt at 120° and 3 h at 165° in a vacuum | $M_W$ = 43 500, yield 93.5%, readily adsorbs $FeCl_3$ in HCOOH | 108 |
| DL-Phenylalanine | $-HNCH(CH_2C_6H_5)CO-$ | in benzene with pyridine, 200 h at 80° | $M_W$ = 59 400, yield 38% | 103 |
| L-Phenylalanine | $-HNCH(CH_2C_6H_5)CO-$ | in dioxan, 1000 h at 60–70° | $M_W$ = 16 800, $[\alpha]_D^{18}$ 24.4°($ClCH_2COOH$) | 121 |
| DL-Valine | $-HNCH(CH(CH_3)_2)CO-$ | ditto | $M_W$ = 17 600 | 121 |
| L-Valine | $-HNCH(CH(CH_3)_2)CO-$ | » | $M_W$ = 12 300, $[\alpha]_D^{18}$ 29.3°($ClCH_2COOH$) | 121 |

TABLE 10 (contd.)

| Initial amino-acid | Formula of the structural unit of polypeptide | Conditions of preparation of polypeptide | Properties of polypeptide | References |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| L-Leucine |  | in benzene, 670 h at 80° | $M_W$ = 26 889, yield 63% | 106 |
| L-Aspartic |  | in the melt at 140°, 30 h in a vacuum | $M_W$ = 1500, yield 71% | 119 |
| L-Glutamic acid |  | in the melt at 180°, 20 h in a vacuum | $M_W$ = 2100 | 120 |
| DL-Methionine |  | in dioxan, 1000 h at 60–70° | $M_W$ = 10500, yield 38.7% | 121 |
| L-Methionine |  | ditto | $M_W$ = 23 700, $[\alpha]_D^{19}$ + 2.6° ($ClCH_2COOH$) | 121 |
| ξ-Aminohexanoic acid |  | 23 h in the melt at 130° followed by vacuum treatment at 160° | $M_W$ = 26 000, yield 77%, $[\eta]$ = 0.194 in 1 : 1 $CH_3COOH$ + $ClCH_2COOH$ | 109 |
| *O*-Benzylserine |  | in benzene with pyridine, 150 h at 70° | $M_W$ = 4900–5300, m.p. 185–190°, readily debenzylated by HBr in dioxan to poly-DL-serine | 116 |
| ε-*N*-Benzyloxycarbonyl--DL-lysine |  | in benzene with pyridine, 400 h at 70° | $M_W$ = 4000, yield 48% | 117 |
| L-Nitroarginine |  | in dioxan with pyridine, 16 days at 70° | $M_W$ = 1040, $[\alpha]_D^{13}$ – 14.1° | 118 |
| Glycine + L-leucine |  | in dioxan with pyridine, 1000 h at 60° | ~1 : 1 copolymer, $M_W$ = 11 457, yield 36% | 106 |
| L-Leucine + + DL-phenylalanine |  | in benzene, 1000 h at 60° | copolymer, $M_W$ = 16 000, yield 47.8% | 106 |
| L-Leucyl-L-alanine |  | in dioxan, 1500 h at 60–70° | $M_W$ = 14 300, yield 24.6% | 111 |
| Glycyl-DL-alanine |  | in dioxan with pyridine, 1000 h at 60° | $M_W$ = 34 813 | 107 |
| Glycyl-DL-phenyl-alanine |  | ditto | $M_W$ = 30 603 | 107 |
| Glycyl-L-leucine |  | » | $M_W$ = 38 000 | 107 |
| β-Alanyl-DL-alanine |  | 27 h in dioxan at 135° and 2 h at 150° in a vacuum | $M_W$ = 26 100, yield 52% | 108 |
| ε-Aminohexanoyl-L--phenylalanine |  | in dioxan, 30 h at 130–140° | copolymer, $M_W$ = 51 200, yield 79% | 109 |
| ε-Aminohexanoyl-DL--alanine |  | 27 h in dioxan at 135° and 2 h at 150° in a vacuum | copolymer, $M_W$ = 65 000, yield 82.8%; the copolymer undergoes reversible thermal denaturation, which is a maximum at 50°, heat of denaturation 45 kcal mole$^{-1}$ | 110, 112 |
| γ-Aminobutyric acid |  | in dioxan, 1.7 h at 70° | $M_W$ = 15 000 ($CH_3COOH$), m.p. 230°, yield 28.6% | 113 |
| γ-Aminobutyryl-γ--aminobutyric acid |  | in dioxan, 100 h at 140° | $M_W$ = 16 500 | 113 |
| γ-Aminobutyryl-DL--alanine |  | ditto | copolymer, $M_W$ = 71 500 | 113 |
| δ-Aminovaleryl-δ--aminovaleric acid |  | » | $M_W$ = 13 100, yield 69.5% | 114 |
| δ-Aminovaleryl-DL--alanine |  | » | copolymer, $M_W$ = 26 000 | 114 |
| ε-Aminohexanoyl-glycine |  | in dioxan, 100 h at 140° in an atmosphere of $CO_2$ | copolymer, $M_W$ = 19 300 | 115 |
| ε-Aminohexanoyl-leucine |  | ditto | copolymer, $M_W$ = 22 300, $[\eta]$ = 0.257 (30° in $CH_3COOH$), $[\alpha]_D^{18}$ = 32.7° ($CH_3COOH$) | 115 |
| ε-Aminohexanoyl-α--aminobutyric acid |  | » | copolymer, $M_W$ = 34 900, $[\eta]$ = 0.3 (30° in $CH_3COOH$), undergoes reversible thermal denaturation in aqueous solutions | 115 |

* $M_W$ is the weight-average molecular weight.

TABLE 11. Polycondensation of $XC_6H_4OCOHNCH(CH_3)$. .COOH.

| X | Medium | Temperature, °C | Time, h | Yield, % | Intrinsic viscosity* |
|---|---|---|---|---|---|
| H | pyridine–benzene | 80 | 10 000 | 83.4 | 0.134 |
| H | pyridine–toluene | 100 | 50 | 92.8 | 0.150 |
| H | nitrobenzene | 100 | 16 | 87.1 | 0.286 |
| H | » | 120 | 4.5 | 96.8 | 0.274 |
| H | » | 125 | 8 | 73.6 | 0.367 |
| o-$CH_3$ | » | 110 | 30 | 79.0 | 0.280 |
| p-$CH_3$ | » | 110 | 56.5 | 82.0 | 0.295 |
| o-$NO_2$ | pyridine–toluene | 100 | 8.0 | 85.3 | 0.113 |
| o-$NO_2$ | nitrobenzene | 100 | 12.0 | 62.7 | 0.119 |
| p-$NO_2$ | pyridine–toluene | 100 | 36 0 | 57.4 | 0.155 |
| p-$NO_2$ | nitrobenzene | 100 | 12.0 | 38.4 | 0.203 |

* The viscosity of 0.2% solution in 80% dichloroacetic acid was determined.

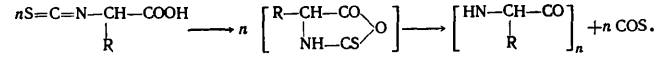
second half of the solution was treated similarly after the addition of triethylamine. In order to isolate the free polymeric acid, the polypeptides were treated in the cold with alkali and purified via the copper salt with subsequent dialysis. The molecular weight of the polypeptide obtained without triethylamine was 12 180 and that obtained with triethylamine was 20 000.

The polypeptides very tenaciously retain water and after drying in a vacuum over phosphorus pentoxide at room temperature contain one molecule of water per glutamic acid residue. Both products were colourless powders, readily soluble in water and gave positive biuret reactions and a weak ninhydrin reaction.

The amino-group can also be activated by treating amino--acids with isocyanates. The resulting amide of the alkanecarbamic acid, with the general formula

RNHCONHCRHCOOH,

where R = t-alkyl, breaks down at a temperature above 175° with the formation of a polypeptide in more than 80% yield. The degree of polycondensation of polypeptides prepared in this way reaches 100.[131] An interesting synthesis of polypeptides is by the polycondensation of the isothiocyanates of aliphatic carboxylic acids, prepared by treating α-amino-acids with carbon disulphide and then decomposing the dithiocarbamic derivatives with mercuric chloride[132]. However, in this case it is assumed that heating of the isothiocyanate leads to the formation of the anhydride of the *N*-thiocarboxy-acid and its polymerisation and not the removal of the substituent from the nitrogen atom:



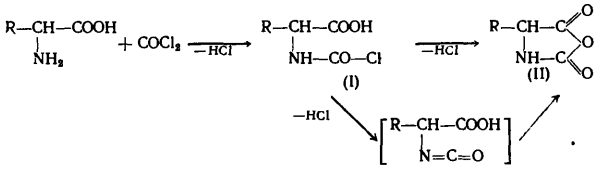
## IV. SYNTHESIS OF POLYPEPTIDES BY THE POLYMERISATION OF THE ANHYDRIDES OF *N*-CARBOXY--α-AMINO-ACIDS

### 1. Synthesis of the Anhydrides of *N*-Carboxy-α-amino--Acids

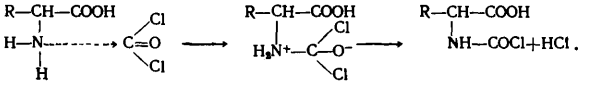
The most usual synthesis of polypeptides is by the polymerisation of the anhydrides of *N*-carboxy-α-amino-acids, which permit the preparation of polymers with a specified molecular weight, capable of being varied over a very wide range, with complete elimination of the racemisation of the amino-acids.

The most widely used procedure for the preparation of the cyclic anhydrides of *N*-carboxy-α-amino-acids is that proposed by Fuchs[133], Farthing[134], and Levy[135]. Finely ground amino-acids, their chlorides, or sodium salts, suspended in an inert solvent (dioxan, ethyl acetate) are treated with phosgene at 30–50°. The reaction may be carried out with simultaneous addition of equivalent amounts of a solution of phosgene in dioxan and a suspension of the amino-acid in dioxan to an excess of the solvent[136]. The anhydrides of the *N*-carboxy-acids and their thio-analogues are also obtained on heating the chlorides of amino-acids with $COCl_2$ or $CSCl_2$ in nitrobenzene[137].

The reaction of α-amino-acids with phosgene proceeds as follows:



The first stage, the formation of the carbamoyl chloride (I) begins with the nucleophilic attack by the amino-nitrogen on the carbonyl carbon in phosgene:

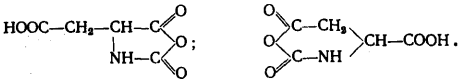


The rate of this process should increase with increase in the electron-donor effect of the R group in the amino-acid, which enhances the basicity of the amino-group. This hypothesis agrees satisfactorily with the observed increase in the rate of reaction with phosgene in the series glycine < alanine < < α-aminobutyric acid ≃ phenylalanine < norleucine < < leucine < isoleucine < pseudoleucine (*C*-t-butylglycine), where the substituent R varies from H to $(CH_3)_3C-$.[138,139]

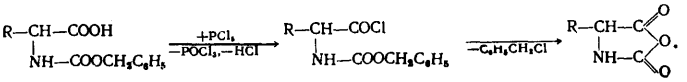
Preliminary saturation of dioxan with sulphur dioxide[140] and also the addition of small amounts of acetic anhydride increase the rate of reaction with phosgene, while impurities may retard it to a large extent[138].

The stage of the cyclisation of the carbamoyl chloride (I) to the anhydride (II) of the *N*-carboxy-α-amino-acid occurs spontaneously and only in the case of proline and its derivatives, where the closure of the second ring involves considerable stresses in the molecule, is additional treatment of the carbamoyl chloride with triethylamine[141] or silver oxide[142,143] necessary.

In the synthesis of the anhydrides of trifunctional *N*-carboxy-α-amino-acids it is necessary to protect the functional groups capable of reacting with phosgene[144]. In the absence of protection aspartic acid gives a mixture of five- and six-membered anhydrides of the *N*-carboxy--acid[145]:



The anhydrides of *N*-carboxy-α-amino-acid are also obtained by treatment of *N*-alkoxycarbonyl- and particularly *N*-benzyloxycarbonyl-α-amino-acids with thionyl chloride, phosphorus pentachloride, or phosphorus tribromide:

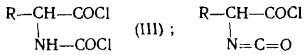
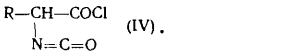


This method[3] is usually employed for β-amino-acids, the *N*-carboxy-derivatives of which yield six-membered anhydrides capable of polymerising[148].

An interesting method of preparation of the anhydrides of the *N*-carboxy-derivatives of various amino-acids[149,150] involves the reaction of thionyl chloride or phosgene with the disodium salt of the *N*-carboxy-amino-acid which is readily obtained from sodium carbonate and the amino-acid or by the simultaneous treatment of the amino-acid with sodium methoxide and carbon dioxide[134,147,148].

The synthesis of the anhydrides of *N*-carboxy-α-amino--acids from the malonic ester[151,152] is suitable only for the preparation of racemic products and has not been used in recent years.

High-molecular-weight polypeptides can be synthesised only from thoroughly purified anhydrides of *N*-carboxy-α--amino-acids which in their synthesis by the reaction of phosgene with α-amino-acids are usually contaminated with the dichloride (III) of the *N*-carboxy-α-amino-acid and the isocyanate (IV) formed from it:

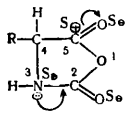

(III);

(IV).

However, the impurities are readily removed on recrystallisation[153] or sublimation in a high vacuum. The removal of chlorine-containing impurities by treating a solution of the anhydride of the *N*-carboxy-α-amino-acid in ethyl acetate with the copolymer of ethyl β-(formyl-*N*-methylamino)-acrylate and divinylbenzene has been described[154]. The anhydrides of *N*-carboxy-α-amino-acids are kept at a temperature not exceeding -30°. The anhydrides of *N*-carboxy--α-amino-acids whose synthesis has been described in recent years are listed in Table 12.

The anhydrides of *N*-carboxy-α-amino-acids are determined quantitatively by titration in a non-aqueous medium with sodium methoxide[155,156] or by the determination of the carbon dioxide evolved on their acid hydrolysis[157,158]; the carbon dioxide is absorbed by an ethanol–dioxan solution of benzylamine to form the benzylammonium salt of toluene--ω-carbamic acid, and then titrated with a solution of sodium methoxide using Thymol Blue as the indicator.

## 2. Chemical Properties of the Anhydrides of *N*-Carboxy--α-amino-Acids

The anhydrides of *N*-carboxy-α-amino-acids are extremely reactive. They have the structure of 2,5-dioxo-oxazolidine substituted in position 4.



The electronegativity of the oxygen atom gives rise to partial positive charges on carbon atom 5 and the nitrogen atom which results in a weakening of the N–H bond and great enhancement of the reactivity of the carbonyl carbon atom 5 towards nucleophilic reagents compared with carbon atom 2. Indeed, nucleophilic addition to the carbonyl carbon atom 5 and reactions involving the participation of the N–H group are the most characteristic reactions of the anhydrides of *N*-carboxy-α-amino-acids.

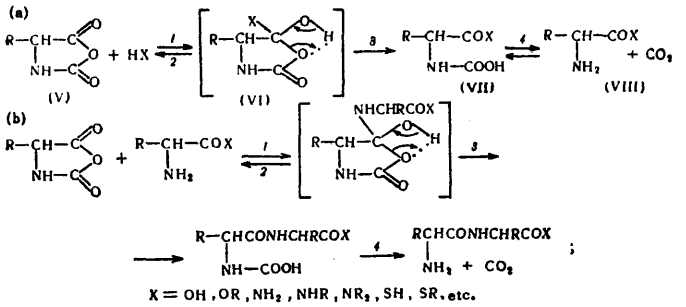
TABLE 12. Synthesis of the anhydrides of *N*-carboxy-α-amino--acids not included in the monograph of Bamford et al.[4] and the review of Katchalski and Sela[5].

| Initial α-amino-acid | Method of preparation | Method of purification | M.p., °C | References |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| Glycine | phosgene treatment | | | 138,140 |
| » | Na salt of *N*-carboxy-glycine + $SOCl_2$ | sublimation | | 150 |
| Sarcosine | Na salt of *N*-carboxy-sarcosine + $SOCl_2$ | » | | 150 |
| DL-*C*-Phenylglycine | Na salt of *N*-carboxy-phenylglycine + + $SOCl_2$ | » | | 150 |
| DL-*C*-(*p*-Nitrophenyl)-glycine | phosgene treatment | ethyl acetate | 135 | 150 |
| DL-*C*-Propargylglycine | ditto | tetrahydrofuran–petroleum ether | 125–127 | 299 |
| DL-Alanine | » | | 42–44 | 138,140 |
| Dehydroalanine | *N*-benzyloxycarbonyl-dehydroalanine + $PCl_5$ | ethyl acetate–petroleum ether, sublimation | 111–113 | 303 |
| DL-Phenylalanine | phosgene treatment | | 126 | 138,279 |
| » | Na salt of *N*-carboxy-phenylalanine + + $SOCl_2$ | sublimation | | 150 |
| » | *N*-benzyloxycarbonyl-phenylalanine + $PCl_5$ | ether | 123–125 (decomp.) | 173 |
| DL-α-Aminobutyric acid | phosgene treatment | | 112–113 | 138 |
| DL-Valine | ditto | | | 140 |
| » | *N*-benzyloxycarbonyl-valine + $PCl_5$ | ether | 80–81 (decomp.) | 173 |
| DL-Norvaline | *N*-benzyloxycarbonyl-norvaline + $PCl_5$ | ether | 67–69 (decomp.) | 173 |
| L-Leucine | phosgene treatment | | | 138 |
| DL-Leucine | *N*-benxyloxycarbonyl-leucine + $PCl_5$ | ether | 48–50 | 173 |
| DL-Norleucine | *N*-benzyloxycarbonyl-norleucine + $PCl_5$ | ether | 78–80 | 173 |
| » | phosgene treatment | | 79 | 138 |
| DL-Isoleucine | ditto | | 70–71 | 138 |
| DL-Pseudoleucine | » | | 120 | 138 |
| L-Proline | phosgene treatment, with $(C_2H_5)_3N$ | ethyl acetate or sublimation | 45 | 141 |
| DL-Serine | phosgene treatment | ethyl acetate–hexane | 82–83 | 286 |
| » | ditto | benzene | 115 (decomp.) | 286 |
| *O*-Acetyl-DL-serine | » | ethyl acetate–hexane | 62.5–63.5 (decomp.) | 286 |
| *O*-Acetyl-L-serine | » | ditto | 50–51 | 286 |
| *O*-Benzyl-L-serine | » | ether–petroleum ether | 72 (decomp.) | 301 |
| *O*-Benzyl-L-tyrosine | » | | 142 (decomp.) | 308 |
| *O*-Benzyloxycarbonyl--L-tyrosine | » | | | 140 |
| *O*-Phenyl-DL--homoserine | » | ethyl acetate–petroleum ether | 105–106 | 310 |
| » | *N*-benzyloxycarbonyl--*O*-phenylhomoserine + + $PCl_5$ | ditto | 105 | 310 |
| ε-*N*-Benzyloxycarbonyl--L-lysine | phosgene treatment | ethyl acetate–hexane | 101–101.5 | 281 |
| » | ditto | | 98.5–99.5 | 140 |
| ε-*N*-Benzyloxycarbonyl--DL-lysine | » | | 100 | 305 |
| δ-*N*-Benzyloxycarbonyl--L-ornithine | » | | 86 | 307 |
| β-Benzyl L-aspartate | » | dichloroethane | 126 | 297 |
| Ditto | » | ethyl acetate–hexane | 127–128 | 144 |
| » | β-benzyl *N*-benzyl-oxycarbonylaspartate + + $PCl_5$ | ditto | 127–128 | 144 |
| β-Benzyl DL-aspartate | phosgene treatment of dibenzyl ester | » | 126–127.5 | 144 |
| β-*p*-Nitrobenzyl L-aspartate | phosgene treatment | | | 302 |
| β-Peptido-DL-aspartic acid | ditto | | | 300 |
| γ-Ethyl L-glutamate | γ-ethyl *N*-benzyloxy-carbonylglutamate + + $SOCl_2$ | ethyl acetate | | 182 |

TABLE 12 (contd.)

| Initial α-amino-acid | Method of preparation | Method of purification | M.p., °C | References |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| δ-Methyl DL-α-amino-adipate | phosgene treatment | chloroform–petroleum ether | 94–95 | 309 |
| DL-Methionine | ditto | | | 138 |
| *S*-Methyl-L-cysteine | » | ethyl acetate–petroleum ether | 74 | 311 |
| *S*-Ethyl-L-cysteine | » | | 69 | 311 |
| *S*-Propyl-L-cysteine | » | | | 311 |
| *S*-Isopropyl-L-cysteine | » | | | 311 |
| *S*-Butyl-L-cysteine | » | ethyl acetate–petroleum ether | 55–56 | 311 |
| *S*-Pentyl-L-cysteine | » | | | 311 |
| *S*-Hexyl-L-cysteine | » | ether–petroleum ether | 42–43 | 311 |
| *S*-(α-Methylnaphthyl)-L-cysteine | » | ethyl acetate–petroleum ether | 105 | 311 |
| *S*-Dodecyl-L-cysteine | » | ditto | 66–67 | 311 |
| *S*-Benzyl-L-cysteine | » | | | 298 |
| *S*-Phenyl-L-cysteine | » | | | 298 |
| *S*-*p*-Tolyl-L-cysteine | » | | | 298 |
| *S*-Phenylthio-L-cysteine | » | ethyl acetate–petroleum ether | 117–119 | 304 |
| γ-Benzyl ester of *S*-carboxy-L-cysteine | » | | | 306 |
| δ-Benzyl ester of *S*-methoxycarbonyl-L-cysteine | » | | 109 | 306 |
| ε-Benzyl ester of *S*-ethoxycarbonyl-L-cysteine | » | | | 306 |
| Mono-*N*-Benzyloxy-carbonyl-L-cysteine | » | ether–petroleum ether | 30–32 | 312 |
| Monoethyl ester of *N*-acetyllanthionine | » | | | 312 |
| Benzyl ester of *N*-benzyloxycarbonyl-lanthionine | » | | | 312 |
| *S*-Benzyloxycarbonyl-DL-homocysteine | » | ether–petroleum ether | 75–76 | 313 |
| *S*-Benzyl-DL-homocysteine | » | ditto | 95–96 | 313 |
| *S*-Benzylhomo-DL-cysteine | » | » | 57 | 313 |
| *S*-Ethyl-DL-homocysteine | » | | | 313 |
| *S*-Propyl-DL-homocysteine | » | | | 313 |
| *S*-Butyl-DL-homocysteine | » | | | 313 |
| *S*-Allyl-DL-homocysteine | » | | | 313 |

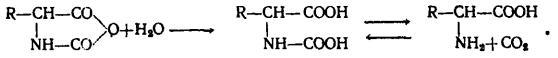
The reaction with nucleophilic reagents HX usually proceeds as follows:



X = OH, OR, $NH_2$, NHR, $NR_2$, SH, SR, etc.

Compound (VIII) has a free amino-group and may react with another molecule of the anhydride like any nucleophilic reagent. Therefore in the presence of a large excess of the anhydride of the *N*-carboxy-α-amino-acid this reaction results in the formation of a polypeptide. In the presence of an excess of HX only compounds of the type of (VIII) are formed.

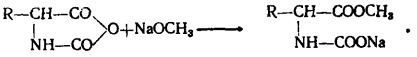
In the reaction with water, in which many anhydrides of *N*-carboxy-α-amino-acids are quite soluble, the following equilibrium is established at low temperatures [3,159-162]:



It has been shown that the decomposition of the anhydrides of *N*-carboxy-α-amino-acid is catalysed by bases and acids [163].

Hydrogen sulphide, alcohols, phenols, and mercaptans react in the presence of triethylamine [164,165] similarly to water with the formation of α-amino-thioacids, esters, and thioesters.

Anhydrous hydrogen chloride in an inert medium reacts with the anhydrides of *N*-carboxy-α-amino-acids to yield the hydrochlorides of the amino-acid chlorides [166,167] while in alcoholic medium it accelerates alcoholysis, a fact which has been used for the preparation of the esters of various α-amino-acids [168-172]. Alcoholysis is also accelerated by alkoxides, a finding on which the titration of the anhydrides of *N*-carboxy-α-amino-acids with sodium methoxide is based [155]:



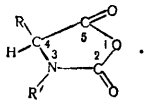
Since primary and secondary amines are nucleophilic agents, they react with the anhydrides of *N*-carboxy-α--amino-acids according to mechanism (a) given above with the formation of peptides and amino-acid amides [133,173-177]. The thio-analogues of the anhydrides of *N*-carboxy-α--amino-acids are capable of the formation of a number of other products [178].

The rate of reaction with nucleophilic reagents decreases with decreasing basicity in the following order: $CH_3O^-$, $OH^-$, $RNH_2$, $ArNH_2$, ROH, $H_2O$. In the reaction with the last three members of the series the free amino-group formed after their addition is more nucleophilic and readily reacts with the free molecules of the anhydrides of *N*-carboxy-α--amino-acids according to mechanism (b) with the formation of oligomers and polymers even in the presence of an excess of the above reagents [175].

The rate of reaction depends also on the nature of the *N*-carboxy-α-amino-acid anhydride and is greater the greater the partial positive charge on the carbonyl carbon atom 5 and the lower the steric hindrance for the attacking nucleophilic agent. For this reason, the reactivity and the rate of polymerisation of the anhydride diminish with increase in the electron-donor effect and particularly with increase in the size of the substituent R, in the following series: glycine, alanine, α-aminobutyric acid, phenylalanine, norleucine, leucine, isoleucine, pseudoleucine, and α-methylalanine [138,139,179].

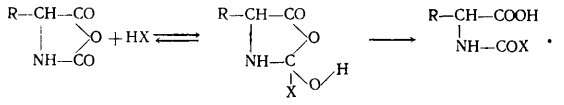
The considerable influence of steric factors on the rate of reaction of the anhydrides of *N*-carboxy-α-amino-acids with primary and secondary amines has been demonstrated by Ballard and Bamford [179]. The usual five-membered ring of the *N*-carboxy-α-amino-acid anhydride, which incorporates nitrogen, oxygen, and two trigonal carbon atoms, is planar and unstrained, the substituent R lying to one side or another of the molecule depending on the asymmetry of carbon atom 4. In the case of *N*- substituted

anhydrides the substituent R′ at the nitrogen is located in the *trans*-position relative to R.



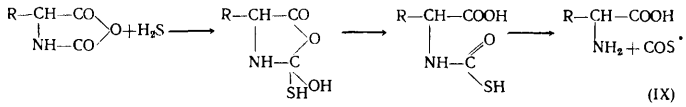
The attacking reagent approaches the carbon atom 5 from the side opposite to that of the carbonyl oxygen along the line passing at a small angle to the plane of the ring in the immediate vicinity of the nitrogen atom. The presence of the substituents R and R′ gives rise to considerable steric hindrance to attack from both sides of the ring, particularly in the case of bulky nucleophilic agents such as secondary amines, and sharply reduces the rate of reaction. In the anhydrides of *N*-carboxyproline and its derivatives both substituents lie on one side of the plane of the ring, which is responsible for the enhanced rate of their reaction with secondary amines.

Similarly, the second carbonyl group can also react with nucleophilic agents: with the formation of urethanes, thiourethanes, and urea derivatives in the case of alcohols, mercaptans, and amines respectively.



However, by virtue of the smaller positive charge of carbon atom 2 the activation energy for this reaction is much higher and it becomes important only at high temperatures and concentration, and when the reactivity of the nucleophilic reagent is high; steric factors can also have an appreciable effect.

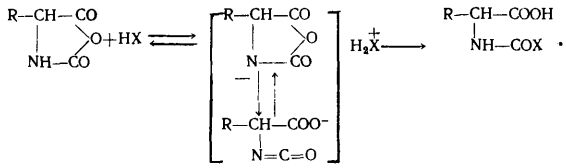
The addition to the carbonyl carbon atom 2 is usually referred to as "erroneous", leading to the disappearance of the amino-group at the end of the growing chain and termination of the polymerisation. The possibility of this reaction was confirmed by Berger et al.[155], who observed the formation of urethane in the reaction of the anhydride of *N*-carboxyphenylalanine with a solution of sodium methoxide. Wieland and Euler[165] allowed the anhydrides of *N*-carboxy-α-amino-acids to react with dry hydrogen sulphide in the presence of triethylamine and obtained α-aminothio-acids, which were always contaminated with α-amino-acids, whose formation can be explained by the decomposition of the corresponding thiocarbamic acids (IX):



(IX)

In the presence of a large excess of amines the addition to carbon atom 2 can occur to a considerable extent[180,181] but the amount of the product of the normal addition rapidly increases when the concentration and basicity of the amine are reduced[180].

However, the anhydride of *N*-carboxysarcosine combines even with nucleophilic agents as powerful as methoxide ions only at carbonyl carbon atom 5.[181] Possibly, the formation of compounds of the type RCH(COOH)NHCOX requires a hydrogen atom linked to the nitrogen atom. In this case nucleophilic attack can occur not only at the carbonyl carbon atom 2 but also at the hydrogen atom, with formation of carbamic acid derivatives via the isocyanate stage[165,181]:



The increase of the affinity of the base HX for a proton should favour this reaction, which agrees with experimental findings[181,182].

The active role of the NH group is particularly evident in the reaction of the anhydrides of *N*-carboxy-α-amino--acids with Grignard reagents[183]. In the *N*-substituted *N*-carboxy-α-amino-acid anhydrides the carbonyl group in position 2 does not react with RMgX and the anhydride of *N*-carboxy-*N*-phenylglycine gives only the following compounds:

$$C_6H_5NHCH_2—COOR,\quad C_6H_5NHCH_2—C(OH)R_2\ (R=CH_3,\ C_2H_5,\ C_6H_5).$$

At the same time the anhydride of *N*-carboxyphenylalanine forms under the same conditions *N*-acylated amino-ketones and amino-alcohols:

$$C_6H_5CH_2CH(COR)NHCOR\quad C_6H_5CH_2CH(NHCOR)C(OH)R_2.\ (R=C_2H_5,\ C_6H_5)$$

Among other reactions of the anhydrides of *N*-carboxy--α-amino-acids unrelated to their polymerisation, their reduction with lithium aluminium hydride[184] and their application in the Friedel–Crafts synthesis have been described[185,186].

## 3. Polymerisation of the Anhydrides of *N*-Carboxy-α--amino-Acids†

The anhydrides of *N*-carboxy-α-amino-acids readily polymerise both in the solid and in solution. The molecular weight and the polydispersity of the polypeptides formed are determined by the nature of the initiator and the polymerisation conditions. Solid polymerisation is usually carried out at elevated temperatures and low-molecular--weight products are obtained. Inert solvents are used for polymerisation in solution, which is carried out at low temperatures, the initiators being amines, alkoxides, alkalis, or water. The initiators and inhibitors of radical type polymerisation do not have any influence on the polymerisation of the anhydrides of *N*-carboxy-α-amino-acids[187,188]. Primary and secondary amines yield polymers with the degree of polymerisation up to 200, depending on the amount of amine.

Using excess amounts of amino-acid esters in the reaction with the anhydrides of *N*-carboxy-α-amino-acids, it is possible to obtain dipeptides[175,189,190]. However, in this case it is difficult to avoid the formation of higher

† It should be noted that the polymerisation of the anhydrides of *N*-carboxy-α-amino-acids differs considerably from the classical example of polymerisation and polycondensation. A better name for it would be polyaddition with subsequent removal of some of the molecules.

oligopeptides [191] and urea derivatives [192]. At low temperatures (-40°) in the presence of triethylamine, which stabilises by salt formation the carbamic acid (VII) formed in the first addition reaction, it proved possible to synthesise di- and tri-peptides in good yields [193-198]. The use of the thio-analogues of the anhydrides of *N*-carboxy-α-amino-acids is also promising for stepwise polypeptide synthesis of this kind [178].

Polypeptides of the highest molecular weight are obtained in the polymerisation of the anhydrides of *N*-carboxy-α-amino-acids in the presence of tertiary amines, alkoxides, and alkali metal hydroxides. However, the reproducibility of the results and the molecular weight of the polypeptides depend also on the purity of the initial compounds and solvents. Impurities, for example chloride ions at concentrations of about 0.01%, can completely vitiate the results of the experiment [199].

Because it is impossible to determine the impurities at such concentrations by the usual methods, it is recommended that the purity of the anhydrides of *N*-carboxy-α-amino-acids be checked by their polymerisation under standard conditions. Thus Idelson and Blout [200] regarded the anhydride of γ-benzyl *N*-carboxy-L-glutamate to be pure if at room temperature in 4% dioxan solution it gave a polymer with a molecular weight not less than 360 000, using sodium methoxide as the initiator with $[I_0]/[M_0] = 1:200$ (see below).

The polymerisation of the anhydrides of *N*-carboxy-α-amino-acids is inhibited by a large number of compounds: boric and dichloroacetic acids [201], hydrogen chloride [202], aldehydes [203,204], phenyl isocyanate, acetic anhydride, etc. Acids inhibit the reaction [205], even if it is initiated by inorganic salts [206,207]. Acetyl chloride, thionyl chloride, aluminium chloride, etc. fully inhibit the polymerisation of the anhydride of *N*-carboxyglycine when present in concentrations up to 0.2 mole %. [208]

The polypeptides obtained under different conditions by the polymerisation of the anhydrides of *N*-carboxy-α-amino-acids, and some of their properties, are listed in Table 13.

A. Polymerisation in the solid form. The anhydrides of *N*-carboxy-α-amino-acids are stable only at temperatures below -30°. At room temperature under the influence of atmospheric moisture the anhydrides of the *N*-carboxy-derivatives of glycine [3,174,210], L-alanine [211], L-leucine [209,211], *C*-phenylglycine, and phenylalanine [209] are converted into polymers. The rate of polymerisation is

TABLE 13. Preparation of polypeptides by the polymerisation of the anhydrides of the *N*-carboxy-derivatives of α-amino-acids (examples not included in the monograph of Bamford et al. [4] and the review of Katchalski and Sela [5]).

| Anhydride of *N*-carboxy-derivative of | Solvent | Initiator | Mol. weight of polypeptide | Removal of protecting groups | References |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| Glycine | dioxan | *p*-bromoaniline | | | 227 |
| » | » | water | | | 138 |
| DL-*C*-Propargylglycine | nitrobenzene | ammonia | $n = 32$ | | 299 |
| DL-Alanine | | dodecylamine | | | 229 |
| » | dioxan | water | | | 138 |
| » | tetrahydrofuran | methanol, menthol, borneole, Al, Zn, Cd, Li compounds | | | 295 |
| L- and D-Alanine | benzene | tri-n-butylamine | | | 288 |
| Dehydroalanine | toluene, pyridine | triethylamine | | | 315 |
| DL-Phenylalanine | dioxan | water | | | 138 |
| » | » | $NaOCH_3$ | ⩽140 000 | | 279 |
| » | chloroform | $NaOCH_3$ | ⩽120 000 | | 279 |
| » | chloroform, benzene | water | ⩽70 000 | | 279 |
| DL-α-Aminobutyric acid | dioxan | » | | | 138 |
| DL- and D-α-aminobutyric acid | nitrobenzene | benzylamine | | | 288 |
| DL- and L-Leucine | benzene | tri-n-butylamine | | | 288 |
| DL-Norleucine, DL-isoleucine, and DL-pseudoleucine | dioxan | water | | | 138 |
| L-Proline | pyridine | | | | 141 |
| » | acetonitrile | $NaOCH_3$ | 50 000–90 000 | | 316 |
| *O*-Acetoxy-L-proline | » | | | $NH_3$ or $NaOCH_3$ | 143 |
| L-Serine | nitrobenzene | $NaOCH_3$ | | | 286 |
| *O*-Acetyl-L-serine | » | triethylamine | | $NaOCH_3$ | 286 |
| *O*-Acetyl-DL-serine | » | $NaOCH_3$ | | $NaOCH_3$ | 286 |
| *O*-Benzyl-L-serine | chlorobenzene | $NaOCH_3$ | | HBr + dioxan | 301 |
| *O*-Benzyl-DL-serine | dioxan | triethylamine | $n = 28–30$ | ditto | 314 |
| *O*-Phenyl-DL-serine | | 100–135°, vacuum | | | 310 |
| *O*-Benzyl-L-tyrosine | dioxan | triethylamine | | $HBr + CH_3COOH$ | 308 |
| *O*-Benzyloxycarbonyl-L-tyrosine | benzene | water | | $HBr + CH_3COOH$ | 318 |
| ε-*N*-Benzyloxycarbonyl-L-lysine | » | » | | $HBr + CH_3COOH$ | 318 |
| » | dioxan | $NaOCH_3$ | 2 000 000 | dioxan + $CHCl_3$ + + HCl + HBr | 281 |
| ε-*N*-Benzyloxycarbonyl-DL-lysine | » | triethylamine | $n = 31–41$ | | 305 |

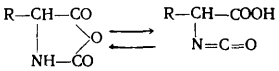
TABLE 13 (contd.)

| Anhydride of *N*-carboxy-derivative of | Solvent | Initiator | Mol. weight of polypeptide | Removal of protecting groups | References |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| δ-*N*-Benzyloxycarbonyl-L-ornithine | dioxan | | $n = 125$ | HCl + $CH_3COOH$ | 307 |
| β-Benzyl L-aspartate and D-aspartate | chloroform, methylene chloride, dichloroethane | $NaOCH_3$, benzylamine | 50000 | | 144, 296, 297 |
| β-*p*-Nitrobenzyl-L-aspartate | dimethylformamide | diethylamine | | | 302 |
| β-Peptido-DL-aspartate | | heating in a vacuum | | LiOH + $C_2H_5OH$ | 300 |
| γ-Methyl L-glutamate and D-glutamate | ethyl acetate | $NH_4OH$ | 13000 | NaOH + $Cu(OH)_2$ | 317 |
| γ-Methyl L-glutamate | chloroform | $CH_3COOH$ | $n = 500–600$ | | 292 |
| γ-Benzyl L-glutamate and D-glutamate | dioxan, benzene, dimethylformamide | $NaOCH_3$, NaOH, trimethylamine | 15000–100000 | | 288, 289 |
| δ-Methyl D-α-aminoadipate and L-α-aminoadipate | ethyl acetate | triethylamine | | | 309 |
| *S*-Methyl-L-cysteine | pyridine | | | | 311 |
| *S*-Ethyl-L-cysteine | pyridine, ethanol | | $n = 11–25$ | | 311 |
| » | | 130–140°, vacuum | $n = 53$ | | 311 |
| *S*-Propyl-, *S*-isopropyl-, *S*-butyl-, *S*-pentyl-, *S*-hexyl-, *S*-dodecyl-, and *S*-methylnaphthyl-L-cysteine | pyridine, dioxan, nitrobenzene, ethanol, acetic acid | heating with or without vacuum | | | 311 |
| *S*-Phenylthio-L-cysteine | ethyl thioglycolate | heating | | simultaneous removal of thiophenol | 304 |
| γ-, δ-, and ε-Benzyl esters of *S*-carboxy-, *S*-methoxycarbonyl-, and *S*-ethoxycarbonyl-L-cysteine | | heating in a vacuum | | | 306 |
| Mono-*N*-Benzyloxycarbonyl-L-cysteine | | ditto | | HBr + $CH_3COOH$ | 312 |
| *S*-Ethyl-, *S*-propyl-, *S*-butyl-, *S*-pentyl-, *S*-benzyl-, *S*-benzoyl-, and *S*-benzyloxycarbonyl-DL-homocysteine | dioxan, pyridine | triethylamine, heating in a vacuum | | | 313 |
| Monoethyl ester of *N*-acetyllanthionine | | heating in a vacuum | | | 312 |
| Monobenzyl ester of *N*-benzyloxycarbonyllanthionine | pyridine | ditto | | | 312 |

determined by the structure and the temperature. The mechanism of the polymerisation of crystalline anhydrides of *N*-carboxy-α-amino-acids initiated by atmospheric moisture is as yet unknown. The shape of the crystals remains unchanged during polymerisation and only X-ray diffraction analysis can detect the alterations in the crystal lattice [212]. Wessely and Siegmund [213] isolated from the polymerisation products of the anhydride of *N*-carboxysarcosine 4% of 1,4-dimethyl-2,5-dioxopiperazine in addition to 7% of polysarcosine.

In the molten state all the anhydrides of *N*-carboxy-α-amino-acids rapidly split off carbon dioxide and are converted into polymers with a relatively low degree of polymerisation [171,214–217].

The mechanism of thermal polymerisation is obscure. Possibly the α-isocyanatocarboxylic acid, capable of polymerising with subsequent removal of carbon dioxide, is an intermediate [218].



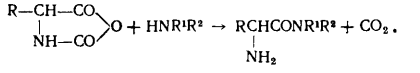
$$OCN—CHRCOOH + OCN—CHRCOOH \longrightarrow OCN—CHR—CO—O—CO—$$
$$—NHCHRCOOH \longrightarrow OCN—CHRCO—NHCHRCOOH + CO_2 .$$

The termination of the growing chain can occur as a result of the deactivation of the isocyanato-end-group.

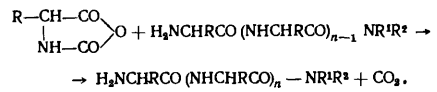
Heyns and Brockmann [219] showed that in the thermal polymerisation of [$^{13}$C]-*N*-carboxyglycine anhydride the carbon dioxide split off contains exclusively the second carbon atom of the ring. However, this is insufficient to settle the problem whether the polymer forms as a result of normal chain growth at the amine end or via the intermediate isocyanatocarboxylic acid, which is probably present in equilibrium with the anhydride of the *N*-carboxy-α-amino-acid [165,181]. The detection of considerable amounts of 2,5-dioxopiperazines in the polymerisation of the anhydrides of *N*-carboxyglycine and *N*-carboxyalanine at 100–165° [220] also prevents final conclusions concerning the mechanism of the reaction.

B. Polymerisation in solution. Initiation with primary and secondary amines. All the known anhydrides of *N*-carboxy-α-amino-acids, except for the anhydride of *N*-carboxy-α-methylalanine [179,247] readily polymerise in the presence of amines in inert solvents (dioxan, benzene, nitrobenzene, chloroform, acetophenone, dimethylformamide, etc.) at relatively low temperatures. The polymerisation can be divided into three main stages.

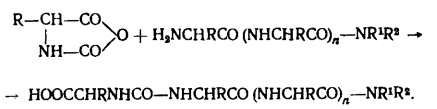
Initiation:



Chain growth:

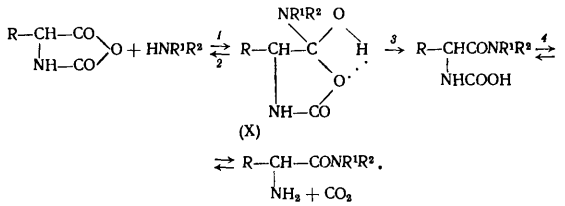


Chain termination:



The initiation and chain growth correspond to "normal" addition of nucleophilic agents to the carbonyl group in position 5, and chain termination to "erroneous" addition. The average degree of polymerisation $\overline{P}_n$ of the polypeptides formed (10–200) is usually equal to the ratio of the initial concentrations of the monomer $[M_0]$ and initiator $[I_0]$, variation of which permits the preparation of polypeptides of the required molecular weight.

*Initiation* proceeds according to the usual mechanism involving the addition of nucleophilic agents to the anhydrides of *N*-carboxy-α-amino-acids:



The rate of initiation depends on the rate of the individual reactions *1*, *2*, and *3*. If among the three stages reaction *3* is the slowest, equilibrium is established between the anhydride of the *N*-carboxy-α-amino-acid and compound (X). On the other hand, if the rate of reaction *1* is slow, i.e. because of its low basicity or because of steric hindrance, the initiator $HNR^1R^2$ adds with difficulty to the carbonyl group in position 5 and is readily split off again, stage *1* determining the rate of the overall initiation process. On the basis of measurements of the isotopic effect (see below) Heyns and Schultze [150] concluded that the anhydrides of the *N*-carboxy-derivatives of phenylalanine and sarcosine react in this way with aniline. The ratios of the rate constants of reactions *1*, *2*, and *3* are 0.08 : 75 : 15 in the case of phenylalanine and 0.07 : 86 : 10 in the case of sarcosine.

The rate of initiation may be measured in the reaction with a large excess of the amine, when the polymerisation does not have a significant effect on the rate of consumption of the anhydride. It was found that in this case the reaction is of second order.

Ballard and Bamford [221] measured the rate constants $K_1$ for the reactions of various anhydrides of *N*-carboxy-α-amino-acids with amines of the type $RHNCH_2CON(CH_3)_2$. The results, which are presented in Table 14, indicate a considerable effect of steric hindrance, due to substituents at the nitrogen and carbon atom 4, on the rate of reaction with secondary amines.

Direct determination of the rate of initiation in polymerisation is very difficult. It can be only approximately estimated from the overall rate of initiation and polymerisation during early stages of the process. It was thus

TABLE 14. Rate constants $K_1$ (litre $mole^{-1}$ $s^{-1}$) for the initiation of the polymerisation of the anhydrides of *N*-carboxy-α-amino-acids with amines of the type $RNHCH_2CON.(CH_3)_2$ in nitrobenzene at 15°.

| Anhydride of *N*-carboxy-derivative of / R | Alanine | Sarcosine | *N*-methyl-alanine | Phenyl-alanine | *N*-isopropyl-glycine | α-Methyl-alanine | L-Proline |
|---|---|---|---|---|---|---|---|
| R= H | 1.13 | 0.82 | 0.45 | 1.0 | 0.83 | 0.29 | 2.68 |
| R= $CH_3$ | 0.48 | 0.57 | 0.16 | 0.40 | 0.48 | $8.4\cdot10^{-4}$ | 2.00 |
| R=$CH(CH_3)_2$ | 0.10 | 7.4 | $2\cdot10^{-5}$ | 0.30 | $<10^{-7}$ | $1\cdot10^{-6}$ | 0.12 |

shown that initiation with n-hexylamine is approximately ten times faster than the polymerisation of the anhydride of γ-benzyl *N*-carboxy-L-glutamate in dioxan [200]. The rate constant for initiation is in this case $K_1 = 0.2 \pm 0.1$ litre × × $mole^{-1}$ $s^{-1}$. [199] The rate of initiation with *p*-chloroaniline of the polymerisation of the anhydride *N*-carboxy-DL-phenylalanine is smaller by a factor of 6000 than the rate of polymerisation itself, while in the case of initiation with *N*-ethylglycine diethylamide in benzene and nitrobenzene the two rates are approximately equal [222]. Relatively rapid initiation has been observed in the systems comprising the anhydride of α-*N*-carboxy-ε-*N*-benzyloxycarbonyl-L-lysine and ammonia and dioxan [223] and the anhydride of *N*-carboxy-DL-phenylalanine or *N*-carboxy-DL-leucine and the sodium salt of DL-phenylalanine [224].

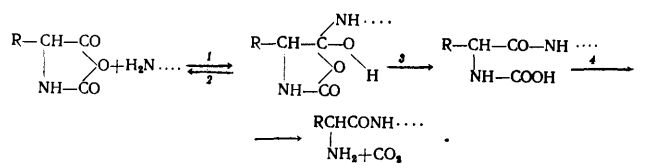
Ballard and Bamford [225] studied the effect of the peptide chain length on the rate of initiation of the polymerisation of the anhydrides of *N*-carboxy-DL-leucine and *N*-carboxy-DL-phenylalanine in nitrobenzene. They found that the dimethylamide of leucine is 3–4 times more active than the dipeptide, tripeptide, and higher peptides, the chain growth having begun proceeds at a constant rate since the reactivity of the amine of the amino-group at the chain end remains virtually constant, starting with the dimer.

It is evident from the mechanism of the initiation reaction that the initiator remains at the end of the polypeptide chain. This enabled Ritschard [226] to follow directly by means of paper chromatography the rate of consumption of the initiator in the polymerisation of γ-benzyl L-glutamate. He employed a coloured initiator — 2,4-dinitrophenylethylenediamine. From photometric measurements on such coloured polymers, their molecular weights were calculated [228]; this can also be done by determining, for example, the halogen content of polypeptides obtained in the presence of halogen-containing initiators [227].

Using as initiators polypeptides with free amino-groups or amines of large molecular weight [229], it is possible to obtain various block copolymers. The rate of initiation and chain growth are usually equal and independent of the degree of polymerisation ($\overline{P}_n$) of the initiator [225]. However, in the case of the polymerisation of the anhydride of *N*-carboxy-DL-phenylalanine initiated with polysarcosine Ballard and Bamford [230,231] observed a direct relation between the rate of polymerisation and initiator chain length up to $\overline{P}_n = 20$, polysarcosine being a hundred times more effective than the monomeric sarcosine dimethylamide. Further increase of $\overline{P}_n$ did not raise the rate of polymerisation. According to the authors, polysarcosine, which does not have intramolecular hydrogen bonds, forms hydrogen bonds with the NH groups of the anhydrides of *N*-carboxy-α-amino-acids, and this increases their concentration on the surface of polysarcosine and as a result increases the rate of polymerisation. This hypothesis has

not as yet been adequately confirmed, since the behaviour of polyproline and polyhydroxyproline, which also do not have NH groups, has not been investigated.

*Chain growth.* The mechanism of chain growth is similar to that of initiation:



Using radioactive carbon, it was shown that, as was to be expected, the carbon dioxide evolved during polymerisation contains carbon originating exclusively from the carbonyl in position 2 of the *N*-carboxy-$\alpha$-amino-acid anhydride ring [149]. From a study of the time variation of the isotopic composition of the carbon dioxide evolved, Heyns and Schultze [150] established that the removal of carbon dioxide (stage *4*) in the polymerisation of the anhydrides of the *N*-carboxy--derivatives of glycine, sarcosine, phenylalanine, and *p*-nitrophenylglycine is relatively rapid. The slowest stage in the polymerisation of the anhydrides of the *N*-carboxy--derivatives of phenylalanine, phenylglycine, and *p*-nitrophenylglycine is reaction *1*, while in the case of glycine the stage involving ring opening (reaction *3*) is slower, and in the case of sarcosine the rates of both reactions are approximately the same. Thus the rate of polymerisation is determined by stage *1* or *3*, depending on the nature of the anhydride of the *N*-carboxy-$\alpha$-amino-acid.

This conclusion agrees with earlier observations. The polymerisation of *N*-carboxy-$\alpha$-amino-acid anhydrides usually is accelerated by increase of temperature [225]. In the polymerisation of sarcosine in nitrobenzene and in acetophenone initiated by sarcosine dimethylamide or poly-(sarcosine dimethylamide) a negative temperature effect was observed [232,233]. According to Heyns' findings [150], the rate of polymerisation in this case is determined not by only one individual reaction but by all the reactions at once.

The removal of carbon dioxide from the growing chain (stage *4*) is reversible. An increase in carbon dioxide pressure slows down the breakdown of the terminal carbamic acid group; this group can be further stabilised by the formation of carbamates with free terminal amino--groups, which reduces their concentration and the rate of polymerisation. For this reason, measurements of the rate of reaction from the carbon dioxide evolved using constant pressure [225] and constant volume [232] apparatus usually differ from one another.

In a homogeneous medium at constant carbon dioxide pressure the rate of polymerisation should also be constant, since the reactivity of the terminal amino-group does not vary with chain growth. Indeed, after the termination of the initiation stage, the polymerisation is a first-order reaction with respect to the anhydride. This was confirmed by Ballard and Bamford for the polymerisation of the anhydrides of the *N*-carboxy-derivatives of DL-leucine, DL-phenylalanine [225], and sarcosine [234], by Breitenbach and Allinger [222] for the polymerisation of the anhydride of *N*-carboxyl-DL-phenylalanine in nitrobenzene, and by Lundberg and Doty [199] for the polymerisation of the anhydride of $\gamma$-benzyl *N*-carboxy--L-glutamate in dimethylformamide.

Short chains [235-237] of poly($\gamma$-benzyl L-glutamate) have the random $\beta$-conformation in inert solvents, while in the case of long chains the $\alpha$-spiral conformation is more stable. It might have been expected that during polymerisation the polypeptide chains undergo changes in conformation on attainment of a certain length and that these changes will be reflected in the polymerisation process. Indeed [199,238], the rate of polymerisation of the anhydride of $\gamma$-benzyl *N*-carboxy L-glutamate in dioxan, nitrobenzene, dichloroethane, chloroform, and benzene in the presence of n-hexylamine increases approximately fivefold when the growing chains reach a length equivalent to eight structural units (Fig. 11). In the presence of a larger amount of hexylamine ($[M_0]/[I_0] = 4$) the appearance of the second, more rapid stage is not observed, since in this case only short chains are formed, while in the initiation with a polypeptide having $\bar{P}_n = 10$ there is only the rapid stage of chain growth.

It has been demonstrated by infrared spectroscopy that the formation of the poly($\gamma$-benzyl L-glutamate) $\alpha$-spiral begins on attaining a chain length equivalent to 7–13 units [200], and certainly not less than 5 units [239]. For this reason, Lundberg and Doty attribute the sharp increase in the rate of polymerisation to changes in the conformation of the growing polypeptide chain.

The formation of a new polypeptide fraction in the second stage of the reaction has been convincingly demonstrated by paper chromatography [226] and the measurements of the electric double refraction (Kerr effect) [240]. Additional confirmation that the polymerisation proceeds in two stages was obtained in a study of the polydispersity of poly-($\gamma$-benzyl L-glutamate) [199,203,241]. In dimethylformamide, where only one stage is observed, the polymer exhibits a very narrow molecular weight distribution. In dioxan and chloroform, where the reaction takes place in two stages, the various polymeric chains grow at different rates, depending on their conformation, and give rise to a polypeptide with a very wide molecular weight distribution. The average degree of polymerisation is much higher than the theoretical value, calculated from the relation $\bar{P}_n = [M_0]/[I_0]$, and is in no way related to it.

From a study of the dispersion of optical rotation [242,244], it has been shown that poly($\gamma$-benzyl L-glutamate) has the configuration of a right-hand spiral, while its antipode should have the configuration of a left-hand spiral. If the configuration is important, the rate of polymerisation should depend also on the relative concentrations of the

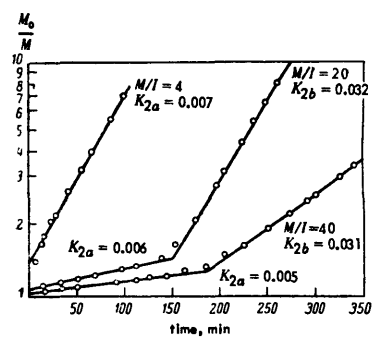



Fig. 11. The rate of polymerisation of the anhydride of $\gamma$-benzyl *N*-carboxy-L-glutamate in dioxan at 25°; initial concentration of the monomer $[M_0] = 4\%$; the units of $K_2$ are litre mole$^{-1}$ s$^{-1}$.

optical antipodes in the initial mixture. Indeed, the pure optical isomers polymerise twice as fast as the racemic mixture of the D- and L-antipodes. The second stage begins in the latter case much later, which is due to the much later formation of the stable racemic $\alpha$-spiral[199,245].

When poly($\gamma$-benzyl L-glutamate) is used as the initiator, the polymerisation of the anhydride of the *N*-carboxy--L-derivative proceeds at a high rate and the optical rotation of the system steadily increases with the growth of the $\alpha$-spirals. In the case of the racemic anhydride the polymerisation proceeds at a rate smaller by a factor of two, but the form of the spirals does not change when D-units are incorporated in it. In the L-polymer (initiator)–D-anhydride system a different relation obtains (Fig. 12). Initially D-units enter into the composition of the right--hand spiral of the L-polymer without changing its form, but as the D-units accumulate inversion of the optical rotation of the system takes place with simultaneous increase of the rate of polymerisation, which is probably due to the transformation of the right-hand $\alpha$-spiral of the L-polymer into the left-hand $\alpha$-spiral characteristic of the D-polymer. Comparison of the relative rates of addition of the D- and L-antipodes to the right-hand $\alpha$-spiral of the L-polymer shows that the L-anhydride is almost five times more reactive than the D-anhydride.

Two stages were also observed in the polymerisation, initiated by n-hexylamine, of the anhydrides of the *N*-carboxy--derivatives of L-leucine in nitrobenzene[199], *O*-benzyloxycarbonyl-L-tyrosine[246], glycine, $\epsilon$-*N*-benzyloxycarbonyl-L--lysine, $\gamma$-benzyl L-glutamate, DL-alanine, DL-$\alpha$-aminobutyric acid, DL-leucine, and DL-valine in dioxan[247]. However, in these cases the polymer is usually precipitated in the form of a gel, the reaction being accelerated simultaneously with the appearance of the new phase.

Ballard and Bamford[248] questioned the existence of two stages in homogeneous polymerisation of the anhydride of $\gamma$-benzyl *N*-carboxy-L-glutamate. According to their observations, the reaction is of first order with respect to the anhydride, and has a constant rate whether it is initiated by n-hexylamine or oligopeptides with $\overline{P}_n$ = 4.5 and 15. Doty and Lundberg[249] indicate that the second, rapid stage is observed only in experiments with thoroughly purified anhydrides. Impurities at low concentrations, for example 0.67 mole % of hexylammonium chloride, completely eliminate the second stage. Furthermore, an additive of this kind results in the formation of a polymer with a much lower molecular weight and a much narrower molecular weight distribution.

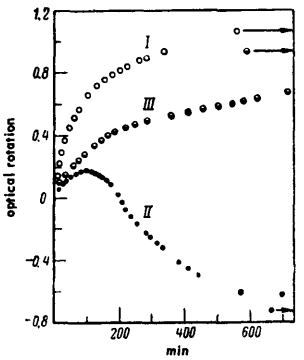


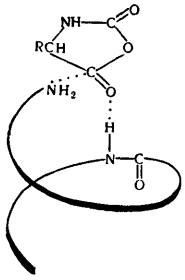

Fig. 12. Variation of the optical rotation of the system during the polymerisation of the anhydrides of $\gamma$-benzyl *N*-carboxy-glutamate [I) L-isomer; II) D-isomer; III) DL-isomer] initiated by the L-polymer; solvent — dioxan; temperature 25°; initial concentration 2%; optical pathlength of the cell $l$ = 20 cm.

In the latest papers[234,250] Ballard and Bamford state that in most systems homogeneous conditions do not obtain, since polypeptides are poorly soluble and form a gel even at the trimer and tetramer stage, the rate of polymerisation increasing by a factor of 5–8 at the same time. Further coagulation of the gel into denser formations lowers the rate. Probably this is due to the adsorption of the polymerising anhydride on the polymeric gel. The polymerisation of the anhydride of $\gamma$-benzyl *N*-carboxy-L-glutamate, whose polymer does not form true solutions in dioxan according to the above authors, has been assigned to reactions of the same class.

Adsorption can occur also in true solutions as a result of the formation of hydrogen bonds between monomer molecules and the polymeric chain, which probably in fact explains the "chain effect" in polysarcosine[231], poly-*N*-ethylglycine, and poly-*N*-benzylglycine[250], their reactivity increasing with increase in $\overline{P}_n$ in the initiation of the polymerisation of the anhydrides of *N*-carboxy-derivatives with free NH groups. The polymerisation of the anhydride of *N*-carboxysarcosine itself is not autocatalytic in a homogeneous medium, since polysarcosine does not form hydrogen bonds with the monomer[250].

However, the single-stage polymerisation of $\gamma$-benzyl *N*-carboxy-L-glutamate in dimethylformamide, in which the polymer is readily soluble and forms $\alpha$-spirals, contradicts both the hypothesis of Lundberg and Doty that the conformation of the growing chain influences the rate of polymerisation and the hypothesis of Ballard and Bamford that adsorption on polymeric chains takes place.

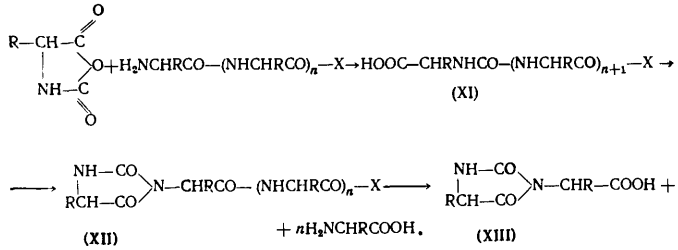
The two hypotheses have been in a way combined in the mechanism proposed by Weingarten[247], according to which activating adsorption of anhydride molecules is possible only at the ends of the growing chains when these have the spiral conformation:




Thus the molecule of the anhydride of the *N*-carboxy--derivative being added assumes a definite orientation even before its reaction with the terminal amino-group. Below yet another attempt will be made to explain the occurrence of the two stages in the polymerisation of the anhydride of $\gamma$-benzyl *N*-carboxy-L-glutamate.

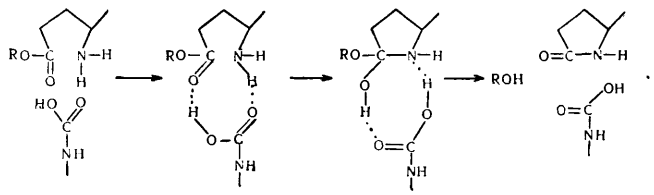
*Chain termination.* The disappearance of the free amino-group at the end of the polypeptide chain, for any reason, results in the cessation of its growth. The cessation of chain growth occurs as a result of the "erroneous"

addition of the terminal amino-group to the carbonyl group in position 2 of the anhydride ring [192,251,252] with formation of the urea derivative (XI), which is capable of cyclising into the hydantoin derivative (XII). In the acid hydrolysis of polypeptides this derivative may be isolated in the form of the substituted hydantoin-3-acetic acid (XIII).



Possibly the cyclisation takes place only during hydrolysis, which is indicated by the presence of free carboxy--groups in polypeptides [241,251,253].

Chain termination can also occur in the intramolecular interaction of the terminal amino-group with any reactive group in the polymeric chain. Thus in the preparation of poly($\gamma$-benzyl L-glutamate) great importance attaches to the intramolecular cyclisation due to the reaction of the terminal amino-group with the ester group of the same structural unit, benzyl alcohol being eliminated [199,241,254]. Recently it has been shown that the cyclisation is catalysed by weak acids, including carbamic acid, and has the following mechanism [164]:



Intramolecular chain termination as a result of the migration of the acetyl group from the oxygen to the nitrogen was noted in the polymerisation of the anhydride of the *N*-carboxy-derivatives of *O*-acetoxyproline [255] and *O*-acetylserine [257,258].

*Polymerisation kinetics.* The polymerisation of the anhydrides of *N*-carboxy-derivatives is very convenient for the investigation of the kinetics of the process, the rate of which may be determined both by the titration of the monomer which failed to react [158,247] and from the amount of carbon dioxide evolved during polymerisation. In the latter case more reliable results are obtained at constant carbon dioxide pressure [206,225]. Closed systems of constant volume [187,232,233,259] are less suitable for kinetic studies. A convenient method is one in which the carbon dioxide evolved is swept by dry nitrogen into an absorption vessel where the change in the concentration of sodium hydroxide [222], barium hydroxide [199], or benzylamine [158] is determined conductimetrically [199,222] or by titration [158]. Idelson and Blout [200] studied the kinetics of the polymerisation of the anhydride of $\gamma$-benzyl *N*-carboxy-L-glutamate by infrared spectroscopy, which makes it possible to follow the disappearance of the monomer, the formation of the polymer, and the changes in the conformation of the polymeric chain.

In most cases of homogeneous polymerisation with fairly high basicity of the initiator and low rate of chain termination there is direct proportionality between the rate of reaction and the initial concentration of the monomer $[M_0]$ and initiator $[I_0]$. The kinetics of this process were examined theoretically by a group of English workers [225,232] and in a general form by Katchalski and coworkers [260,261]. Three stages of the process are distinguished: initiation ($K_1$), chain growth ($K_2$), and chain termination ($K_3$); the process can take place in one of the following possible ways.

If the rate of initiation is equal to the rate of chain growth ($K_1 = K_2$) and chain termination may be neglected ($K_3 = 0$), the rate of polymerisation is given by

$$-\frac{d[M]}{dt} = \frac{d[CO_2]}{dt} = K_2[I_0][M].$$

These conditions are satisfied by the homogeneous polymerisation of the anhydrides initiated by the amides or esters of amino-acids, peptides, or polypeptides, in solvents where the process takes place in one stage only and at low temperatures when chain termination does not play a significant role. The number-average degree of polymerisation of the polymer formed is defined by the relation $\bar{P}_n = ([M_0] - [M])/[I_0]$, or $\bar{P}_n = [M_0]/[I_0]$ on completion of polymerisation when $[M] = 0$. The molecular weight distribution should be of the Poisson type, i.e. the polydispersity is low with $\bar{P}_w/\bar{P}_n \simeq 1$.

The actual molecular weight distribution has been determined in only a few cases. It proved to be fairly narrow for polysarcosine [262], poly($\gamma$-benzyl L-glutamate) [199,263], and poly-$\epsilon$-*N*-benzyloxycarbonyl-L-lysine [246], obtained in dimethylformamide.

If the rates of initiation and chain growth differ from one another ($K_1 \neq K_2$), then when the rate of chain termination is low ($K_3 = 0$) the rate of polymerisation is given by the expression

$$-\frac{d[M]}{dt} = \frac{d[CO_2]}{dt} = K_1[I][M] + K_2\sum_{i=1}^{\infty} N_i^*[M],$$

where $[I]$ represents the concentration of the initiator at any instant, and $N_i^*$ the concentration of growing polymer chains containing at a given instant the following number of $i$-units: $[I] + \sum_{i=1}^{\infty} N_i^* = [I_0]$. At the early stages of the process when $[I_0] \simeq [I] \gg \sum_{i=1}^{\infty} N_i^*$, the overall rate of reaction is determined mainly by the first term of the equation, and on completion of polymerisation, when $[I] \ll \sum_{i=1}^{\infty} N_i^* \simeq [I_0]$, by the second term. Thus in this case polymerisation is of first order with respect to the anhydride and the rate of evolution of carbon dioxide is determined by the constants $K_1$ at the beginning and $K_2$ at the end of polymerisation. If $K_1 > K_2$, which occurs when the initiators are strong bases, the initiation process terminates rapidly and the rate of chain growth remains constant throughout the process. The molecular weight distribution of the polymer is very narrow and $\bar{P}_n = [M_0]/[I_0]$. When weak initiators are used, with $K_1 < K_2$, the initiation process is protracted and the overall rate of the reaction increases with increase in the number of new chains, and the polymer formed is polydisperse. $\bar{P}_n = [M_0]/[I_0]$ obtains only in the case where the entire initiator is able to react before the end of polymerisation.

If in the case of rapid initiation ($K_1 > K_2$, $K_3 \simeq 0$) two stages are observed in the chain propagation process ($K_{2a}$ and $K_{2b}$), the transition from $K_{2a}$ to $K_{2b}$ being completed

after the attainment of a chain length equivalent to $s$-units, the rate of the process is given by the expression

$$-\frac{d[M]}{dt}=\frac{d[CO_2]}{dt}=K_1[I][M]+K_{2a}\sum_{i=1}^{i=s}N_i^*[M]+K_{2b}\sum_{i=s}^{\infty}N_i^*[M].$$

This case was examined by Katchalski[246] on the basis of the kinetic data obtained by Lundberg and Doty[199] for two-stage polymerisation of the anhydride of $\gamma$-benzyl $N$-carboxy-L-glutamate in dioxan. Similarly to the preceding case, the polymerisation is again of first order with respect to the anhydride, its rate being determined mainly by the constant $K_{2a}$ at the beginning and $K_{2b}$ at the end: $-d[M]/dt = K_2[I_0]/[M]$. The polymer fractions with a degree of polymerisation less than $s$ exhibit the Poisson distribution. The fractions with $\overline{P}_n > s$ are more polydisperse the greater the difference between $K_{2a}$ and $K_{2b}$. On the basis of mathematical analysis, the authors believe that the number of $\beta$-chains diminishes during the polymerisation at a slower rate the greater the value of $s$, and the weight fraction of the $\beta$-polymer falls after reaching a maximum proportional to $s$. It is reasonable that the time of transition from $K_{2a}$ to $K_{2b}$ depends only on $[M_0]$ and not on $[I_0]$, since the rate of formation of the polymer with $\overline{P}_n = s$ depends on the concentration of the monomer $[M_0]$ and not on the number of chains $[I_0]$.

However, the relation observed by Doty and Blout[199,200] between $[M_0]$ and the time of transition from $K_{2a}$ to $K_{2b}$ is the opposite of that which would be expected on the basis of Katchalski's conclusions (Fig. 11). Furthermore, in one of his latest papers Katchalski[256] notes that the polydispersity found by Doty ($\overline{P}_w/\overline{P}_n = 8.5$) is much greater than the theoretical value. Thus the conclusions derived from an analysis of the polymerisation kinetics on the basis of the hypothesis of Doty and Lundberg, that chain conformation influences the rate of chain growth, is in poor agreement with experiment. On the other hand, no conclusion can be reached about the hypothesis of Ballard and Bamford that the adsorption of the monomer on polymer chains affects the rate of polymerisation, since the example examined by Katchalski assumes that $K_{2a}$ and $K_{2b}$ are constant, a possibility which is excluded in Ballard's hypothesis.

If in the case of a high rate of initiation and a single-stage process ($K_1 > K_2$) some of the polymerising chains are terminated ($K_3 \neq 0$) as a result of a bimolecular reaction with the anhydride, the amount of carbon dioxide evolved is less than that of the anhydride which has reacted ($[M_0] - [M]$). The difference $[M_0] - [M] - [CO_2]$ corresponds to the amount of terminal carboxy-groups. Katchalski[260,261] showed that in this case the molecular weight distribution of the growing chains remains of the Poisson type, but the polymer fraction with terminal carboxy-groups is polydisperse with $\overline{P}_w/\overline{P}_n \simeq 2$. The maximum attainable degree of polymerisation of the polymer as a whole is then $\overline{P}_n = K_2/K_3$.

This case is close to real polymerisation conditions. The chain termination reaction, which is rare at low temperatures (one reaction for 300 addition reactions)[199,241] plays a considerable role at elevated temperatures, since the activation energy for chain termination is somewhat higher than that for chain propagation, which in the case of $\gamma$-benzyl L-glutamate is only 6.6 kcal mole$^{-1}$.[199,200]

The kinetics of the polymerisation of the anhydrides of the $N$-carboxy-derivatives of trifunctional acids, for which intramolecular chain termination is possible, have not been examined theoretically.

TABLE 15. Rate constants $K_{2(a)b}$ (litre mole$^{-1}$ s$^{-1}$) for the polymerisation of the anhydrides of various $N$-carboxy--$\alpha$-amino-acids.

| Anhydride of $N$-carboxy-derivative of | Solvent | Initiator | t, °C | $10^2K_{2(a)b}$ | References |
|---|---|---|---|---|---|
| Glycine | dioxan | $p$-bromoaniline | 37 | 18 | 227 |
| Sarcosine | benzene | n-hexylamine | 25 | (12)60 | 234 |
| L-Alanine | » | » | 25 | (6.3)54 | 234 |
| » | nitrobenzene | » | 25 | (4.8)26.4 | 234 |
| L-Leucine | » | » | 25 | (1.3)9 | 199 |
| Phenylalanine | » | » | 25 | (1.6) | 234 |
| » | benzene | » | 25 | (5) | 234 |
| $\gamma$-Benzyl L-glutamate | dioxan | » | 34 | 2.5–5.2 | 200 |
| Ditto | dichloroethane | » | 25 | (1.5)14 | 199 |
| » | dimethylformamide | » | 25 | 5.7 | 199 |
| » | » | » | 0 | 1.9 | 199 |
| » | » | » | 40 | 8.7 | 199 |
| » | dioxan | $NaOCH_3$ | 34 | 430–630 | 277 |
| $\gamma$-Benzyl DL-glutamate | » | n-hexylamine | 25 | (0.4)1.5 | 199 |
| Ditto | dimethylformamide | » | 25 | 2.2 | 199 |
| $\gamma$-Methyl L-glutamate | chloroform | $CH_3COOH$ | 30 | (0.35)2.9 | 292 |

Table 15 lists the latest data on the rates of polymerisation of the anhydrides of $N$-carboxy-derivatives, from which it follows that the rate of polymerisation is a maximum in the case of glycine and proline. Racemates polymerise more slowly than enantiomers. Non-polar solvents, which cannot form hydrogen bonds, accelerate the reaction[199].

The determinations of the rates of polymerisation are not very accurate because of the difficulty of purifying the anhydrides of $N$-carboxy-derivatives and the solvents, and because of failure to achieve the conditions of a homogeneous reaction[247]; the fact that the reaction is homogeneous is established with difficulty by a visual procedure (cf. Refs. 199 and 250). Furthermore, because the reaction of the anhydrides of $N$-carboxy-derivatives with strong amines proceeds in different ways, the true concentration of growing chains is only approximately equal to the initial concentration of the initiator. When the process takes place in two stages, the constant $K_{2b}$ is much too low, since not all the growing chains attain a length necessary for the acceleration of the reaction. Finally, polymerisation initiated by primary and secondary amines must proceed in several ways simultaneously. Otherwise it would have to be of first order with respect to the initiator and the rate of chain propagation would be independent of the nature of the initiator.

In fact $K_2$ does depend on the initiator. Thus diethylamine leads as a rule to polymerisation twice as fast as that given by hexylamine[247]. Furthermore, the order of the reaction with respect to the initiator is sometimes other than unity. In the polymerisation of the anhydrides of the $N$-carboxy-derivatives of DL-valine, DL-leucine, $\epsilon$-$N$-benzyloxycarbonyl-DL-lysine, and DL-$\alpha$-aminobutyric acid in dioxan a fractional reaction order was found[247]. In the polymerisation of the anhydride of $N$-carboxysarcosine Heyns and Schultze[150] found the reaction to be of second order with respect to the initiator, and later it was shown that the rate is proportional to the expression

$$a[I_0]+b[I_0]^2 \quad ,$$

where $a$ and $b$ are constants[232,247].

In an investigation of the two-stage polymerisation of the anhydride of $\gamma$-benzyl $N$-carboxyl-L-glutamate the slow stage was found to be of first order with respect to the

anhydride and its rate proved to be independent of the initiator. On the other hand, the second, rapid stage was of fractional order (3/2) with respect to the anhydride and its rate did depend on the initiator [228].

The authors propose the following mechanism for chain propagation which explains the peculiarities of this process:

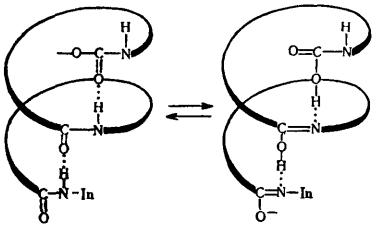
$$P_n\text{—}NH_2 + M \xrightarrow{K_{2a}} P_n\text{—}NHCOCHRNHCOOH, \quad (c)$$

$$P_n\text{—}NHCOCHRNHCOOH \xrightarrow{K_4} P_n\text{—}NHCOCHRNH_2 + CO_2, \quad (d)$$

$$P_n\text{—}NH_2 + P_m\text{—}NHCOOH \xrightarrow{K} P_n\overset{+}{N}H_3 + P_mNHCOO^-, \quad (e)$$

$$P_mNHCOO^- + M \xrightarrow{K_{2b}} P_mNHCOCHRNHCOO^- + CO_2. \quad (f)$$

Chain propagation can proceed according to the generally accepted mechanisms (c)–(d) with a rate constant $K_{2a}$ or by reaction (f) with a higher rate constant $K_{2b}$. Usually the contribution of reaction (f) is small because of the instability of carbamic acid and the resulting low concentration of the carbamate anion. However, on formation of the $\alpha$-spiral the stability of the anion may be significantly increased because of the distribution of the charge throughout the spiral:



As a result, the initiator can influence the stability of the carbamate anion and hence the rate of polymerisation. The rate of reaction (f) is defined by the equation

$$\frac{d[M]}{dt} = K_{2b}\left(\frac{K_{2a}}{K_4}\right)^{\frac{1}{2}} K^{\frac{1}{2}} [I_0]\,[M]^{\frac{3}{2}},$$

i.e. the reaction is of order 3/2 with respect to the anhydride, which agrees with experiment.

The mechanism proposed constitutes a very interesting attempt to account for the effect of spiral conformation and the initiator on the rate of polymerisation. However, we feel bound to point out that according to this mechanism secondary amines should not affect the reactivity of the terminal amino-group of the growing chain, since they are incapable of participating in the suggested system of hydrogen bonds.

Bamford and Block [264] proposed another mechanism for the effect of the initiator on the rate of polymerisation, which will be examined below.

C. Initiation with water. Polymerisation in the presence of water proceeds similarly as the polymerisation initiated by amines [265]. However, the initiation stage is slower because of the lower basicity of water, and the ionisation of free carboxy- and amino-groups in the system greatly slows down chain growth, particularly in the first polymerisation stage [224,266–270]. The use of water as the initiator is of interest for the preparation of polypeptides with terminal carboxy- and amino-groups capable of further condensation, for example by the carbodiimide method [271].

In the case of initiation by water side-reactions are possible. The polyglycine obtained in this way contains up to 2% of 2,5-dioxopiperazine [253]. Polymerisation in polar solvents, for example dimethylformamide, probably takes place by a different mechanism and leads to considerable amounts of hydantoin derivatives [207,272].

In many cases water can be used not only as the initiator but also as the polymerisation medium [174]. In recent years the dependence of the rate of polymerisation of various anhydrides of *N*-carboxy-derivatives on the pH of the medium has been studied in detail [163,269,273–275].

D. Initiation with strong bases. Sodium hydroxide [276], sodium methoxide, sodium borohydride [203], and triphenylmethylsodium [277], which have been proposed by Blout and coworkers as the initiators of the polymerisation of the anhydrides of *N*-carboxy-derivatives, yield exclusively high-molecular-weight polypeptides [poly($\gamma$-benzyl L-glutamate, $M$ = 600 000; poly-$\epsilon$-*N*-benzyloxycarbonyl--L-lysine, $M$ = 2 000 000], which are of low dispersity and are free of 2,5-dioxopiperazine and other cyclic compounds [278,279]. A detailed study of this process [203,277,280,281] has shown that polypeptides with the maximum molecular weights are formed in solvents such as dioxan, chloroform, and benzene at temperatures below 30° and monomer concentrations below 4%. In nitrobenzene the rate of polymerisation is smaller by a factor of almost 30 and the polymer has a much lower molecular weight. There is no proportionality between the degree of polymerisation and the ratio $[M_0]/[I_0]$, the molecular weight of the polymer being always higher than the calculated value [203,281].

The rate of polymerisation and the molecular weight of polymers increase in the series lithium, sodium, potassium, and caesium methoxides [280]. The polymerisation of the anhydride of $\gamma$-benzyl *N*-carboxy-L-glutamate in dioxan at 34° proceeds after a brief autocatalytic period as a first--order reaction with respect to the monomer at a rate one hundred times greater ($K_2$ = 4.3–6.3 litre mole$^{-1}$ s$^{-1}$) than in the case of initiation by primary or secondary amines [280]. Addition to the reaction system of fresh portions of the anhydride of the *N*-carboxy-derivative does not increase the

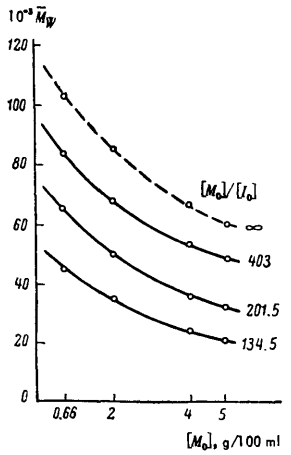



Fig. 13. Dependence of the molecular weight $\bar{M}_w$ of poly-DL-phenylalanine on the initial monomer concentration $[M_0]$ for various values of $[M_0]/[I_0]$.

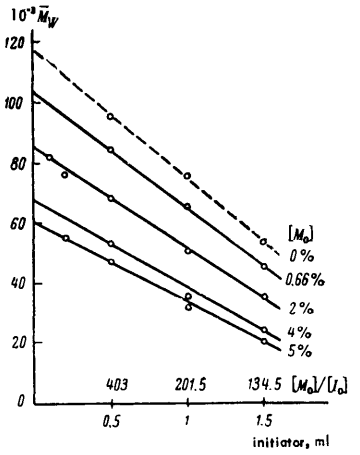
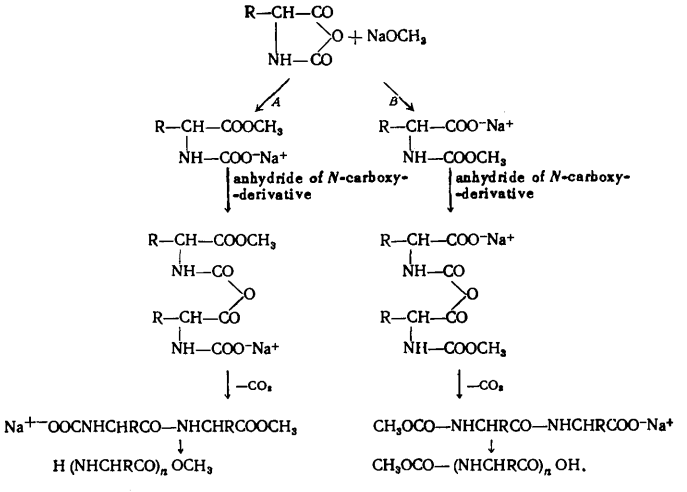



Fig. 14. Dependence of the molecular weight $\bar{M}_W$ of poly-DL-phenylalanine on the ratio $[M_0]/[I_0]$ for various initial monomer concentrations $[M_0]$.

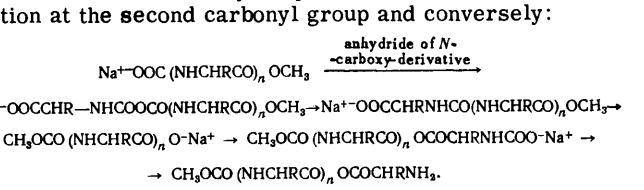
molecular weight of the polymer. The replacement of the L-anhydride by the racemate lowers the rate of polymerisation by a factor of seventeen and the molecular weight of the polymer by a factor of about five.

The above features of the process have also been found for the neutral amino-acid DL-phenylalanine[279]. Figs. 13 and 14 show the experimental dependence of the molecular weight $\bar{M}_W$ of the polypeptide on the concentration of the anhydride $[M_0]$ and the ratio $[M_0]/[I_0]$. The polymerisation was carried out at 40° in chloroform in the presence of sodium methoxide. The dashed lines, corresponding to $[M_0] = 0$ and $[M_0]/[I_0] = \infty$ (0 ml of initiator) were obtained by extrapolation. The molecular weights were found from the light scattering.

These results led Blout and Idelson[280] to the hypothesis that the polymerisation in this case has an ionic mechanism:

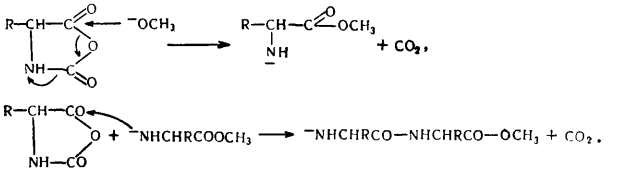



The growth of the polymeric chain proceeds by successive addition of the polymeric anions to the anhydride of the *N*-carboxy-derivative either at the carbonyl in position 5 (pathway *A*) or at the carbonyl in position 2 (pathway *B*) with formation of mixed anhydrides which readily eliminate carbon dioxide. Chain termination occurs when the addition at the carbonyl in position 5 is followed by the addition at the second carbonyl group and conversely:




In the first case the polymer should contain urea and in the second anhydride and urethane groups.

A more probable mechanism[282] for chain propagation[280], also proposed by the same workers, is one in which the participation of an amine anion is assumed, and the elimination of carbon dioxide is attributed to simple electron pair transfers:



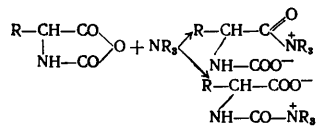

E. Initiation with tertiary amines. Tertiary amines (pyridine[174,182,224,283-285], α-picoline, 2,6-lutidine[182], triethylamine[103,259,286,287], tri-n-butylamine[259,285,288], and trimethylamine[289]) are effective initiators for the polymerisation of the anhydrides of *N*-carboxy-derivatives with a free NH group. However, the resulting polypeptides contain some substituted hydantoin-3-acetic acid[207,283].

As regards the anhydrides of *N*-substituted *N*-carboxy--derivatives, there is no single view concerning their ability to polymerise under the action of tertiary amines. In contrast to the anhydride of *N*-carboxy-*N*-cyclohexylglycine[284], the anhydride of *N*-carboxy-*N*-phenylglycine does not polymerise in pyridine even at an elevated temperature[174,175]. The anhydride of *N*-carboxysarcosine polymerises at room temperature in pyridine[175,283] even when it is most thoroughly purified by means of phenylmagnesium bromide[284]. The anhydrides of the *N*-carboxy--derivatives of L-proline[141,290], L-hydroxyproline, and *O*-(*p*-toluenesulphonyl)-L-hydroxyproline[290] also polymerise readily in pyridine. Nevertheless, Ballard and Bamford[182,206,259,285] believe that the polymerisation of sarcosine and proline and their derivatives is due to impurities and that after thorough purification it is possible to reduce to a minimum the initial rate of polymerisation[259].

Tertiary amines give rise to rapid polymerisation of the anhydrides of *N*-carboxy-derivatives in organic solvents even in the case of high $[M_0]/[I_0]$ ratios, yielding high--molecular-weight polypeptides, the degree of polymerisation of which is independent of the $[M_0]/[I_0]$ ratio[203]. These features resemble in many ways the polymerisation initiated by strong bases.

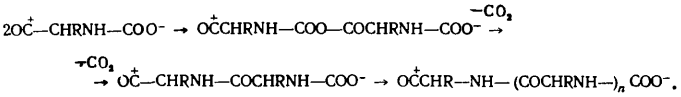
The polypeptides obtained in an anhydrous medium with tertiary amines as the initiators cannot have terminal amino- and carboxy-groups, i.e. they must have a cyclic structure. Thorough analysis of polysarcosine ($M$ = 22 000) and poly-*N*-cyclohexylglycine, prepared in dry pyridine, showed that these polymers have virtually no end-groups[284]. Cyclic dipeptides, substituted 2,5-dioxopiperazines, have been isolated, the yield reaching 35% in the case of poly--*N*-cyclohexylglycine. According to Wieland[291], in this

case the anhydride ring is opened by the tertiary amine with formation of a zwitter-ion:

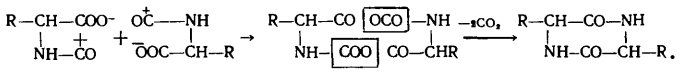


The formation of polypeptides, 2,5-dioxopiperazines and substituted hydantoin-3-acetic acid can be explained by different possibilities of combining the zwitter-ions.

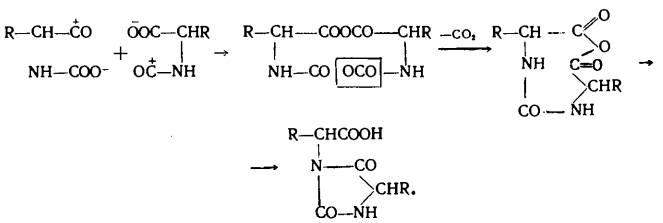
Formation of polypeptide:



Formation of 2,5-dioxopiperazine:

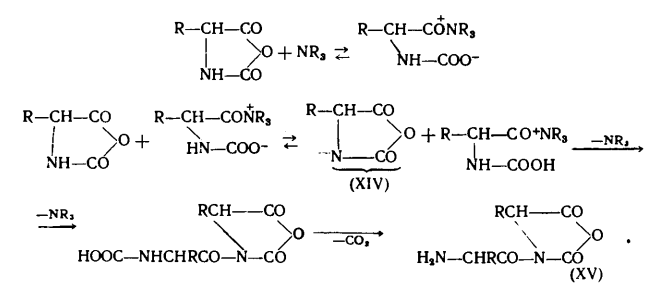


Formation of substituted hydantoin-3-acetic acid:

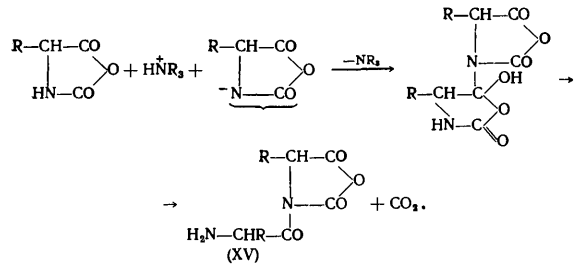


The rapid polymerisation of the anhydrides of *N*-carboxy-derivatives in organic solvents in the presence of catalytic amounts of tertiary amines [203] shows, however, that the growth of the polypeptide chain proceeds mainly not as a result of the interaction of two zwitter-ions but as a result of their reaction with the anhydrides of *N*-carboxy--derivatives.

The mechanism proposed by Ballard and Bamford [182,259,285] for the reaction between the anhydrides of *N*-carboxy--derivatives and tertiary amines excludes the possibility of the polymerisation of the anhydrides of *N*-substituted *N*-carboxy-derivatives, since the primary products of the reaction are believed to be the anhydride anion (XIV) and 3-(α-aminoacyl)-2,5-dioxooxazolidine (XV):

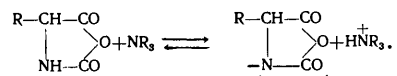


Subsequently the anion (XIV) can also react with a molecule of the anhydride by the mechanism



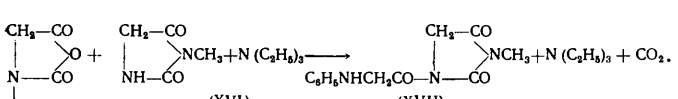
Compound (XV) initiates chain growth both at the amine end and at the *N*-carboxy-derivative anhydride end.

However, measurements of the rate of polymerisation of the anhydrides of the *N*-carboxy-derivatives of γ-ethyl L-glutamate in dimethylformamide and of DL-phenylalanine in nitrobenzene in the presence of pyridine, α-picoline, and 2,6-lutidine as the initiators [182] showed that the anion (XIV) does not form as a result of the nucleophilic attack by the tertiary amine on the carbonyl group in position 5 but as a result of direct attack by the amide hydrogen (cf. Ref. 181):



Otherwise the rate of reaction of the tertiary amines with the anhydrides of the *N*-carboxy-derivatives should decrease in the series pyridine, α-picoline, 2,6-lutidine due to increasing steric hindrance, while experiment showed that the rate actually increases in this series because of the increasing basicity of the amines.

Chain termination occurs also as a result of intramolecular cyclisation of the bifunctional polymeric chain or as a result of deactivation of the terminal amino-group. The formation of substituted hydantoin-3-acetic acid is explained by a rearrangement of compound (XV). In the authors' view [259] the mechanism proposed is proved by the fact that the rapid polymerisation of the anhydride of *N*-carboxy-sarcosine proceeds only in the presence of 3-methylhydantoin (XVI), an analogue of the anhydride of the *N*-carboxy--derivative not substituted at the nitrogen atom, and also by the fact that it proved possible to isolate 3-methyl-1--(*N*-phenylglycyl)hydantoin (XVII) from the products of the reaction of the anhydride of *N*-carboxy-*N*-phenylglycine, triethylamine, and 3-methylhydantoin:



As already pointed out, the suggested mechanism excludes the possibility of the polymerisation of *N*-substituted anhydrides, which cannot be regarded as completely proved. Furthermore, it entirely fails to account for the extremely rapid rate of polymerisation, which is comparable with the rate of ionic polymerisation. The chain growth of the anhydride end cannot increase significantly the rate of polymerisation, since it involves interaction either with

activated molecules of the anhydride of the *N*-carboxy--derivative, the concentration of which is extremely low, or with terminal amino-groups, which would reduce the concentration of the active centres for chain propagation.

It has been shown[264] that the polymerisation in the presence of secondary and primary amines also frequently proceeds by the mechanism characteristic of the initiation by tertiary amines. Blout[203] observed a considerable similarity between the polymerisations of the anhydride of $\gamma$-benzyl *N*-carboxy-L-glutamate initiated by diethylamine and triethylamine. In both cases the polymerisation was rapid and the molecular weight of the polymer was independent of the $[M_0]/[I_0]$ ratio.

Bamford found (Fig. 15) that the polymerisation of the anhydrides of the *N*-carboxy-derivatives of sarcosine and $\gamma$-ethyl L-glutamate in the presence of n-hexylamine and diisopropylamine takes a normal course only when initiated by n-hexylamine (curves *B* and *C*). Because of the considerable steric hindrance caused by the isopropyl groups, the initiation of the polymerisation of sarcosine by diisopropylamine is slow and the reaction becomes accelerated only as active terminal amino-groups appear in the growing chain (curve *D*). It would appear that this should also hold for other anhydrides. However, in the case of the anhydride of the *N*-carboxy-derivative not substituted at the nitrogen atom (curve *A*) the sterically hindered diisopropylamine gives rise to much more rapid polymerisation than does hexylamine, which can be explained only by the preferential occurrence of the process involving the mechanism characteristic of tertiary amines. This conclusion is also confirmed by the analysis of the molecular weights of the polymers. Whereas poly($\gamma$-ethyl L-glutamate) obtained in the presence of hexylamine has $\overline{P}_n = 60$, in the initiation with diisopropylamine $\overline{P}_n$ reaches 150 under the same polymerisation conditions with $[M_0]/[I_0] = 15$. It is interesting that in the latter case the amount of carbon dioxide evolved is much smaller than the theoretical value.

F. Initiation with salts. Inorganic salts were proposed by Ballard as the initiators of the polymerisation of the anhydrides of *N*-carboxy-derivatives as early as 1954 [206,207] but did not find wide application, since the resulting polypeptides contained up to 30–40% of hydantoin derivatives. However, this type of initiation is very interesting from the chemical point of view, because it is believed that there is considerable similarity in the mechanisms of the reaction of the anhydrides of *N*-carboxy--derivatives with salts and tertiary amines[207,259].

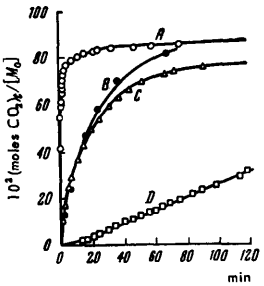
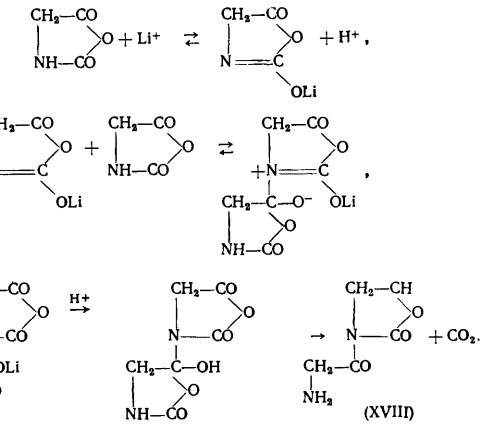
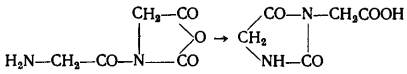



Fig. 15. Rate of evolution of carbon dioxide in different systems in diethylformamide solution at 25°:
*A*) anhydride of $\gamma$-ethyl *N*-carboxy-L-glutamate–diisopropylamine; *B*) anhydride of *N*-carboxysarcosine–n-hexylamine; *C*) anhydride of $\gamma$-ethyl *N*-carboxy-L-glutamate–n-hexylamine; *D*) anhydride of *N*-carboxysarcosine–diisopropylamine; $[M_0] = 0.224$ M; $[I_0] = 0.015$ M.

The following mechanism has been proposed for the initiation of polymerisation:

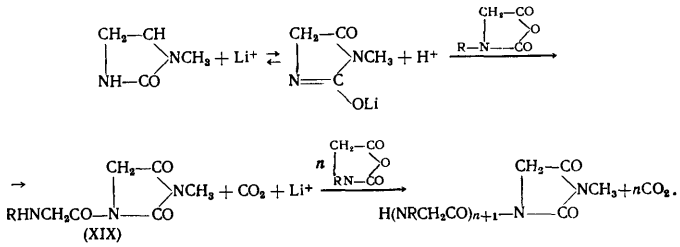


An intermediate compound, 3-aminoacetyl-2,5-dioxooxazolidine (XVIII), is formed and initiates chain growth or is converted into hydantoin-3-acetic acid:

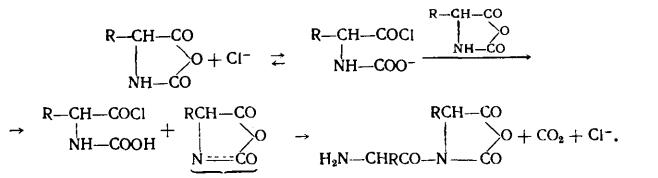


The polypeptide chains have reactive end-groups and can react with one another or form macro-rings.

The anhydrides of *N*-substituted *N*-carboxy-derivatives do not react with salts, but they readily polymerise in the presence of 3-methylhydantoin:



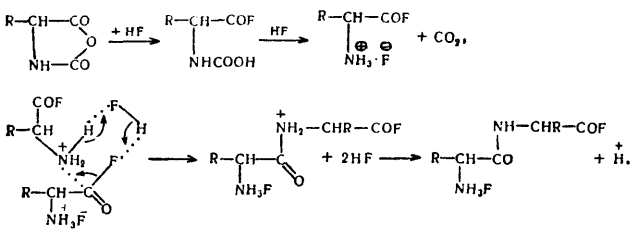
The first chain unit, 3-methyl-1-(*N*-phenylglycyl)hydantoin (XIX) was isolated from the products of the reaction of the anhydride of *N*-carboxy-*N*-phenylglycine, 3-methylhydantoin, and lithium chloride[259]. Later it was found that lithium perchlorate does not initiate the polymerisation of the anhydrides[250], which means that the active component of lithium chloride is not the cation $Li^+$ but the anion $Cl^-$.[259]



G. Initiation with acids. Acids usually inhibit the polymerisation of the anhydrides of *N*-carboxy-derivatives. However, the anhydride of γ-methyl *N*-carboxy-L--glutamate rapidly polymerises in chloroform in the presence of acetic acid[292]. With $[M_0]/[I_0] = 2$ the reaction is initially slow ($K_{2a} = 0.0035$), but after 30 min the rate increases sharply ($K_{2b} = 0.029$) and the polymerisation terminates in 2 h with formation of a polypeptide having $\overline{P}_n = 500-600$. The increase in rate corresponds to $\overline{P}_n = 50-60$, which the authors of this investigation attribute to the gel effect.

It is interesting that in dioxan polymerisation does not take place, the addition of 10% of dioxan to chloroform causing the appearance of an induction period (70 min). In the pure acid tripeptides are formed slowly. Acylated products and 2,5-dioxopiperazines have not been detected in the reaction products. The polymerisation of the anhydrides of *N*-carboxy-derivatives in chloroform is also induced by a number of other acids[201].

H. Polymerisation in anhydrous hydrogen fluoride. Anhydrous hydrogen fluoride readily dissolves the anhydrides of *N*-carboxy-α-amino-acids and polypeptides[293]. An attempt was made to use it as a polymerisation medium[294]; the polymerisation then proceeds without additional initiators but involves the racemisation of the amino-acids and the formation of considerable amounts of 2,5-dioxopiperazines. The degree of polymerisation reaches 25–30. The following mechanism has been suggested for this reaction:



I. Initiation with organometallic compounds. The polymerisation of the anhydride of *N*-carboxy-DL-alanine in tetrahydrofuran in the presence of a number of organometallic compounds was investigated recently[295]. Diethylcadmium and triethylaluminium proved to be the most effective compounds. Diethylzinc, phenylmagnesium bromide, and butyllithium were less effective, and tributylboron did not initiate the polymerisation at all. In contrast to other polymers, the polyalanine obtained in the presence of triethylaluminium was insoluble in water. Since poly-D-alanine and poly-L-alanine are also insoluble in water, the authors of this investigation suggested that triethylaluminium causes stereospecific polymerisation of the anhydride of the *N*-carboxy-derivative.

A similar property is shown by aluminium isopropoxide and by catalytic systems consisting of triethylaluminium and methanol or borneol, although in this case the insoluble fraction forms only part of the product. On the other hand, mixtures of diethylzinc with methanol and water and of diethylcadmium with methanol give only the water-soluble poly-DL-alanine.

When the optically active (+)-borneol and (-)-menthol were used as initiators, polyalanine exhibiting optical activity in solution was obtained, but the polymerisation of the monomer was incomplete.

4. Copolymerisation of the Anhydrides of *N*-Carboxy-α--amino-Acids

The available methods for the synthesis of the copolymers of α-amino-acids starting with the anhydrides of the *N*-carboxy-derivatives do not permit the preparation of copolypeptides with a specified sequence of the amino-acid residues. Usually the synthesis of copolypeptides reduces to the polymerisation in the solid state or in solution of a mixture of the anhydrides of the *N*-carboxy-derivatives using as the initiators the same compounds as in homopolymerisation, i.e. primary, secondary, and tertiary amines, sodium methoxide, amino-acid amides, polypeptides with free amino-groups, water, etc.

It is quite reasonable that copolymerisation should be a more complex process than the polymerisation of a pure *N*-carboxy-α-amino-acid anhydride and that it should have a number of specific features. Most of the published studies on copolymerisation were undertaken in order to elucidate the effect of the polypeptide composition on the conformation of macromolecules in solution; less attention was given to problems of the kinetics and mechanism of the reaction. For this reason, a considerable part of these investigations will be examined very briefly in this Section.

Katchalski and Sela[5] considered the copolymerisation of two anhydrides of *N*-carboxy-α-amino-acids as a system of the following reactions:

$$\cdots A + A \xrightarrow{K_1} \cdots A,$$
$$\cdots A + B \xrightarrow{K_2} \cdots B,$$
$$\cdots B + A \xrightarrow{K_3} \cdots A,$$
$$\cdots B + B \xrightarrow{K_4} \cdots B,$$

where A and B are monomers, ....A and ....B the growing peptide chains containing the terminal amino-group of the amino-acids A or B and $K_1$, $K_2$, $K_3$, and $K_4$ are the rate constants. The anhydrides of *N*-carboxy-derivatives of various amino-acids greatly differ in their reactivity and therefore the above reactions can proceed at different rates. However, Shalitin and Katchalski[319] found that the rates of copolymerisation are determined by the nature of the monomer and not of the terminal amino-acid residue of the growing chain, and therefore $K_1 = K_3$ and $K_2 = K_4$. It has been found that the rates of copolymerisation with diethylamine as the initiator, of the anhydrides of the *N*-carboxy-derivatives of γ-benzyl L-glutamate and ε-*N*-benzyloxycarbonyl-L-lysine in dimethylformamide, which is a good solvent both for homopolymers and copolymers at 25°, are equal to the sum of the rates of polymerisation of the individual monomers (Figs. 16 and 17).

On the basis of the data obtained, the rate of copolymerisation $-d[G + L]/dt$ can be represented thus:

$$-\frac{d[G+L]}{dt} = K_G[I_0][G] + K_L[I_0][L], \quad (1)$$

or

$$-\frac{d[G+L]}{dt} = K_{cop}[I_0][G+L],$$

where

$$K_{cop} = \frac{K_G[G] + K_L[L]}{[G] + [L]}. \quad (2)$$

Since $K_G$ is greater than $K_L$, the anhydrides of γ-benzyl *N*-carboxy-L-glutamate ($G$) will be consumed more rapidly

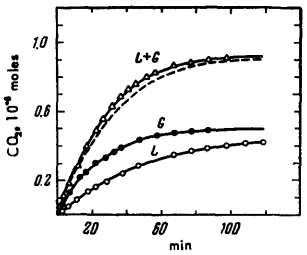



Fig. 16. Polymerisation of the anhydrides of the *N*-carboxy-derivatives of ϵ-*N*-benzyloxycarbonyl-L-lysine (*L*) and γ-benzyl L-glutamate (*G*) and their mixture (*G* + *L*) in dimethylformamide at 25° with diethylamine as the initiator; the dashed curve represents the sum of curves *L* and *G*.

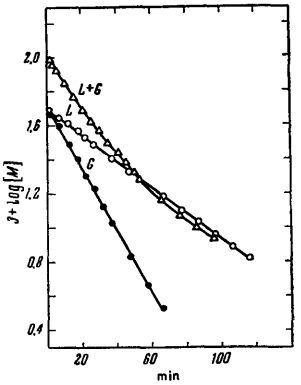



Fig. 17. Consumption of the monomers *L* and *G* as a function of time; [*M*] is the molar concentration of the monomer which has not reacted.

during copolymerisation than the anhydride of ϵ-*N*-benzyloxycarbonyl-α-*N*-carboxy-L-lysine (*L*). For this reason, the reaction mixture at the end of the process will contain only traces of the first anhydride and relatively large amounts of the second, and $K_{cop}$ will be virtually equal to $K_L$. The time variation of the composition of the copolymer formed is clearly shown in the electrophoretic pattern obtained in phosphate buffer at pH 7.8 for glutamic acid, lysine, and the copolymers of glutamic acid and lysine in the initial and final stages of copolymerisation (Fig. 18).

It is seen that the copolymers isolated at the beginning of the reaction were negatively charged and migrated towards the anode, like glutamic acid, while those isolated at the end of the reaction were positively charged and migrated towards the cathode, like lysine. The copolymers isolated after 25, 50, and 93% of conversion of the monomers contained glutamic acid and lysine residues in molar ratios of 3.0, 1.3, and 0.22 respectively.

The hypothesis concerning the mechanism of copolymerisation made it possible to derive an equation for the composition of the resulting copolymer as a function of

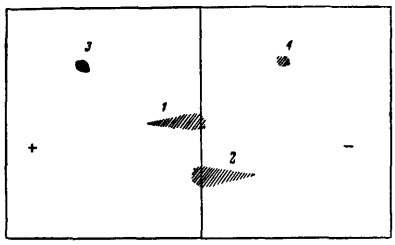



Fig. 18. Electrophoretic pattern of the copolymer of lysine and glutamic acid:
1) copolymer after 20% conversion; 2) copolymer after completion of reaction; 3) glutamic acid; 4) lysine.

time *t* and the initial composition of the reaction mixture $[G_0]/[L_0]$:

$$\frac{[G]_x}{[L]_x} = \frac{[G_0]}{[L_0]} \frac{1-\exp(K_G[I_0])t}{1-\exp(K_L[I])t}, \qquad (3)$$

where $[G]_x/[L]_x$ is the ratio of the glutamic acid and lysine residues in the copolymer.

Investigation of the copolymerisation of other anhydrides of *N*-carboxy-α-amino-acids (L-phenylalanine and ϵ-*N*-benzyloxycarbonyl-L-lysine, L-phenylalanine and γ-benzyl L-glutamate, glycine and ϵ-*N*-benzyloxycarbonyl-L-lysine, ϵ-*N*-benzyloxycarbonyl-L-lysine and DL-alanine, and γ-benzyl L-glutamate and DL-alanine) in dimethylformamide with diethylamine as the initiator established that the copolymerisation of these monomeric pairs proceeds similarly to the copolymerisation of the anhydrides of the *N*-carboxy-derivatives of γ-benzyl L-glutamate and ϵ-*N*-benzyloxycarbonyl-L-lysine, i.e. the rates of copolymerisation are equal to the sum of the rates of polymerisation of the corresponding individual monomers. The resulting copolypeptides had a molecular weight distribution close to the molecular weight distribution of the corresponding homopolymers.

A number of copolypeptides with different contents of L-glutamic acid, L-lysine, L-tyrosine, and L-phenylalanine have been synthesised[320] from the anhydrides of the corresponding N-carboxy-derivatives in absolute benzene at 25° using sodium methoxide as the initiator ($[M_0]/[I_0]$ = = 400). The molecular weights of the resulting copolymers were in the range 50 000–100 000. On the basic of kinetic data, the authors concluded that up to 90% conversion the copolymerisation is of first order, the reaction order departing from unity subsequently. Table 16 presents data on the composition of the initial reaction mixture and the copolypeptides.

A number of copolymers with *M* = 30 000–550 000 containing different amounts of L-glutamic acid, L-lysine, L-tyrosine, L-phenylalanine, and L-alanine were prepared later[321,322]. Blout and Idelson[323] obtained four high-molecular-weight copolypeptides of L-lysine and L-glutamic acid with a disordered structure and different molar ratios of the components (7 : 3, 6 : 4, 5 : 5, and 4 : 6) from the anhydrides of the *N*-carboxy-derivatives of γ-benzyl L-glutamate and ϵ-*N*-benzyloxycarbonyl-L-lysine in 1% solution of absolute benzene at room temperature using sodium methoxide as the initiator ($[M_0]/[I_0]$ = 200); the benzyl and benzyloxycarbonyl groups were subsequently removed with dry hydrogen bromide. The resulting copolypeptides had an average molecular weight ranging from 36 000 to 110 000,

TABLE 16. Dependence of the composition of copolypeptides on the composition of the initial mixture.

| Molar composition of initial mixture, % | | | | Molar composition of copolypeptides, % | | | |
|---|---|---|---|---|---|---|---|
| L-glutamic acid | L-lysine | L-phenyl-alanine | L-tyrosine | L-glutamic acid | L-lysine | L-phenyl-alanine | L-tyrosine |
| 50.0 | 33.3 | — | 16.7 | 49.8 | 34.3 | — | 15.9 |
| 47.6 | 38.4 | — | 4.0 | 56.4 | 37.8 | — | 5.8 |
| 58.0 | 42.0 | — | — | 59.0 | 41.0 | — | — |
| 58.0 | 41.0 | — | 1.0 | 56.1 | 42.6 | — | 1.3 |
| 58.0 | 38.0 | 4.0 | — | 61.6 | 33.4 | 5.0 | — |
| 56.0 | 36.0 | 8.0 | — | 57.1 | 33.9 | 9.0 | — |
| — | 100.0 | — | — | — | 100 | — | — |
| 100 | — | — | — | 100 | — | — | — |

and were readily soluble in water both at low and high pH, the solubility being a minimum in the region of neutral pH and depending on the composition and charge of the polypeptide, i.e. as regards their solubility they resembled polyamphoteric compounds and certain proteins.

In order to elucidate the dependence of the conformation of macromolecules on the composition of copolymers, the copolypeptides of *S*-methyl-L-cysteine and L-methionine with molar ratios of 1 : 9, 2 : 8, 3 : 7, and 5 : 5 and the copolymers of L-valine and L-methionine with the same molar ratios were synthesised[324] from the anhydrides of the corresponding *N*-carboxy-derivatives in nitrobenzene solution (4%) using sodium methoxide as the initiator ($[M_0]/[I_0]$ = = 200). For the same purpose, Karlson et al.[144] synthesised poly-$\beta$-benzyl esters of L- and D-aspartic acid, the poly-$\gamma$-benzyl ester of glutamic acid, and also a series of their copolymers by the polymerisation of a mixture of the anhydrides of the *N*-carboxy-derivatives in methylene chloride solution using sodium methoxide as the initiator ($[M_0]/[I_0]$ = 200) with different monomer ratios (1 : 9, 2 : 8, 3 : 7, 5 : 5, 7 : 3, 9 : 1). It was established that poly($\beta$-benzyl L-aspartate) and poly($\gamma$-benzyl L-glutamate) have an $\alpha$-spiral conformation but with the opposite direction of turns.

To study the effect of the ester group on the conformation and properties of poly-$\beta$-aryl esters of L-aspartic acid, a number of copolymers with different molar ratios of ester residues were prepared[302] by the copolymerisation of the anhydrides of $\beta$-*p*-nitrobenzyl and $\beta$-benzyl esters of *N*-carboxy-L-aspartic acid in dimethylformamide using diethylamine as the initiator. It was found that the copolymers have a spiral conformation, the introduction of more than 35–40% *p*-nitrobenzyl residues into poly($\beta$-benzyl L-aspartate) reversing the direction of the turns of the spiral.

By the copolymerisation of the anhydride of $\gamma$-benzyl *N*-carboxy-L-glutamate with the anhydrides of the *N*-carboxy-derivatives of L-alanine, L-leucine, and L-methionine at different ratios, Kulkarni and Blout obtained copolypeptides of interesting structure[325]. The $\gamma$-ester groups in the copolymers were replaced by 2-morpholinoethylamine residues. Such copolypeptides were readily soluble in water and showed a high content of the spiral conformation in solution. Addition to the solution of denaturing agents (urea) and salts caused their transition to a randomly coiled conformation.

To elucidate the influence of the steric configuration of the monomers and their ratio on the molecular weight and properties of the resulting copolypeptides[326], a number of polypeptides were synthesised by the copolymerisation of a 3% solution of a mixture of the anhydrides of the *N*-carboxy-derivatives in benzene saturated with water (70°, 24 h). The anhydrides of the *N*-carboxy-derivatives of the strongly basic D- or L-lysine and the acidic L-tyrosine were taken in 1 : 1 and 3 : 1 ratios. For the 3 : 1 monomer ratio, the resulting copolymers had a mean molecular weight of about 18 000 regardless of the configuration of the lysine. When the monomer ratio was 1 : 1, copolymers with the molecular weight $\overline{M}_W$ = 18 000 and $\overline{M}_W$ = 40 000 were obtained in the case of DL-lysine and D-lysine respectively as well as two polymers with different molecular weights in the case of L-lysine. The product with the higher molecular weight ($\overline{M}_W$ = 600 000) had a much higher content of L-tyrosine than the copolymer with the lower molecular weight ($\overline{M}_W$ = = 13 000).

To synthesise polypeptides having a structure similar to that of proteins, polypeptides were prepared[327] by the copolymerisation (using 0.5 mole % of sodium methoxide) of an equimolar mixture of the anhydrides of the *N*-carboxy-derivatives (4% solution in dimethylformamide) of L-lysine and L-glutamic acid, whose homopolymers have the $\alpha$-spiral conformation at pH above 10.5 and below 4.5 respectively. It was expected that such copolymers would have the $\alpha$-spiral conformation at a neutral pH. The resulting copolymers had a molecular weight of about 40 000 and were soluble in water. Up to 15% of the spiral conformation was detected in a neutral 0.15 M sodium chloride solution, the amount increasing to 50% at pH 4 and falling to zero at pH 12 or on removal of sodium chloride.

In an attempt to synthesise soluble amphoteric polypeptides, a study was made of the copolymerisation of the anhydrides of the *N*-carboxy-derivatives of L-glutamic acid, L-lysine, and L-phenylalanine in the ratios 1 : 1 : 3 and of L-glutamic acid, L-lysine, and L-leucine in the ratios 1 : 1 : 1.9.[328–330] The resulting polypeptides had typical amphoteric properties. They dissolved in dilute mineral acids and alkalis but not in water at pH between 4.0 and 10.8, which the authors of these studies explained by the aggregation of the copolypeptides on approach to the isoelectric point, which for the second polymer is 7.3.

Later Yuki[329] found that, in order to increase the solubility in the region of neutral pH, it is necessary to introduce serine residues, which together with threonine residues are responsible for the solubility of albumin. Copolypeptides containing L-glutamic acid and DL-serine in molar ratios of 4 : 1, 3 : 2, 2 : 3, and 1 : 4 were obtained. The last two copolymers were soluble even in water. The free copolymer containing L-glutamic acid, L-lysine, and DL-serine in the proportions 1 : 1 : 2 dissolved at any pH. The specific viscosity of this copolymer was found to be related to the pH (Fig. 19). The viscosity is a minimum at the isoelectric point (pH 7), which is characteristic of amphoteric polyelectrolytes.

Linear water-soluble copolypeptides of L-glutamic acid, L-lysine, and L-tyrosine in the proportions 2.8 : 2.6 : 1.0 have also been obtained[331], by the polymerisation of the anhydrides of the corresponding *N*-carboxy-derivatives in benzene solution using sodium methoxide as the initiator ($[M_0]/[I_0]$ = 400), with subsequent removal of the benzyloxycarbonyl group. The copolymer had $\overline{M}_W \simeq$ 49 000 and was soluble in water, but it dissolved in 0.15 M sodium chloride solution only at pH $>$ 10.

The following tyrosine-containing copolymers have been prepared[332] from the anhydrides of the corresponding *N*-carboxy-derivatives: glycine–L-tyrosine with molar ratios 1 : 1 ($\overline{M}_W$ = 7390) and 2 : 1 ($\overline{M}_W$ = 6520); L-phenylalanine–L-tyrosine with molar ratios 1 : 1 ($\overline{M}_W$ = 6370) and 2 : 1 ($\overline{M}_W$ = 8780); and glycine–DL-alanine–L-tyrosine with molar ratios 8 : 4 : 1 ($\overline{M}_W$ = 2360).

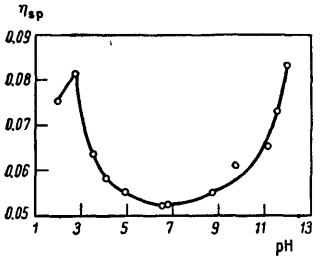



Fig. 19. Dependence of the intrinsic viscosity of the 1 : 1 : 2 glutamic acid–L-lysine–DL-serine copolymer on the pH of the medium.

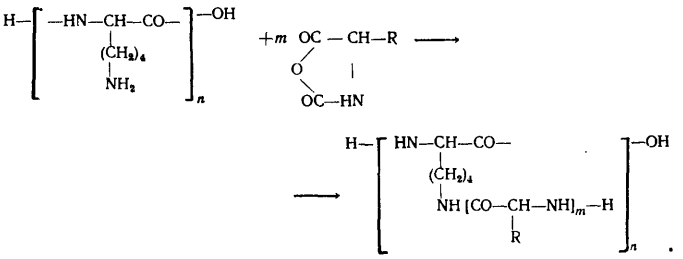
Since many physical and chemical properties of collagen and gelatine are determined by their large content of proline and hydroxyproline, model polypeptides containing the above amino-acid residues were synthesised [333]. Copolymers with the following monomer ratios were obtained by the copolymerisation at room temperature of a mixture of the anhydrides of the corresponding *N*-carboxy-derivatives in dioxan solution with diethylamine and triethylamine as the initiators or in pyridine without initiator: L-proline : glycine = 1 : 1, 1 : 2, and 1 : 3; L-proline : glycine : L-hydroxyproline = 1 : 2 : 1.

Copolypeptides containing L-arginine and L-leucine (2.3 : 1), which have a weak inhibiting effect on blood coagulation [334], and L-glutamic acid, 2,5-dihydroxyphenylalanine, and 3,4-dihydroxyphenylalanine, with weak catalytic properties [335], have been described.

Patents dealing with the method of preparation of copolypeptides and their application in various branches of industries have appeared in recent years. Thus a patent describes the preparation of copolypeptides by the treatment of solutions of the sodium salts of amino-acids (obtained from proteins, for example serum albumin) with the esters of chloro-acids, for example methyl chloroformate, and then with thionyl chloride, which yields a mixture of the anhydrides of the *N*-carboxy-derivatives; the latter is polymerised by the usual methods and converted into fibres and films [336]. Another patent [337] describes the method of preparation of copolypeptides from a mixture of the anhydrides of the *N*-carboxy-derivatives of L-leucine and phenylalanine. The molecular weight of the resulting copolypeptides exceeds 7000. These copolymers can be used for the preparation of fibres, sheets of various types, and moulds.

## 5. Preparation of Graft and Block Copolymers

Proteins react under mild conditions with the anhydrides of *N*-carboxy-derivatives of $\alpha$-amino-acids with the formation of polypeptidyl proteins. Like synthetic polypeptides with free amino-groups, proteins with free amino-groups function as polyinitiators in these reactions. Branched polyamino-acids have been prepared [338] by the polymerisation of the anhydrides of the *N*-carboxy-derivatives of DL-alanine, sarcosine, and L-lysine in the presence of poly-L-lysine, which functioned as the polymerisation initiator. Poly($\epsilon$-*N*-poly-DL-alanyl)-L-lysine with $n$ = 20 and $m$ = 20, water-soluble poly($\epsilon$-*N*-polysarcosyl)-L-lysine with $n$ = 20 and $m$ = 7, and branched poly($\epsilon$-*N*-poly-L-lysyl)-L-lysine with $n$ = 30 and $m$ = 15 have been obtained.



Similarly an aqueous solution of the hydrobromide of poly-L-lysine was used as a polyvalent initiator [339] for the polymerisation of the anhydride of $\gamma$-benzyl *N*-carboxyglutamate; the product was a branched polypeptide with $n$ = 280 and $m$ = 40, whose molecular weight was 1 500 000.

Poroshin [340] studied the reaction of the products of the primary degradation of casein (peptone hydrolysis mixture) with the anhydrides of the *N*-carboxy-derivatives of glycine, DL-alanine, and DL-proline in cooled dioxan solutions or in phosphate buffer. The reaction products were dialysed and then examined for their amino-acid content. It was established that in the case of polyglycylpeptone the degree of polymerisation ($m$) of glycine was 8–10 while for poly-DL-alanylpeptone $m$ was 18–20. The poly-DL-alanylpeptone was used for the polymerisation of the anhydride of *N*-carboxy-DL-proline, the products being poly-DL-alanyl--poly-DL-prolylpeptone which was readily soluble in water.

Konigsberg and Becker [341] grafted the anhydrides of the *N*-carboxy-derivatives of glycine and phenylalanine, with a [$^{13}$C]carboxyl carbon atom, on to a number of proteins (albumin, egg albumin, chymotrypsin, chymotrypsinogen, and lysosyme) in 0.067 M phosphate buffer at pH 6.2–7.8, in 0.1 M borate buffer at pH 8.2–9.1, and in sodium bicarbonate solution saturated with carbon dioxide, at pH 6.9–7.6. A gradual increase in the amount of grafted glycine was observed when the pH was altered from 6.2 to 9. Among the above solutions, the bicarbonate solution proved to be the most effective. For example, in phosphate buffer 41 moles of glycine residues were grafted on to one mole of protein, while under otherwise the same conditions in sodium bicarbonate solution 72 moles of glycine residues were grafted on to one mole of protein.

Kley et al. [342,343] treated bovine and rabbit blood albumin in bicarbonate solution or in phosphate buffer with the anhydrides of the *N*-carboxy-derivatives of glycine, leucine, phenylalanine, glutamic acid, and lysine. Microtitration showed an appreciable change in the amounts of carboxy-, imidazole, and $\alpha$- and $\epsilon$-amino-groups and established that grafting takes place partly (to the extent of 30%) at $\epsilon$-amino-groups.

A water soluble gliadine fraction was obtained by peptidylation [344]. For this purpose, DL-alanine and $N^4$-(3-hydroxypropyl)-L-asparagine were grafted on to gliadine. In the first case the reaction was carried out with the anhydride of *N*-carboxy-DL-alanine and gliadine in a mixture of dioxan and 0.05 M phosphate buffer (pH 6.8, 2°, 48 h), and water soluble poly-DL-alanylgliadine was isolated. The alanine content increased from 1.4% in gliadine to 23.6% in poly-DL-alanylgliadine, which corresponds to the grafting, on average, of 4.1 millimoles of alanine residues per gramme of gliadine. In the second case the reaction was

carried out with the anhydride of benzyl *N*-carboxyaspartate and gliadine in dimethylformamide (20°, 48 h). After its isolation, the polybenzyloxy-L-aspartylgliadine was kept for 30 min at 40° in propanolamine; the water-soluble *N*-(3-hydroxypropyl)-L-aspartylgliadine, enriched in aspartic acid residues up to 6.3 millimoles per gramme of gliadine, was then isolated by precipitation with 4 M acetic acid.

As pointed out by Katchalski and Sela[5], peptidylation does not interfere in most cases with the biological properties of proteins, but modifies a number of their other properties. Bearing in mind the stability of valine peptides towards acid hydrolysis, a study was made of the effect of grafting valine on to proteins on the biological and chemical properties of the latter[345]. Poly-DL-valylchymotrypsin, poly-DL-valyllysosyme, and poly-DL-valylinsulin were obtained by the reaction of the anhydride of *N*-carboxy-DL-valine with proteins at 4° in phosphate (pH 7.6) and borate (pH 8.5) buffers. The modified proteins are unusually stable towards acid hydrolysis. Hydrolysis is complete only after boiling with hydrochloric acid for 96 h. The enzymic activity of poly-DL-valylchymotrypsin is reduced only by 60% compared with the activity of the natural protein, while in the case of polyglycylchymotrypsin the activity is the same as that of the natural enzyme.

The effect of grafting L-tyrosine, L-tryptophan, L-phenylalanine, L-cysteine, L-proline, L-glutamic acid, L-lysine, L-alanine, L-serine, L-cyclohexylalanine, a mixture of L-glutamic acid and L-tyrosine, and of L-glutamic acid and L-cyclohexylalanine on the physiological activity of gelatine has been investigated[346]. It was found that when amino-acids with aromatic and cyclohexane rings in the side-chains are grafted on to gelatine, the physiological activity of the latter increases.

The problem of converting certain enzymes into water-insoluble products, with specific catalytic activity, is interesting because the "water-insoluble enzymes" can be readily removed from the reaction sphere. They can also be used for the preparation of columns with enzymic activity. For this purpose, Atara Bar-Eli and Katchalski[347] prepared polytyrosyltrypsin which was completely soluble and retained the enzymic activity of trypsin. When it was combined by diazotisation with the copolymer of *p*-aminophenylalanine and leucine, trypsin which was completely insoluble in water but nevertheless retained its enzymic activity was obtained. The latter could be used for the preparation of an active trypsin column for systematic amino-acid analysis.

Polytyrosyltrypsin containing 20–28 tyrosine residues grafted per mole of trypsin was prepared[348] by the polymerisation of the anhydride of *N*-carboxy-L-tyrosine in aqueous solution using trypsin as a polyvalent initiator. It was established that approximately half of the $\epsilon$-amino-groups of trypsin were acylated by the anhydride of *N*-carboxy-L-tyrosine, the average chain length of the grafted tyrosine being about 2.5. In contrast to trypsin, polytyrosyltrypsin is moderately soluble at pH 5–9. In its response to denaturing agents (urea, soya bean oil) and in its enzymic activity polytyrosyltrypsin is indistinguishable from trypsin.

A water-soluble block polypeptide consisting of a central poly-L-alanine block and two side poly-DL-glutamic acid blocks was synthesised[349]. The synthesis was carried out in benzene solution, the initial concentration of the anhydride of $\gamma$-benzyl *N*-carboxy-DL-glutamate being 2%. The initiator was n-hexylamine to which the anhydrides of *N*-carboxy-L-alanine and then of $\gamma$-benzyl *N*-carboxy-DL-glutamate were added in succession. The course of polymerisation was followed from the carbon dioxide evolved. According to the amino-acid analysis, the molar ratio of glutamic acid to alanine was 1.54. It was established that the molecule of the block polymer had a block consisting of 175 residues of L-alanine and two DL-glutamic acid blocks consisting of 325 residues altogether.

Any polymeric material containing free primary or secondary amino-groups can be used as a polyvalent initiator of the polymerisation of the anhydrides of *N*-carboxy-derivatives and not only natural proteins or synthetic poly-$\alpha$-amino-acids. Thus polymerisation of styrene in liquid ammonia with sodium as the initiator at -40°, with subsequent addition of ammonium chloride and removal of ammonium by distillation, yielded polystyrene containing 11% of nitrogen. The polymerisation of the anhydride of *N*-carboxyl-DL-valine in benzene solution of this polystyrene gave a product containing 24–29% of polystyrene and soluble only in *m*-cresol. The copolymers styrene–glycidyl methacrylate–DL-phenylalanine and styrene–glycidyl acrylate–DL-phenylalanine were prepared similarly[350]. These unusual polyamides are thermoplastic and exhibit exceptional stability towards solvents.


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# COPOLYMERISATION OF HYDROCARBONS IN THE PRESENCE OF IONIC CATALYSTS

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## 1. INTRODUCTION

Comparison of the relative activities of monomers in copolymerisation has been successfully used to study the mechanism of chain growth in radical polymerisation. The copolymerisation constants yield quantitative estimates of the relative reactivities of monomers and of the corresponding active centres.

During recent years a great deal of attention has been paid to catalysts which bring about polymerisation by an ionic mechanism, in connection with the use of catalysts of ionic type for the synthesis of several polymers having valuable properties, especially stereoregular polymers. Data on copolymerisation provide a deeper insight into the mechanism of chain formation in cationic, anionic, and coordination–ionic polymerisation.

## 2. THEORETICAL CONCEPTS

A theoretical treatment of the problems involved in radical copolymerisation has been given, and we must therefore examine the possibility of applying to ionic polymerisation the relations obtained. Scheme (1), suggested by Alfrey and Goldfinger[1], considers four possible modes of chain growth in the copolymerisation of two monomers: i.e. the reactivity of the growing polymeric ion is assumed to depend on the nature of the terminal active unit in the chain, and the rate constant for chain growth to be determined by the reactivity both of the monomer and of the active centre. Here M* denotes a cation in the case of cationic polymerisation, and an anion in anionic polymerisation, while in the case of coordination-complex polymerisation it represents a catalytic complex bound to the active end of the growing chain.

$$\begin{aligned} &\sim M_1^* + M_1 \xrightarrow{k_{11}} \sim M_1^*, \\ &\sim M_1^* + M_2 \xrightarrow{k_{12}} \sim M_2^*, \\ &\sim M_2^* + M_2 \xrightarrow{k_{22}} \sim M_2^*, \\ &\sim M_2^* + M_1 \xrightarrow{k_{21}} \sim M_1^*. \end{aligned} \qquad (1)$$

When the concentration of growing chains is constant, we can apply the relationship that has been termed the fundamental equation of copolymerisation[1,2]

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]}\right), \qquad (2)$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are copolymerisation constants for the first and second monomers, representing the relative activities of the monomers towards addition to the active centres $\sim M_1^*$ ($r_1$) and $M_2^*$ ($r_2$). Eqn. (2) is applicable to ionic copolymerisation only if the concentration of active centres remains constant during such processes. The necessity for this condition had already been noted by Landler[3,4], who was the first to generalise data on ionic polymerisation.

The presence of a constant concentration of active centres in several cases of cationic[5,6] and anionic[7-9] polymerisation has now been established by direct measurement, from the ultraviolet absorption spectrum, of the concentration of growing polymeric cations and anions during polymerisation. In the presence of complex organometallic catalysts, too, the concentration of active centres is usually constant as a result of the catalytic character of the process[10]. Consequently the general equation of copolymerisation is applicable to most cases of ionic copolymerisation. The relative reactivity of monomers in the growth reaction can be measured by the copolymerisation constants calculated from experimental data by the usual procedures developed for radical copolymerisation — by the intersection method based on the integral or differential equation of Mayo and Lewis[2,11] by Alfrey's method of trial and error[1], or by the method of Fineman and Ross[12].

Constancy of the concentration of active centres has different causes in radical and in ionic polymerisation. In the former case it arises from the fact that, during a given period of time, equal quantities of radicals are formed by initiation and disappear by termination reactions which lead to the destruction of active centres. In ionic processes, active centres cannot be destroyed by interaction with one another, because the polymer chains bear charges of the same sign[13]. Therefore the constancy of the concentration of active centres is not due to a balance between processes of creation and destruction but to the fact that many ionic processes are unaccompanied by the destruction of active centres — by processes of chain termination[6,10,13,14] — and active centres, once formed, can cause chain growth until no monomer remains. If in such cases initiation is sufficiently rapid, and formation of all the active centres is complete within a time which is considerably shorter than the duration of the whole process of polymerisation, a constant concentration of active centres will be established during the process[5-10].

In cationic polymerisation, initiation is usually rapid, and all the active centres begin to take part in chain growth almost at the same time[6,15]. With anionic polymerisation cases are known in which initiation occurs throughout the process of polymerisation, and then the condition that the concentration of active centres should be constant is not satisfied. This is observed when polymerisation occurs under the influence of organolithium compounds in hydrocarbon solvents at a catalyst concentration exceeding 0.02 M.[9,16] The low rate of initiation in these cases is explained by the high degree of association of the organolithium compound[9]. When copolymerisation is carried out under such conditions, account must be taken, in deriving the equation for the composition of the copolymer, of the initiation stage[17] (i.e. of the rate of interaction with the catalyst of each of the two monomers)

$$A^- + M_1 \xrightarrow{k_1} AM_1^-, \qquad A^- + M_2 \xrightarrow{k_2} AM_2^-, \qquad (3)$$

and only after this are the usual four possible growth reactions (1) considered.

Even in this case, however, the Alfrey–Goldfinger equation (2) is incapable of giving the composition of the copolymer correctly only when the anions formed from the different monomers differ greatly in activity. If the initiator can react with both monomers, while the anion $AM_2^-$ is practically unable to add on the monomer $M_1$, the composition of the copolymer in the initial stages of polymerisation will be represented by the equation

$$\frac{d[M_1]}{d[M_2]} = (k_{11}/k_{12})(k_1/k_2)\left(\frac{[M_1]}{[M_2]}\right)^2, \qquad (4)$$

instead of by the fundamental equation of copolymerisation.

In the copolymerisation of styrene with methyl methacrylate, for example, the polystyrene anion initiates the polymerisation of both these monomers[18], whereas the poly(methyl methacrylate) anion does not bring about the polymerisation of styrene[19]. In this case — Eqn. (4) — the ratios of the mole fractions of styrene and methyl methacrylate in the copolymer and the monomer mixture are actually linked by a relation of the second degree[17].

The above can be summarised in the statement that equations obtained from an examination of radical processes of copolymerisation are general for all mechanisms of polymerisation, being inapplicable only in isolated special cases.

We at once adopted Alfrey and Goldfinger's scheme (1) to represent processes of ionic copolymerisation, i.e. we took into account the different reactivities both of the monomers and of the active centres formed from them. Differing activities of two polymeric anions is clearly exhibited in the above case of the copolymerisation of styrene and methyl methacrylate[18,19], in which the less active anion — the poly(methyl methacrylate) anion — does not initiate polymerisation of the less active monomer (styrene). Comparison based on quantum-mechanical calculations[20] of the reactivities of various monomers and of the ions obtainable from them has shown that, in cationic and anionic polymerisation, the more active monomer always yields the less active ion, just as in radical polymerisation the more active monomer gives the less active radical[21,22]. The correctness of this conclusion is confirmed by measurements of the absolute rate constants of all four stages of the growth reaction in copolymerisation. In the case of cationic polymerisation such data have been obtained[23] for the copolymerisation of isobutyl vinyl ether with chloroethyl vinyl ether under the influence of iodine in dichloroethane solution (Table 1). The less active monomer — 2-chloroethyl vinyl ether ($k_{12} < k_{11}$) — forms the more active cation ($k_{22} > k_{12}$).

TABLE 1. Absolute rate constants (in litre × × mole$^{-1}$ min$^{-1}$) for the growth reactions in the copolymerisation of isobutyl vinyl ether ($M_1$) and 2-chloroethyl vinyl ether ($M_2$) in the presence of iodine in dichloroethane solution at 30°.

| $k_{11}$ | $k_{12}$ | $k_{22}$ | $k_{21}$ |
|---|---|---|---|
| 390 | 195 | 520 | 260 |

In the case of anionic polymerisation under the influence of "live" polymers, monomers which are less active than styrene ($k_{12} < k_{11}$) give an anion to which styrene adds on more rapidly than to the anion of polystyrene ($k_{21} > k_{11}$) (Table 2)[24]. Thus with anionic polymerisation, too, the less active monomer forms the more active anion. The only exception is provided by the anion of the dimer of 1,1-diphenylethylene, but this is due to the greater steric hindrance to the addition of styrene caused by the two phenyl groups of the anion.

Until recently most investigators, when discussing experimental data on ionic copolymerisation, ignored differences in reactivity between polymeric ions differing in their

TABLE 2. Absolute rate constants (in litre mole$^{-1}$ s$^{-1}$) for the growth reactions in the copolymerisation of styrene ($M_1$) with other monomers in the presence of "living" polymers with Na as counter-ion in tetrahydrofuran solution. (Concentration of active centres 0.003 M at 25°.)

| $M_2$ | $e_1$ | $e_2$ | $k_{11}$ | $k_{12}$ | $k_{22}$ | $k_{21}$ |
|---|---|---|---|---|---|---|
| α-Methylstyrene | —0.80 | —1.27 | 550 | 26 | 2.5 | 800 |
| β-Methylstyrene | —0.80 | | 550 | 18 | | |
| 2,4-Dimethylstyrene | —0.80 | | 550 | 160 | | |
| p-Methylstyrene | —0.80 | —0.88 | 550 | 180 | 220 | 1000 |
| o-Methylstyrene | —0.80 | —0.78 | 550 | 330 | | |
| 1,1-Diphenylethylene | —0.80 | | 550 | 350 | | 1 |
| 2-Vinylpyridine | —0.80 | —0.50 | 550 | 30000 | 3500 | very low rate |

active terminal units ($\sim M_1^*$ and $\sim M_2^*$). It was usually accepted that the rate of addition of a monomer is independent of the nature of the end group in the polymeric ion[23-33]. Only two chain-growth reactions were then taken into account in copolymerisation[34]. Such a simplified view of ionic copolymerisation arose from an incorrect interpretation of the frequently observed cases of ideal copolymerisation in ionic processes[4,33]. In ideal copolymerisation $r_1 r_2 = 1$, i.e. $k_{11}/k_{12} = k_{21}/k_{22}$. Although it is sufficient, for this equation to be valid, that the rates of addition of monomer $M_1$ to the two polymeric ions should differ from the rates of addition of $M_2$ to these ions by the same factor ($k_{11} = Xk_{21}$ and $k_{12} = Xk_{22}$), Flory concluded that each monomer adds on to any ion at the same rate, i.e. $k_{11} = k_{21}$ and $k_{12} = k_{22}$, and thus the equation for the composition of the copolymer assumes the form of Wall's equation[34]

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1]}{k_{22}[M_2]}. \qquad (5)$$

It follows from these concepts that the copolymerisation constant for monomer $M_1$ with monomer $M_2$, $r_1 = 1/r_2 = k_{11}/k_{22}$, should be equal to the ratio of the rate constants for chain growth in the homopolymerisation of these monomers. However, this conclusion is contradicted by the experimental results. In the copolymerisation of butadiene with isoprene[29] and of butadiene[26,27,32] or isoprene[25,30,31] with styrene under the influence of organolithium compounds, the more active monomer (according to copolymerisation data) possesses the lower rate of homopolymerisation. In order to explain the "reversal of activity" the concept is introduced[25-32,35-48] of a selective solvation of an active centre by one of the monomers, which thus proves more active in copolymerisation. Calculation[26] based on kinetic data for the copolymerisation of butadiene with styrene in the presence of butyllithium has shown that, in order to explain the experimental differences between the copolymerisation constant and the ratio of the rates of homopolymerisation, the ability of butadiene to solvate an active centre must exceed that of styrene by a factor of 80. It is difficult to explain such a large difference in solvating power by the structural differences between butadiene and styrene.

If differences in the activity of polymeric ions towards the same monomer are taken into account, the contradictions discussed above do not arise. The more active monomer yields the less active ion[20]; if the ions exhibit greater differences in activity than do the monomers, the rate of homopolymerisation of the more active monomer will be smaller than that of the less active monomer ("reversal" of activity). Direct measurement of all four rate constants for chain growth in the copolymerisation of butadiene with styrene in the presence of butyllithium[35] has shown that the rates of addition of the butadiene molecule to the anions of polystyrene and of polybutadiene differ by a factor of 75, while the rates of addition of the two different monomers (styrene and butadiene) to the same anion (polystyrene or polybutadiene) differ by factors of 15 and 3 respectively. Thus it is evident that in this case the "reversal of activity" of the monomers in homopolymerisation compared with copolymerisation[26,27] is actually due to the greater differences in activity between the polymeric anions than between the monomers, not to selective solvation of an active centre by one of the monomers. If the simultaneous occurrence of four different reactions of chain growth is taken into account, it is possible[36] by means of the usual kinetic equations to calculate a rate curve for the copolymerisation of butadiene with styrene which agrees with the experimental results. Consequently the results of a kinetic study of copolymerisation also show that, in ionic as in radical copolymerisation, ions with different end-groups, as well as the monomers, show differences in activity.

Copolymerisation constants can be used to compare the relative activities of a series of monomers only when they relate to copolymerisation of all these monomers with the same standard monomer. It is therefore desirable for ionic copolymerisation to generalise all known values of relative reactivity in the form of a scheme resembling the $Q-e$ scheme of Alfrey and Price[21]. With ionic, in contrast to radical, copolymerisation however, the copolymerisation constants are usually found to depend on the nature of the catalyst and of the polymerisation medium[25,26,28,31,32,37-44] (Table 3, pairs 3, 4, 7, 8, and 11; Table 5, pairs 1, 4–6, 10, and 12). As a consequence, it has not yet proved possible to set up a scheme which will take into account all the factors influencing the relative activity of monomers in ionic copolymerisation.

Hammett's rule[45,46] is widely used for the quantitative correlation of the reactivity of monomers in ionic copolymerisation with their structure. This rule links the rate constants for reactions of benzene derivatives with the electronic characteristics of their substituents in the formula

$$\log(K/K_0) = \rho\sigma, \qquad (6)$$

where $K$ and $K_0$ are rate constants (or equilibrium constants) for substituted and unsubstituted benzene derivatives in reactions of a given type, $\rho$ is a constant characteristic of a given reaction (the reaction constant), and $\sigma$ is a constant characterising a given constituent in all types of reactions. The actual value of the substituent constant $\sigma$ depends on the type of reaction taken as standard, and is a quantitative expression of the electron-acceptor or electron-donor character of this substituent. The standard is chosen in such a way that the $\sigma$ constant of electron-acceptor substituents is positive[45,46]. The influence of the polar effects of substituents on the rate constants is associated with a change in the activation energy during the reaction; if steric effects predominate, deviations from the Hammett rule are observed[45,46]. In comparing the activities of monomers undergoing polymerisation, the polar effect can be allowed for, not by means of the Hammett $\sigma$ constant, which is known only for substituents in the benzene ring, but from the magnitude of the polar factor in the $Q-e$ scheme, since the quantity $e$ also characterises the electron-donating or electron-accepting power of a substituent,

TABLE 3. Copolymerisation in the presence of catalysts of cationic type.

| No. of pair | $M_1$ | $M_2$ | Catalyst | Medium | $r_1$ | $r_2$ | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 1 | styrene $e=-0.80$ | *p*-chlorostyrene $e=-0.33$ | $SnCl_4$ | $CCl_4$ | 2.5±0.4 | 0.30±0.03 | 56 |
| | | | $SnCl_4$ | $CCl_4$ | 2.7±0.3 | 0.35±0.05 | 65 |
| | | | $SnCl_4$ | $CCl_4$–nitrobenzene (1 : 1) | 2.2±0.2 | 0.45±0.02 | 56 |
| | | | $SnCl_4$ | nitrobenzene | 2.2±0.05 | 0.35±0.05 | 56 |
| | | | $AlBr_3$ | $CCl_4$–nitrobenzene (1 : 1) | 2.2±0.2 | 0.34±0.05 | 58 |
| | | | $FeCl_3$ | ditto | 2.0±0.1 | 0.43±0.03 | 58 |
| | | | $TiCl_4$ | » | 2.2±0.2 | 0.45±0.02 | 58 |
| | | | $TCl_4+CCl_3COOH$ | » | 2.0±0.4 | 0.50±0.05 | 58 |
| | | | $I_2$ | dichloroethylene | 2.5 | 0.45 | 68 |
| 2 | | *m*-chlorostyrene | $SnCl_4$ | nitrobenzene | 3.3±0.4 | 0.3 ±0.05 | 57 |
| 3 | | *p*-methylstyrene | $I_2$ | dichloroethylene | 0.2 | 4.2 | 68 |
| | | $e=-0.88$ | $TiCl_4$ | toluene, 0° | 0.54±0.4 | 3.6 ±0.1 | 37 |
| | | | $TiCl_4$ | toluene, −78° | 0.55±0.06 | 1.18±0.06 | 37 |
| | | | $TiCl_4$ | $CCl_4$ | 0.32±0.10 | 1.08±0.14 | 37 |
| | | | $TiCl_4$ | nitrobenzene | 0.68±0.04 | 1.10±0.05 | 37 |
| | | | $SnCl_4$ | $CCl_4$–nitrobenzene (1 : 1) | 0.48±0.07 | 1.18±0.14 | 37 |
| 4 | | *p*-methoxystyrene $e=-1.11$ | $SnCl_4$ | nitrobenzene | (0.01) | 100 | 57 |
| | | | $SnCl_4$ | $CCl_4$–nitrobenzene (1 : 1) | −0.04±0.04 | 19±3 | 37 |
| | | | $SnCl_4$ | ditto | −0.02±0.07 | 29±5 | 37 |
| | | | $AlCl_3$ | » | 0.34±0.05 | 11±1 | 37 |
| | | | $TiCl_4$ | » | 0.12±0.07 | 14±3 | 37 |
| | | | $TiCl_4$ | $CCl_4$ | 0.05±0.04 | 46±3 | 37 |
| | | | $TiCl_4$ | $CCl_4$ | 0.00±0.03 | 31±6 | 37 |
| | | | $TiCl_4$ | $CCl_4$–nitrobenzene (1 : 1) | −0.12±0.12 | 35±5 | 37 |
| | | | $TiCl_4$ | nitrobenzene | 0.48±0.08 | 5.6 ±0.8 | 37 |
| | | | $TiCl_4$ | nitrobenzene | 0.22 | 7.6 | 37 |
| | | | $TiCl_4$ | toluene | 0.01 | 72 | 37 |
| | | | $TiCl_4$ | toluene | −0.33±0.3 | 12±2 | 37 |
| 5 | | *m*-methoxystyrene | $SnCl_4$ | nitrobenzene | 0.90±0.15 | 1.1±0.15 | 57 |
| 6 | | *m*-nitrostyrene $e=+0.81$ | $SnCl_4$ | » | 20±4.0 | 0.03±0.03 | 57 |
| 7 | | 3,4-dichlorostyrene | $SnCl_4$ | $CCl_4$ | 3.1±0.1 | 0.48±0.08 | 38 |
| | | | $AlBr_3$ | » | 6.8±0.8 | 0.0 ±0.2 | 38 |
| | | | $AlCl_3$ (solid) | » | 2.8±0.2 | 0.45±10 | 38 |
| | | | $TiCl_4$ | » | 7.2±0.5 | 0.38±0.20 | 38 |
| | | | $BF_3\cdot(C_2H_5)_2O$ | » | 5.9±0.2 | 0.27±0.07 | 38 |
| | | | $ZnCl_2+(C_2H_5)_2O$ | » | 4.2±0.2 | 0.10±0.05 | 38 |
| | | | $H_2SO_4$ | nitrobenzene | 3.0±0.5 | 0.20±0.15 | 38 |
| | | | $AlCl_3$ (solid) | » | 3.5±0.5 | 0.0 ±0.2 | 38 |
| 8 | | *α*-methylstyrene $e=-1.27$ | $SnCl_4$ | $C_2H_5Cl$ | 0.05 | 2.90 | 67 |
| 9 | | isoprene $e=-1.22$ | $SnCl_4$ | $C_2H_5Cl$ | 0.8 | 0.1 | 65 |
| 10 | | butadiene $e=-1.05$ | $AlCl_3$ | monomer | $r_1 >$ | $r_2$ | 60 |
| 11 | | chloroprene $e=-0.02$ | $BF_3\cdot(C_2H_5)_2O$ | cyclohexane | 15.6 | 0.24 | 61 |
| | | | $BF_3\cdot(C_2H_5)_2O$ | n-hexane | 12.8±0.3 | 0.06±0.01 | 40 |
| | | | $BF_3\cdot(C_2H_5)_2O$ | nitroethane | 33.0±0.5 | 0.15±0.05 | 40 |
| | | | $AlBr_3$ | benzene | 6.9±0.5 | 0.04±0.01 | 40 |
| | | | $AlBr_3$ | nitrobenzene | 16.0±0.05 | 0.065±0.01 | 40 |
| 12 | | 2-methylpropene $e=-0.96$ | $AlCl_3$ | $CH_3Cl$ | 1.99±0.24 | 9.02±0.77 | 66 |
| | | | $SnCl_4$ | $C_2H_5Cl$ | 0.17 | 1.6 | 67 |
| 13 | *p*-chlorostyrene $e=-0.33$ | *p*-methylstyrene $e=-0.88$ | $SnCl_4$ | nitrobenzene | 0.22±0.05 | 4.5 ±0.7 | 57 |
| | | | $I_2$ | dichloroethylene | 0.19 | 6.5 | 68 |
| 14 | | *m*-methoxystyrene | $SnCl_4$ | nitrobenzene | 0.38±0.05 | 2.6 ±0.4 | 57 |
| 15 | | *p*-bromostyrene $e=-0.35$ | $SnCl_4$ | » | 1.0 ±0.1 | 1.0 ±0.1 | 57 |
| 16 | | *p*-ethylstyrene | $SnCl_4$ | $CCl_4$–nitrobenzene (1 : 1) | 0.29±0.04 | 4.1 ±0.5 | 59 |
| 17 | | *α*-methylstyrene $e=-1.27$ | $SnCl_4$ | ditto | 0.35±0.05 | 15.0±1.5 | 59 |
| | | | $SnCl_4$ | $CCl_4$ | 0.3 ±0.05 | 15.5±1.5 | 57 |
| 18 | | *trans*-*β*-methylstyrene | $SnCl_4$ | $CCl_4$–nitrobenzene (1 : 1) | 0.74±0.06 | 0.32±0.04 | 59 |
| 19 | | *cis*-*β*-methylstyrene | $SnCl_4$ | ditto | 1.0 ±0.1 | 0.32±0.2 | 59 |
| 20 | | *β*-ethylstyrene | $SnCl_4$ | » | 0.88±0.33 | 0 | 59 |
| 21 | *p*-chlorostyrene $e=-0.33$ | 2-methylpropene $e=-0.96$ | $SnCl_4$ | benzene | 2.8 ±0.3 | 12.2±1.0 | 39,40 |
| | | | $SnCl_4$ | nitrobenzene | 1.25±0.1 | 8.6±0.2 | 39,40 |
| | | | $AlBr_3$ | benzene | 0.99±0.10 | 1.14±0.10 | 39,40 |
| | | | $AlBr_3$ | n-hexane | 1.02 | 1.01 | 39,40 |
| | | | $AlBr_3$ | dichloroethylene | 0.89 | 2.80 | 39,40 |
| | | | $AlBr_3$ | nitrobenzene | 0.53±0.04 | 14.9±0.2 | 39,40 |
| | | | $AlBr_3$ | benzene–nitrobenzene (1 : 1) | 0.75 | 18.0 | 39,40 |
| | | | $AlBr_3$ | nitromethane | 0.73±0.05 | 22.2±0.5 | 39,40 |
| 22 | *α*-methylstyrene $e=-1.27$ | *p*-methoxystyrene $e=-1.11$ | $SnCl_4$ | nitrobenzene | 0.30±0.1 | 15±5 | 57 |
| 23 | | *p*-dimethylaminostyrene $e=-1.37$ | $SnCl_4$ | » | 0.035±0.015 | 31±19 | 57 |
| 24 | | *m*-methoxystyrene | $SnCl_4$ | » | 5±1 | 0.3±0.1 | 57 |
| 25 | | isoprene $e=-1.22$ | $SnCl_4$ | $C_2H_5Cl$ | 7.1 | 1.6 | 62 |
| 26 | *p*-methylstyrene $e=-0.88$ | *p*-methoxystyrene $e=-1.11$ | $TiCl_4$ | nitrobenzene | 0.58±0.06 | 1.54±0.10 | 37 |
| | | | $TiCl_4$ | $CCl_4$ | −0.03±0.07 | 3.7 ±0.4 | 37 |
| | | | $SnCl_4$ | $CCl_4$–nitrobenzene (1 : 1) | 0.14±0.14 | 1.9 ±0.3 | 37 |
| | | | $I_2$ | dichloroethylene | 0.30 | 4.3 | 68 |
| 27 | isoprene $e=-1.22$ | propene | $AlCl_3$ | $C_2H_5Cl$ | 0.50 | 0.23 | 64 |
| 28 | | 2-methylpropene $e=-0.96$ | $AlCl_3C_2H_5$ | benzene | $r_1$ | $<r_2$ | 66 |
| 29 | | butadiene $e=-1.05$ | $AlCl_3C_2H_5$ | » | 3.4±0.4 | 0.12±0.015 | 69 |
| 30 | butadiene $e=-1.05$ | 2,3-dimethylbutadiene $e=-1.81$ | $AlCl_3C_2H_5$ | » | 0.053±0.005 | 4.24±0.41 | 70 |

and is linearly related with $\sigma$, as has been shown for substituted styrenes[47,48].

Work on ionic copolymerisation is discussed in greater detail below. Results on copolymerisation in the presence of alkali metals and of the sodium–naphthalene complex are not included, since these processes involve the intermediate formation of ion-radicals[13,49,50], and may be complicated by simultaneous polymerisation by ionic and radical mechanisms[51-54].

## 3. COPOLYMERISATION BY MEANS OF CATALYSTS OF CATIONIC TYPE

In polymerisation by a cationic mechanism the growing chain is a carbonium ion[5,15,55]. Various Lewis acids are catalysts for cationic polymerisation. Results obtained for processes of copolymerisation occurring by a cationic mechanism are given in Table 3.[37-41,56-70]. Comparison of the copolymerisation constants shows that, when reacting with the same polymeric cation, the more active monomer is usually that in which the electron density on the double bond is the greater, in agreement with the view that growth of the polymer chain takes place with the latter in the form of a cation. The above rule is observed in the copolymerisation of styrene (Table 3, pairs 1–8), *p*-chlorostyrene (pairs 13–20), and $\alpha$-methylstyrene (pairs 22-24) with nuclear-substituted styrenes, of styrene with chloroprene (pair 11) and with methylpropene (pair 12), of *p*-chlorostyrene with methylpropene (pair 21), of $\alpha$-methylstyrene with isoprene (pair 25), of *p*-methylstyrene with *p*-methoxystyrene (pair 26), and of butadiene with isoprene and with 2,3-dimethylbutadiene (pairs 29 and 30). An exception is observed only in the copolymerisation of styrene with isoprene and with butadiene (pairs 9 and 10), when styrene is the more active monomer, although it has the lower value of $e$ in the $Q$–$e$ scheme (and hence a lower electron density on the double bond). Gantmakher and Medvedev[62] explain this exception by the participation of double bonds of the polymer in interaction with the active centres, as a result of which data on the composition of the copolymer do not reflect the true relation between the activities of the monomers in chain growth.

By means of the Hammett rule it is possible to obtain a quantitative estimate of the variation in copolymerisation constants with the electron-donor or electron-acceptor character of the substituent. The copolymerisation of *para*-substituted styrenes satisfies the relationship

$$\ln r_1 = \ln (k_{11}/k_{12}) = \ln k_{11} - \ln k_{12} = \rho_1(\sigma_1 - \sigma_2), \qquad (7)$$

where $\sigma_1$ and $\sigma_2$ are the constants of the substituents in the monomers $M_1$ and $M_2$. Table 4, taken from a paper by Tobolsky and Boudreau[37], gives values of $\rho_1$ for the copolymerisation of substituted styrenes in the presence of various catalysts (from data for the pairs 2–6 and 13–15 in Table 3). The negative value of the reaction constant $\rho_1$ also agrees with the concept of cationic chain growth in the presence of Lewis acids as catalysts. Furthermore, the linear dependence of $\ln r_1$ on $\sigma$ shows that differences in the relative activity of *para*-substituted styrenes are determined not by steric but by polar factors — by differences in electron density on the double bonds of the monomers.

TABLE 4. Reaction constants $\rho_1$ in the cationic copolymerisation of substituted styrenes.

| Catalyst | Medium | $\rho_1$ | Monomer $M_1$ |
|---|---|---|---|
| $TiCl_4$ | nitrobenzene | −1.5±0.4 | styrene |
| $TiCl_4$ | » | −2.2±0.4 | *p*-methoxystyrene |
| $TiCl_4$ | » | −1.1±0.5 | *p*-methylstyrene |
| $SnCl_4$ | $CCl_4$–nitrobenzene (1:1) | −4.0±0.5 | styrene |
| $SnCl_4$ | ditto | −3.3±1.0 | *p*-methylstyrene |
| $TiCl_4$ | $CCl_4$ | −4.2±0.8 | styrene |

Steric hindrance determines the relative activity of the monomers only when $\beta$-substituted styrenes are involved in copolymerisation (pairs 18–20). When reacting with a $\beta$-alkylstyrene end-group, the *p*-chlorostyrene molecule is more active than the $\beta$-alkylstyrene molecule ($r_2 < 1$), although the electron density on the double bond in *p*-chlorostyrene is smaller owing to the presence of an electron-acceptor substituent in the ring[59]. In copolymerisation with $\alpha$-methylstyrene the relative activity of the monomers is determined by the relative electron densities on their double bonds (pairs 8, 17, and 22–25). This difference in steric hindrance, produced by substituents in the $\alpha$- and $\beta$-positions of the vinyl group in styrene, is consistent with the view that attack by the polymeric carbonium cation is directed mainly on the $\beta$ carbon atom of styrene (since the phenyl-substituted cation should be thermodynamically the more stable[71]).

The influence of the gegenion and that of the solvent on the kinetics of cationic homopolymerisation are usually attributed[55] to changes in the concentration of active cations resulting from different degrees of dissociation in solvents differing in dielectric constant or in ion-pairs with different gegenions. However, variation in ionic concentration would probably affect equally all four rates of growth in copolymerisation, and then the copolymerisation constants would not depend on the nature of the solvent or on that of the gegenion. Nevertheless, the relative activities of the monomers depend in several cases (pairs 3, 4, 8, 11, and 21) both on the nature of the gegenion and on that of the medium in which polymerisation is carried out. In the presence of different catalysts in the same solvent, the copolymerisation constants depend to different extents on the polarity of the monomer (this corresponds to different values of the reaction constant $\rho_1$ in the copolymerisation of substituted styrenes, Table 4). Variation in the copolymerisation constants when the process is carried out in different solvents or in the presence of different catalysts shows that, at least in some solvents, chain growth involves not free ions but ion-pairs.

Thus study of copolymerisation in the presence of Lewis acids has shown that — (1) the relationship between the relative activities of the monomers and the electron densities on their double bonds corresponds to a cationic mechanism of chain growth; (2) steric hindrance produced by $\beta$-substituents in styrene is consistent with the view that the styrene molecule adds on to the growing chain by the $\beta$ carbon atom; and (3) since the use of different catalysts and solvents affects not only the kinetics of homopolymerisation but also the copolymerisation constants, the growing chain is usually not a free cation, chain growth probably occurring in ion-pairs.

## 4. COPOLYMERISATION BY MEANS OF CATALYSTS OF ANIONIC TYPE

The polymerisation of hydrocarbon monomers by an anionic mechanism is initiated by various organometallic

compounds and their complexes. According to modern views, first put forward by Ziegler[72], growth of the polymer chain occurs by introduction of monomer at a polarised metal–carbon bond, when separation of the charges on the polarised bond may lead to the formation of an ion-pair in which the active end of the growing chain is the anion[33,72-75]. In a series of organometallic compounds of the alkali metals, the ionic character of the bond increases on passing from lithium to sodium, potassium, rubidium, and caesium[76], as is shown in the polymerisation of dienes by a change in the structure of the polymer. In the presence of organolithium compounds, the polymers formed consist of 1,4 monomeric units; the polymers formed under the influence of organopotassium compounds contain a considerable quantity of 1,2 units[72,73]. The structure of the polydiene chain changes in the same direction if polymerisation under the influence of organolithium compounds is carried out in the presence of substances capable of forming "onium" complexes (ethers, amines, sulphides[72-75,77,78]). Hence it can be concluded that the ionic character of the lithium–carbon bond is enhanced by the coordination with lithium of electron-donor compounds, and in such solvents as tetrahydrofuran the process of polymerisation under the influence of organolithium compounds approaches in character a typically anionic polymerisation (such as, for example, polymerisation under the influence of organopotassium compounds)[74,75,77]. The influence of the counterion on the kinetics of polymerisation and the structure of the polymer shows that, in anionic polymerisation, chain growth involves not the free anion but an ion-pair or the polarised metal–carbon bond. Data on copolymerisation by an anionic mechanism are given in Table 5.[24,25,32,35,37,43,44,69,70,73,79-86]

Study of the composition of isoprene–styrene (Table 5, pair 6 [25]) and butadiene–isoprene (pair 12 [77]) copolymers shows that practically the same composition is obtained in the presence of organopotassium or organosodium compounds as in the presence of complexes of organolithium compounds with electron-donor substances. These results support the view that, under the influence of complexes of organolithium compounds, polymerisation occurs by the same mechanism as in the presence of organopotassium and organosodium compounds, i.e. by a typical anionic mechanism. However, it must be stressed that, even in tetrahydrofuran solution, chain growth by an anionic mechanism occurs in an ion-pair, and does not involve a free anion, since the rate of polymerisation of styrene in tetrahydrofuran depends on the nature of the alkali-metal ion[24].

The dependence of the relative activity of monomers on the electron density at the double bonds in the case of copolymerisation in the presence of organopotassium and organosodium compounds and of complexes of organolithium compounds with tetrahydrofuran supports the view that the active end of the growing chain is anionic in character. Actually, determinations of copolymerisation constants or of the composition of the copolymers indicate that the reactivity of the monomers in the growth reaction of a polymeric anion diminishes in the sequence

*p*-chlorostyrene ($e=-0.33$) > styrene ($e=-0.80$) > butadiene ($e=-1.05$) > isoprene ($e=-1.22$) > 2,3-dimethylbutadiene ($e=-1.81$),

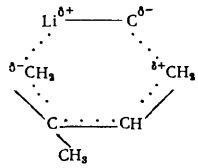
with increasing electron density on the double bonds in the monomer (with increase in $e$ in the $Q-e$ scheme). The rate constants for the addition of various derivatives of styrene to "live" polystyrene in tetrahydrofuran solution obey the Hammett rule, with $\rho = +0.5$ having a positive value in conformity with the assumption of an anionic mechanism for chain growth. In the copolymerisation of butadiene with isoprene and with 2,3-dimethylbutadiene in tetrahydrofuran[69,70,84] or in hexane[28,29] (pairs 11 and 12 in Table 5), and also of styrene with *p*-methylstyrene and with *p*-methoxystyrene (pairs 2 and 3), the Hammett rule is obeyed by quantities representing the reactivities of the monomers towards the same active terminal unit

$$\left(\frac{1}{r_1}=\frac{k_{12}}{k_{11}}\right).$$

Instead of the $\sigma$ constants, let us use the polar factor $e$ in the $Q-e$ scheme, in order to take into consideration results obtained in the copolymerisation of dienes:

$$\log\frac{1}{r_1}=\text{const}\,e. \qquad (8)$$

As noted above, 1,4 polymers of dienes are formed in the presence of organolithium compounds in hydrocarbon medium, in contrast to the 1,2 and 3,4 polymers obtained under the influence of other organometallic compounds of alkali metals[74]. In discussions of this phenomenon the lithium–carbon bond has been regarded as a polarised covalent bond instead of being ionic[76]. Stearns and Forman[87] suggested a mechanism of chain growth in which the first stage involved formation of an intermediate cyclic complex with a coordinate link between $Li^{\delta+}$ and the $\pi$ electrons of the double bond in the monomer, e.g. for isoprene




In the first stage the conformation of the monomeric molecule is fixed by formation of the cyclic complex, which ensures that the second stage — addition of monomer to the negatively polarised end of the chain — shall be stereospecific. In present-day terminology this mechanism of polymerisation is said to be coordinate-anionic[10,81]. With the addition of increasing quantities of an electron-donor complexing agent (or with increasing complexing power of the additive, e.g. on passing from diethyl ether to triethylamine and tetrahydrofuran), the ability of the lithium atom to form a complex with the monomer diminishes, and a transition occurs from coordinate-anionic to typically anionic polymerisation. This change in the mechanism of polymerisation produces a change in structure when isoprene is polymerised in different solvents. The relation between the activities of isoprene and styrene on copolymerisation under the influence of butyllithium changes to the same extent in the presence of different electron-donor additives[25].

Since the changes in the structure of polyisoprene and in the composition of its copolymer with styrene have the same causes, a linear correlation exists between these quantities (Fig. 2 [25]). The change in relative reactivity of the monomers on passing from copolymerisation by means of organolithium compounds in hydrocarbon medium to copolymerisation in the presence of complexes of organolithium compounds with electron-donor substances has been studied on the following pairs of monomers — styrene–butadiene (pair 5 [Table 5]), styrene–isoprene (pair 6), styrene–$\alpha$-methylstyrene (pair 4), and butadiene–isoprene

TABLE 5. Copolymerisation under the influence of catalysts of anionic type.

| No. of pair | $M_1$ | $M_2$ | Catalyst | Medium | $r_1$ | $r_2$ | $M_1$, mole %, in initial mixture | $M_1$, mole %, in copolymer | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 1 | styrene $e=-0.80$ | *p*-chlorostyrene $e=-0.33$ | $LiC_2H_5$ | $N(C_2H_5)_3$ | 0.1±0.1 | 6.5±0.1 | 50 | 23 | 79 |
| | | | $LiC_2H_5$ | $C_6H_6$ | — | — | 50 | 67 | 79 |
| | | | $NaC(C_6H_5)_3$ | $(C_2H_5)_2O$ | — | — | 50 | 61 | 79 |
| | | | $LiC_2H_5$ | $(C_2H_5)_2O$ | — | — | 50 | 48.5 | 79 |
| | | | Na-naphthalene | tetrahydrofuran | — | — | 50 | 18 | 79 |
| | | | $LiC_2H_5$ | tetrahydrofuran | — | — | 50 | 34.4 | 80 |
| 2 | | *p*-methylstyrene $e=-0.88$ | $LiC_4H_9$ | toluene | 2.5±0.1 | 0.26±0.03 | — | — | 37 |
| | | | $LiC_4H_9$ | $C_6H_6 + (C_2H_5)_2O$ | — | — | 50 | 70 | 81 |
| | | | "live" $(M)_n^-Na^+$ | tetrahydrofuran | 3.05 | 0.22 | — | — | 24 |
| | | | ditto | tetrahydrofuran | 5.3 | 0.18 | — | — | 85 |
| 3 | | *p*-methoxystyrene $e=-1.11$ | $LiC_4H_9$ | toluene | 10.9±0.8 | 0.05±0.02 | — | — | 37 |
| | | | "live" $(M)_n^-Na^+$ | tetrahydrofuran | 19 | 0.045 | | | 86 |
| 4 | | *α*-methylstyrene $e=-1.27$ | $LiC_4H_9$ | toluene | — | — | 50 | 98 | 37 |
| | | | $LiC_2H_5$ | toluene | — | — | 82 | 77.5 | 77 |
| | | | $LiC_2H_5$ | toluene + $(C_2H_5)_2O$ | — | — | 82 | 92 | 77 |
| | | | $LiC_2H_5$ | toluene + $N(C_2H_5)_3$ | — | — | 82 | 96 | 77 |
| | | | $NaC(C_6H_5)_2$ | toluene | — | — | 82 | 94 | 77 |
| | | | "live" $(M)_n^-Na^+$ | tetrahydrofuran | 21 | 0.003 | — | — | 24 |
| 5 | | butadiene $e=-1.05$ | $LiC_4H_9$ | n-heptane | 0 | 7 | — | — | 26 |
| | | | $LiC_2H_5$ | toluene | 0.1 | 12.5 | — | — | 32 |
| | | | $LiC_4H_9$ | benzene | 0.05 | 20 | — | — | 37 |
| | | | $LiC_4H_9$ | benzene | 0.035 | 10.0 | — | — | 73 |
| | | | "live" $(M)_n^-Na^+$ | benzene | 0.06 | 3 | — | — | 86 |
| | | | $LiC_4H_9$ | 1 M ether in benzene | 0.11 | 1.78 | — | — | 43 |
| | | | $LiC_4H_9$ | 1 M tetrahydrofuran in benzene | 0.744 | 1.03 | — | — | 44 |
| | | | $LiC_2H_5$ | toluene + $N(C_2H_5)_3$ | 0.3 | 5.5 | — | — | 32 |
| | | | $LiC_2H_5$ | tetrahydrofuran | 8±1 | 0.2±0.1 | — | — | 32 |
| | | | $NaC_2H_5$ | benzene | 0.96 | 1.6 | — | — | 73 |
| | | | $KC(CH_3)_2C_6H_5$ | benzene | 1 | 1 | — | — | 73 |
| | | | $LiC_4H_9$ | hexane | — | — | 50 | 13.6 | 44 |
| | | | $LiC_4H_9$ | 1 M ether in benzene | — | — | 50 | 31 | 44 |
| | | | $LiC_4H_9$ | 1 M dioxan in benzene | — | — | 50 | 30 | 44 |
| | | | $LiC_4H_9$ | 1 M methylal in benzene | — | — | 50 | 31 | 44 |
| | | | $LiC_2H_5$ | toluene + $N(C_2H_5)_3$ | — | — | 50 | 33 | 32 |
| | | | $LiC_4H_9$ | 1 M $(CH_3OCH_2)_2$ in benzene | — | — | 50 | 47 | 44 |
| | | | $LiC_4H_9$ | 1 M tetrahydrofuran in benzene | — | — | 50 | 47 | 44 |
| | | | $LiC_4H_9$ | n-heptane + tetrahydrofuran | — | — | 50 | 30 | 26 |
| | | | $KCH_2C_6H_5$ | toluene | — | — | 50 | 67.5 | 82 |
| 6 | | isoprene $e=-1.22$ | $LiC_4H_9$ | benzene | 0.14±0.02 | 7±0.6 | — | — | 30 |
| | | | $LiC_2H_5$ | toluene | 0.25 | 9.5 | — | — | 83,31 |
| | | | $LiC_2H_5$ | 2.5 M $N(C_2H_5)_3$ in toluene | 0.8 | 1 | — | — | 31,83 |
| | | | $LiC_2H_5$ | tetrahydrofuran | 40 | 0 | — | — | 31,83 |
| | | | $LiC_4H_9$ | benzene | — | — | 50 | 11.5 | 25 |
| | | | $LiC_4H_9$ | monomer | — | — | 50 | 12.5 | 25 |
| | | | $LiC_4H_9$ | $N(C_2H_5)_3$ | — | — | 50 | 49.5 | 25 |
| | | | $LiC_4H_9$ | $(C_2H_5)_2O$ | — | — | 50 | 58.2 | 25 |
| | | | $LiC_4H_9$ | tetrahydrofuran | — | — | 50 | 72.3 | 25 |
| | | | $KCH_2C_6H_5$ | toluene | — | — | 50 | 75 | 82 |
| 7 | | vinylmesitylene | "live" $(M)_n^-Na^+$ | tetrahydrofuran | 1060 | 0.004 | — | — | 85 |
| 8 | *p*-chlorostyrene $e=-0.33$ | *α*-methylstyrene $e=-1.27$ | $LiC_2H_5$ | benzene | — | — | 16 | 26 | 79 |
| | | | $LiC_2H_5$ | $N(C_2H_5)_3$ | — | — | 16 | 87.5 | 79 |
| 9 | *p*-methylstyrene $e=-0.88$ | *p*-methoxystyrene $e=-1.11$ | $LiC_4H_9$ | toluene | 1.93±0.03 | 0.72±0.02 | — | — | 37 |
| 10 | isoprene $e=-1.22$ | penta-1,3-diene | $LiC_4H_9$ | n-hexane | 17±5 | 0.06±0.02 | 20 | 62.8 | 28 |
| | | | $LiC_4H_9$ | 2 M ether in hexane | — | — | 20 | 43.4 | 28 |
| 11 | | 2,3-dimethyl-butadiene $e=-1.81$ | $LiC_4H_9$ | n-hexane | 17±5 | 0.06±0.02 | — | — | 28 |
| 12 | | butadiene $e=-1.05$ | | toluene | — | — | 50 | 29.5 | 77 |
| | | | $LiC_2H_5$ | 2 M $N(C_2H_5)_3$ in toluene | — | — | 50 | 17.5 | 77 |
| | | | $LiC_2H_5$ | toluene | — | — | 50 | 16 | 77 |
| | | | $NaC(C_6H_5)_3$ | hexane | 0.47±0.03 | 3.38±0.14 | — | — | 29 |
| | | | $LiC_4H_9$ | | | | | | |
| | | | $LiC_4H_9$ | hexane, benzene, toluene, benzene soln. of tetrahydrofuran, pyridine, and $N(C_2H_5)_3$ > 0.001 M | 0.5 ±0.1 | 3.6 ±0.3 | — | — | 86 |
| | | | $LiC_4H_9$ | $N(C_2H_5)_3$ | 0.11±0.02 | 3.6 ±0.6 | — | — | 69,84 |
| | | | $LiC_4H_9$ | tetrahydrofuran | 0.13±0.02 | 4.5 ±0.7 | — | — | 69,84 |
| 13 | butadiene $e=-1.05$ | 2,3-dimethyl-butadiene $e=-1.81$ | $LiC_4H_9$ | tetrahydrofuran | 44±11 | 0.65±0.16 | — | — | 70 |

(pair 12). In all these cases the relative activity of the monomer having the lower electron density on the double bonds increases with the complexing power of the electron-donor additive or with its concentration (see e.g. the data on the copolymerisation of butadiene with styrene, pair 5).

In the copolymerisation of butadiene and of isoprene with styrene by means of butyllithium in hydrocarbon medium, the monomer having the higher electron density on the double bonds (isoprene with $e = -1.22$, and butadiene with $e = -1.05$) is even more active than styrene, in which

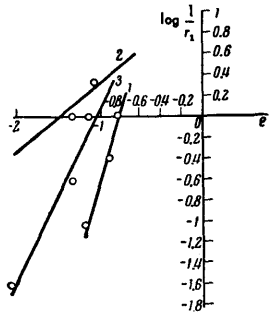



Fig. 1. Dependence, on electron density at double bonds, of reactivity of monomers in the presence of $C_4H_9Li$ towards: 1) styrene, copolymerised with *p*-methyl- and *p*-methoxy-styrenes in toluene[37]; 2) isoprene, copolymerised with butadiene[28] and 2,3-dimethylbutadiene[29] in hexane; 3) butadiene, copolymerised with isoprene and with 2,3-dimethylbutadiene in tetrahydrofuran[68,70,84].

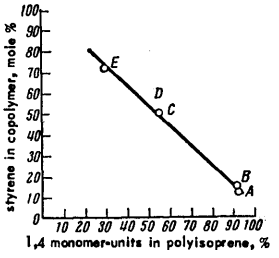



Fig. 2. Relation between structure of homopolymers of isoprene and composition of isoprene–styrene copolymers obtained from an equimolecular mixture by anionic polymerisation[25] in the presence of $C_4H_9Li$ in: *A*) benzene; *B*) monomer; *C*) triethylamine; *D*) ether; *E*) tetrahydrofuran.

the electron density on the double bond is lower ($e$ = -0.80), which would appear to contradict the view that a partial negative charge is present on the end of the growing chain. Actually, these results confirm the coordination nature of chain growth under the influence of organolithium compounds. The first stage — formation of a $\pi$ complex with the lithium atom — should tend to produce a higher electron density on the double bonds of the monomer; the second stage — addition of monomer to the negatively polarised end of the chain — occurs more readily with monomers of lower electron density on the double bonds.

In all the cases mentioned (pairs 4–6 and 12), in conformity with this mechanism, the relative activity of the monomer of greater electron density on the double bonds increases on passing from copolymerisation under the conditions of a typically anionic process (in the presence of organopotassium compounds or of LiR in tetrahydrofuran) to polymerisation of the same monomers in the presence of organolithium compounds without electron-donor additives. The reactivity of the monomers could be changed on reaction via a cyclic complex, in comparison with polymerisation in ion-pairs, for steric reasons; but then the activity of $\alpha$-methylstyrene could have been expected to decrease in comparison with styrene on passing to reaction in the ring, whereas the opposite is observed[77].

Use of the copolymerisation method to study the mechanism of polymerisation in the presence of organometallic compounds has in the first place provided evidence that the active unit in the growing chain is negatively charged, i.e. that polymerisation actually takes place by an anionic mechanism. Data on copolymerisation under the influence of organolithium compounds in various media have shown the coordinate–anionic mechanism of the action of this catalyst in a hydrocarbon solvent.

## 5. COPOLYMERISATION BY MEANS OF COMPLEX ORGANOMETALLIC CATALYSTS OF THE ZIEGLER–NATTA TYPE

Complex organometallic catalysts for the stereospecific polymerisation of alkenes and dienes are prepared from compounds of metals in the secondary subgroups of Groups IV–VI of the Periodic System and organometallic compounds of metals in Groups I–III.[10,88] The ionic and complex nature of these catalysts has now been proved; during growth the active unit in the chain is coordinated with the catalyst, and the act of addition of a new monomeric unit involves heterolytic cleavage of the bond between the catalyst and the terminal unit in the chain, with formation of a new polarised bond[10,75].

Study of copolymerisation enables several details of the mechanism of chain growth to be elucidated. Data on copolymerisation in the presence of Ziegler–Natta catalysts[69,70,89–128] are given in Tables 6 and 7. Investigation has been based mainly on styrene (Table 6, pairs 1–18), ethylene, propene (pair 24), and dienes (pairs 31–33).

The copolymerisation of styrene with nuclear-substituted styrenes is ideal in character, i.e. $r_1r_2 = 1$. Moreover, Wall's condition (5) is satisfied: the copolymerisation constant is equal to the ratio of the growth rate constants for the homopolymerisation of the monomers under the same conditions[129–132]: $r_2 = 1/r_1 = k_{22}/k_{11}$, so that the nature of the terminal unit in the chain does not affect the rate of addition of the monomer unit. The relative activities of *para*-substituted styrenes depend on the electron-donor power of the substituents: the copolymerisation constants obey the Hammett rule $\ln r_2 = \rho\sigma$, the reaction constant $\rho$ being negative. Consequently monomers of higher electron density on the double bond are more active, as in cationic polymerisation. On the other hand, the higher reactivity of ethylene compared with propene, which has a higher electron density on the double bond owing to the presence of an electron-donor substituent, has previously been regarded as an argument in support of the anionic nature of the growing chain[89,90].

In order to remove the contradiction, a mechanism of chain growth has been suggested[81,93] which takes into account the complex nature of stereospecific polymerisation. As in the mechanism quoted earlier for chain

TABLE 6. Copolymerisation under the influence of a Ziegler–Natta catalyst.

| No. of pair | $M_1$ | $M_2$ | Catalyst | Medium | $r_1$ | $r_2$ | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 1 | styrene $e=-0.80$ | *p*-methylstyrene $e=-0.88$ | $TiCl_4+Al(C_2H_5)$ | benzene | 0.90 | 1.15±0.08 | 92,118 |
| | | | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 0.84 | 1.19 | 92 |
| | | | $TiCl_3+Al(C_2H_5)_3$ | » | 0.85 | 1.18 | 92 |
| | | | $TiCl_3+Be(C_2H_5)_2$ | n-heptane | 0.85 | 1.18 | 92 |
| | | | $TiCl_3+Al(i\text{-}C_4H_9)_3$ | » | 1.0±0.12 | 1.0±0.12 | 95,96 |
| 2 | | *o*-methylstyrene $e=-0.78$ | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | benzene | 12.5±1 | 0.10±0.01 | 92–94 |
| | | | $TiCl_3+Al(i\text{-}C_4H_9)_3$ | toluene | mixture of copolymers of different compositions | | 122 |
| 3 | | *m*-methylstyrene $e=-0.72$ | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | benzene | 2.0±0.1 | 0.50±0.1 | 92,93 |
| 4 | | 2,4-dimethylstyrene | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 7.7 | 0.13 | 92,93 |
| 5 | | 2,5-dimethylstyrene $e=-0.84$ | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 33 | 0.03 | 92,93 |
| 6 | | 2,6-dimethylstyrene | $TiCl_3+Al(i\text{-}C_4H_9)_3$ | toluene | — | 0 | 122 |
| 7 | | 2,4,6-trimethylstyrene | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | benzene | — | 0 | 92,93 |
| 8 | | *p*-ethylstyrene | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 0.95±0.1 | 1.05±0.1 | 92–94 |
| 9 | | *p*-cyclohexylstyrene | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 2.08 | 0.48 | 92,93 |
| 10 | | *o*-fluorostyrene | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 5.6 | 0.18 | 92,93 |
| 11 | | *m*-fluorostyrene | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 2.13 | 0.47 | 92,93 |
| 12 | | *p*-fluorostyrene | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 1.50±0.1 | 0.60±0.1 | 92,93 |
| | | | $TiCl_3+Al(i\text{-}C_4H_9)_3$ | toluene | mixture of copolymers of different compositions | | 122 |
| 13 | | *m*-chlorostyrene $e=-0.35$ | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | benzene | 2.34 | 0.43 | 92–94 |
| 14 | | *p*-chlorostyrene $e=-0.33$ | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 2.20±0.2 | 0.50±0.1 | 92–94 |
| 15 | | *p*-bromostyrene $e=-0.35$ | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 1.75±0.1 | 0.55±0.1 | 92–94 |
| 16 | | *p*-methoxystyrene $e=-1.11$ | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 0.625 | 1.6 | 92–94 |
| 17 | | 1-vinylnaphthalene $e=-1.12$ | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 3.3±0.5 | 0.35±0.2 | 92–94 |
| 18 | | *p*-t-butylstyrene | $TiCl_3+Al(i\text{-}C_4H_9)_3$ | n-heptane | mixture of homopolymers | | 95,96 |
| | | | | toluene | mixture of copolymers | | 122 |
| 19 | | *p*-n-butylstyrene | $TiCl_3+Al(i\text{-}C_4H_9)_3$ | n-heptane | mixture of homopolymers | | 95,96 |
| 20 | | propene | $TiCl_3+Al(C_2H_5)_3$ | » | with 42 mole % of $M_1$ in mixture, 4 mole % in copolymer | | 97 |
| 21 | | 5-methylhex-1-ene | $TiCl_3+Al(C_2H_5)_3$ | » | mixture of two copolymers | | 98 |
| 22 | | 4-methylpent-1-ene | $TiCl_3+Al(C_2H_5)_3$ | » | ditto | | 98 |
| 23 | | isoprene $e=-1.22$ | $TiCl_3+Al(C_2H_5)_3$ | benzene | 0.1 | 6 | 99 |
| | | | $TiCl_4+Al(C_2H_5)_3$ | » | 1st fraction 0.63±0.39<br>2nd fraction 11±14 | 1. 8±0.9<br>0.08±0.84 | 100 |
| 24 | ethylene | propene | $VOCl_3+Al(n\text{-}C_6H_{13})_3$ | n-heptane | 17.95±0.27 | 0.065±0.02 | 90,104,105 |
| | | | $VCl_4+Al(n\text{-}C_6H_{13})_3$ | » | 7.08 | 0.088 | 91,104,105 |
| | | | $VCl_3+Al(n\text{-}C_6H_{13})_3$ | » | 6.61±0.20 | 0.145±0.007 | 101,104,105 |
| | | | $TiCl_4+3Al(n\text{-}C_6H_{13})_3$ | » | 33.36 | 0.039 | 101,104,105 |
| | | | $TiCl_3+Al(n\text{-}C_6H_{13})_3$ | » | 15.72 | 0.110 | 101,104,105 |
| | | | $VAcac_3^a+AlCl(C_2H_5)_2$ | » | 15.0 | 0.04 | 107 |
| | | | β-$TiCl_3+Al(C_2H_5)_3$ | solvent naphtha | 3.0±0.5 | 0.25±0.05 | 109 |
| | | | $VO(OR)Cl_2+AlCl_2C_2H_5$ | solvent naphtha | 17.5 | 0.05 | 109 |
| | | | $AlBr_3—VCl_4—Sn(C_6H_5)_4$ | $C_6H_{12}$ | 16 | 0.1 | 110,111 |
| | | | $VCl_4+Al(i\text{-}C_4H_9)_3$ | $C_6H_{12}$ | 16 | 0.063 | 110 |
| | | | $VCl_4+CH_3TiCl_3$ | $C_6H_{12}$ | 16 | 0.063 | 110 |
| | | | $VCl_4+Zn(C_6H_5)_2$ | $C_6H_{12}$ | 16 | 0.063 | 110 |
| | | | $VCl_4+Zn(n\text{-}C_6H_{13})_2$ | $C_6H_{12}$ | 16 | 0.063 | 110 |
| | | | $VOCl_3+Al(i\text{-}C_4H_9)_3$ | $C_6H_{12}$ | 28 | 0.036 | 110 |
| | | | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | $C_6H_{12}$ | 37 | 0.027 | 110 |
| | | | $ZrCl_4+Al(i\text{-}C_4H_9)_3$ | $C_6H_{12}$ | 61 | 0.016 | 110 |
| | | | $HfCl_4+Al(i\text{-}C_4H_9)_3$ | $C_6H_{12}$ | 76 | 0.013 | 110 |
| 25 | | but-1-ene | $VCl_4+Al(n\text{-}C_6H_{13})_3$ | n-heptane | 29.6±0.8 | 0.019±0.001 | 103,105 |
| | | | $VCl_3+Al(n\text{-}C_6H_{13})_3$ | » | 29.96±0.81 | 0.043±0.01 | 103,105 |
| 26 | | hexa-1,5-diene | $VCl_4$ or $VOCl_3+AlR_3$ | n-heptane | $r_1>r_2$ | | 108 |
| 27 | | isoprene $e=-1.22$ | $VOCl_3+Al(i\text{-}C_4H_9)_3$ | tetrachloroethylene | with 90 mole % of $M_1$ in mixture, the copolymer contains 96 mole % | | 119 |
| 28 | propene | but-1-ene | $VCl_4+Al(n\text{-}C_6H_{13})_3$ | n-heptane | 4.39 | 0.227 | 106 |
| | | | $VCl_3+Al(n\text{-}C_6H_{13})_3$ | » | 4.04 | 0.252 | 106 |
| 29 | | isoprene $e=-1.22$ | $TiCl_4+Al(C_2H_5)_3$ | » | formation of copolymers established | | 118 |
| | | | $TiCl_3+Al(C_2H_5)_3$ | » | ditto | | 118 |
| 30 | but-1-ene | 3-methylbut-1-ene | $TiCl_3+Al(i\text{-}C_4H_9)_3$ | » | 8.5 | 0.013 | 120 |
| | | | | | (empirical copolymer) | | |
| 31 | butadiene $e=-1.05$ | isoprene $e=-1.22$ | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | benzene | 1.0±0.05 | 1.0±0.05 | 69,123 |
| | | | $TiCl_4+Al(C_2H_5)_3$ | » | 1.6 | 1.1 | 124 |
| | | | $TiCl_4+LiC_4H_9$ | » | 1.6±0.3 | 0.8±0.2 | 124 |
| | | | $TiI_4+Al(C_2H_5)_3$ | » | 1.88 | 0.55 | 124 |
| | | | $CoAcac_3^a+Al(C_2H_5)_2Cl$ | toluene | 1.0±0.05 | 1.0±0.05 | 125 |
| | | | $CoCl_2\cdot C_5H_5OH+$ $+Al(i\text{-}C_4H_9)_2Cl$ | benzene | 2.3±0.1 | 1.15±0.05 | 69,123 |
| | | | $CoCl_2\cdot C_5H_5OH+Al(C_2H_5)_2Cl$ | » | 0.92 | 1.25 | 126 |
| | | | $CoCl_2\cdot C_5H_5N+Al(C_2H_5)_2Cl$ | » | 0.99 | 1.37 | 126 |
| | | | $NiCl_2\cdot C_5H_5N+Al(C_2H_5)_2Cl$ | » | 1.15 | 0.59 | 126 |
| 32 | | 2,3-dimethylbutadiene $e=-1.81$ | $TiCl_4+Al(i\text{-}C_4H_9)_3$ | » | 2.16±0.2 | 0.39±0.04 | 70 |
| | | | $CoCl_2\cdot C_5H_5OH+Al(i\text{-}C_4H_9)_2Cl$ | » | 2.7 ±0.12 | 1.13±0.05 | 70 |

TABLE 6 (contd.)

| No. of pair | $M_1$ | $M_2$ | Catalyst | Medium | $r_1$ | $r_2$ | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 33 | | *trans*-penta-1,3-diene | $VCl_3 \cdot C_4H_8O + Al(C_2H_5)_2Cl$ | benzene | with 92 mole % of $M_1$ in the mixture, the copolymer contains 69 mole % | | 127 |
| | | | $VAcac_3^* + Al(C_2H_5)_3Cl$ | » | ditto | | 127 |
| | | | $CoCl_2 \cdot C_2H_5OH + Al(i\text{-}C_4H_9)_2Cl$ | » | with 50 mole % of $M_1$ in the mixture, the copolymer contains 61 mole % | | 128 |

* Acac = acetylacetonate.

growth in the presence of organolithium compounds in hydrocarbon medium, chain growth is regarded as a two-stage process, in which the first stage involves formation of a monomer–active centre complex, and the second stage consists in addition of monomer to the end of the growing chain bound to the catalyst. The electron density on the double bonds in the monomers has opposite effects in these stages, and the dependence of the relative activity of a monomer on the polar effect of the substituents is determined by which of the two stages in the growth reaction is the slower. Natta and his coworkers consider that, in the stereospecific polymerisation of styrenes, chain growth takes place by an anionic mechanism, but the overall kinetics of growth is determined by the stage of formation of a $\pi$ complex between the monomer and the transition metal of the active centre: this stage is favoured by a higher electron density on the double bond of the monomer.

Danusso[81] proposes that this mechanism of polymerisation should be termed "anionic polymerisation with counterion attack". As accepted previously, the term "anionic polymerisation" indicates the sign of the partial charge on the active unit in the growing polymer chain; the term "counterion attack" shows that the rate of growth is determined by interaction between the monomer and the counterion.

The proposed scheme makes it clear why the nature of the terminal unit in the chain does not affect the rate of growth in copolymerisation in contrast to cationic and anionic copolymerisation. When styrenes undergo copolymerisation and homopolymerisation in the presence of Ziegler–Natta catalysts, the rate of growth is determined solely by the stage involving formation of a complex between the monomer molecule and the transition metal, and this stage is unaffected by differences in reactivity between the terminal units formed from different monomers.

According to the mechanism of chain growth under consideration, the lower relative activity of propene and but-1-ene compared with ethylène (pairs 24 and 25 in Table 6) is due not to differences in electron density on the double bonds but to steric factors. When polar factors are decisive, differences in copolymerisation constants are due to differences in the activation energy of chain growth[20]. However, the activation energy of growth in the presence of the catalyst $(C_6H_{13})_3Al + VOCl_3$ or $VCl_4$ is the same for the homopolymerisation of ethylene and of propene as for their copolymerisation[105]. Consequently, the difference in activity is associated with steric factors — with the increase in steric hindrance to chain growth in the sequence ethylene–propene–but-1-ene.[10] The decisive role of steric factors in the copolymerisation of ethylene with propene (pair 24) and with but-1-ene (pair 25), as well as of but-1-ene with propene (pair 28), is indicated also by the absence of temperature variation in the copolymerisation constants of these monomers in the presence of any of the catalysts studied[90,91,101–111].

In copolymerisation of ethylene with propene[90,91,101–107,110], the atom of the transition metal present in the catalytic complex takes part in the stage of chain growth, which determines the rate of the overall process, since the copolymerisation constants vary with the nature of the compound of the transition metal. On the basis of the two-stage scheme of chain growth, however, it cannot be concluded from this variation, as is done by Carrick and his coworkers[110], that chain growth involves incorporation of monomer at the transition metal–carbon bond.

The view that in the growth reaction the position of the monomer is fixed in the reaction complex provides at the present time the most widely accepted explanation for the stereospecificity of the action of Ziegler–Natta catalysts[10]. This stereospecific action appears also in copolymerisation: in the presence of $VCl_4$ and $(C_6H_{13})_3Al$, ethylene forms crystalline copolymers with *cis*-but-2-ene and with cycloalkenes in which the monomer units alternate regularly, with the units of the second monomer forming a diisotactic structure[112–116,121] (Table 7). The steric selectivity of these catalysts is shown in the fact that mixtures of some monomers, in the presence of Ziegler–Natta catalysts, yield not copolymers but mixtures of homopolymers or of two copolymers differing in composition[95,96,98,100,120,122] (pairs 2, 12, 18, 19, 21–23, and 30 of Table 6).

Data on the copolymerisation of conjugated dienes (butadiene and isoprene, *cis*- and *trans*-penta-1,3-diene and 2,3-dimethylbutadiene — pairs 31–33 in Table 6) show especially clearly the difference between Ziegler–Natta coordination catalysts and ordinary cationic and anionic catalysts. Whereas when typical cationic and anionic catalysts are employed, the relative reactivity of a diene monomer is determined primarily by the electron density at its double bonds[28,29,69,70,84], in the presence of coordination catalysts the copolymerisation constants differ little among themselves, and are probably almost independent of the electron density on the double bonds in the monomer.

It has now been shown that complex catalysts based on titanium halides effect polymerisation by a coordinate-anionic mechanism[133,134], whereas those based on cobalt halides do so by a coordinate–cationic mechanism[134,135]. However, these distinctions do not lead to any substantial difference in the copolymerisation constants of the dienes in the presence of the two types of complex catalysts

TABLE 7. Copolymerisation of ethylene ($M_1$) with disubstituted ethylenes in the presence of Ziegler–Natta catalysts. [Polymerisation in toluene medium with vanadium tris-acetylacetonate + $(C_2H_5)_2AlCl$ as soluble catalyst, or $VCl_4$ + $(C_6H_{13})_3Al$ as colloidal catalyst. Copolymer formation proved by fractionation. Composition determined from content of radioactive ethylene.)

| No. of pair | $M_2$ | Catalyst | $M_1$, mole %, in | | Ref. |
|---|---|---|---|---|---|
| | | | mixture | copolymer | |
| 1 | *cis*-but-2-ene | soluble | 1 | 51 | 112–116 |
| | | soluble | 3 | 82.3 | 121 |
| | | colloidal | 1 | 67.5 | 112–116 |
| 2 | *trans*-but-2-ene | soluble | 1 | 92 | 112–116 |
| | | soluble | 3 | 94.6 | 121 |
| | | colloidal | 1 | 81 | 112–116 |
| 3 | pent-2-ene | colloidal | 1 | 26 | 112, 116 |
| 4 | cyclopentene | soluble | 1 | 55 | 112, 116, 117 |
| | | soluble | 3 | 58.5 | 121 |
| | | colloidal | 1 | 55 | 112, 116, 117 |
| | | colloidal | 3 | 58 | 121 |
| 5 | cyclohexene | soluble | 3 | 97 | 121 |
| | | colloidal | 3 | 93 | 121 |
| 6 | cycloheptene | soluble | 1 | 51 | 115, 116, 117 |
| | | soluble | 3 | 55.5 | 121 |
| | | colloidal | 1 | 63 | 115, 116, 117 |
| | | colloidal | 3 | 65.5 | 121 |
| 7 | *cis*-cyclooctene | soluble | 3 | 90 | 121 |
| | | colloidal | 3 | 92 | 121 |

(pairs 31 and 32 in Table 6). It may be supposed that the relative activity of diene monomers undergoing copolymerisation is determined primarily by steric factors. This is supported by the inability of *cis*-penta-1,3-diene (in contrast to the *trans* isomer) to polymerise or to form a copolymer with butadiene in the presence of several complex catalysts – $(C_2H_5)_2AlCl + VCl_3$ tetrahydrofuran or $VAcac_3$†,[127] $(iso\text{-}C_4H_9)_3Al + TiCl_4$, and $(iso\text{-}C_4H_9)_2AlCl + CoCl_2.C_2H_5OH$ [128] – as well as by the existence of a relation between the composition and the microstructure of the chain in copolymers obtained in the presence of catalytic systems based on compounds of cobalt and of nickel[69,70,124–126].

Data on copolymerisation in the presence of Ziegler catalysts thus show that in this process the polymer chain is neither a free anion nor a cation. The mechanism of the growth reaction is determined by the nature of the catalytic complex, in which the polymer chain occupies a definite position, and chain growth occurs as a stepwise process consisting of two stages – (1) formation of an active centre–monomer complex, and (2) addition of the monomer unit to the chain. In connection with the coordination character of chain growth, the relative activities of monomers are determined to a considerable extent not by polar but by steric factors.


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† Acac = acetylacetonate.

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# THE QUANTITATIVE INTERPRETATION OF GAS CHROMATOGRAMS

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## I. INTRODUCTION

When attempting a chromatographic analysis, the investigator is faced with three main types of problem. The first group relates to the choice of the best procedures and parameters for the separation process, the second to the identification of the components of the mixture to be analysed, and the third to the quantitative interpretation of the gas chromatograms.

The results of calculations of the concentration of the various constituents from the experimental chromatogram depend on correct choice and accurate measurement of the key parameter of the elution curve (particularly when the peaks are only partially resolved), on correct choice of the method of calculating the concentration, and lastly, on correct evaluation of the sensitivity of the detector towards each of the constituents.

The present review is devoted to a discussion of these problems. It is a continuation of our earlier articles[1,2], which dealt with the choice of separation procedures and with the qualitative analysis of mixtures.

A summary of published correction coefficients and peak areas for various substances and different detectors is given at the end of the review, so as to enable the reader to use these values directly in his experimental work.

Throughout this paper, it will be assumed that a differential detector is used.

## II. PARAMETERS OF THE PEAK AND METHODS OF CALCULATION

When a small enough sample is eluted, a distribution of concentrations (called a layer chromatogram) is formed on the sorption layer. Further elution leads to desorption of the wanted constituent. The resulting distribution of concentrations is called an eluate chromatogram.

If the system of detector and recorder used does not distort the curve, the resulting chromatogram differs from the true eluate chromatogram only by a scale factor.

The main parameters of the chromatographic peak (Fig. 1) are[3]:

1. The height $h$, measured by the length of a perpendicular dropped from the peak maximum to the base line.

2. $h'$, the length of a perpendicular dropped to the base line from the intersection of the tangents to the peak.

3. The width of the peak, which can be measured as the distance between points on the peak at a height of 0.5 ($\mu_{0.5}$), 0.75 ($\mu_{0.75}$), 0.9 ($\mu_{0.9}$), or 1/e ($\mu_e$) of the total peak height,

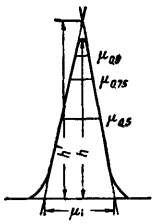



Fig. 1. Parameters of the chromatographic peak.

or alternatively as the distance between the points of inflection ($\mu_p$) or as the intersection ($\mu_i$) on the base line of the tangents at the points of inflection (peak base). It can be readily shown that if the chromatographic peak is sufficiently close to a gaussian distribution curve the following relationships hold between the various $\mu$ values:

$$\mu_e = 1.201\mu_{0.5},$$
$$\mu_{0.75} = 0.645\mu_{0.5},$$
$$\mu_{0.5} = 0.392\mu_{0.5},$$
$$\mu_p = 1.540\mu_{0.5},$$
$$\mu_i = 1.700\mu_{0.5}.$$

4. The peak area $Q$, defined by the outline of the curve and the base line.

5. The retention time $t_R$, the retention volume $V_R$, or the corresponding length $l$ on the chromatogram.

The peak height $h$ is related to the concentration of the substance in the sample. If the column is not overloaded with sample, this relationship is linear, provided of course that the response of the detector is directly proportional to the concentration of the substance in the eluate. However, the peak height is appreciably affected by temperature and by the flow rate of the carrier gas; therefore, the peak height should be selected as the quantitative parameter only if the following conditions are satisfied: (1) high reproducibility of sample size; (2) high stability of temperature and carrier flow; (3) no overloading of the column by the sample; (4) operation in the linear region of the detector and of the recording system.

The use of peak heights for calculating the quantitative composition of a mixture is convenient when the components have small retention times and give narrow peaks on the chromatogram. The method is applicable also to incompletely resolved constituents, provided the band maximum of one component is not affected by its neighbours. Calculations based on peak heights are particularly successful in routine analysis, requiring only moderate precision[4-7]. They are especially convenient in chromatography and in capillary chromatography.

In practice, peak areas are more frequently used as the parameter for calculation. There are various methods for measuring peak areas: planimetry, cutting out and weighing the peak, multiplying the height $h$ by the half-width $\mu_{0.5}$, drawing the tangents to the curve at the points of inflection and calculating the area of the resulting triangle, and the use of integrating devices. The choice of method for measuring peak areas should be guided by the features of the particular elution curve.

When using a planimeter the shape of the curve is immaterial, but the method is inconvenient for very small or very large areas. The precision of the calculation depends very much on subjective factors.

The shape of the peak is likewise unimportant when cutting out and weighing, but in this case significant errors can be introduced by lack of uniformity in the paper as well as by the subjective factor.

The measurement of peak areas as the product of the height $h$ and the half-width $\mu_{0.5}$ is convenient and accurate only if the peaks are symmetrical. Errors are again caused by overloading the column with sample, since the relationship $Q = 1.064h\mu_{0.5}$ (which applies to a gaussian distribution) does not hold when the column is overloaded. The method is difficult to use for small areas of negligible height and long retention time, or for large height and small $t_R$, because the half-width cannot be measured accurately. This method is accurate only when the peaks are adequately resolved.

When the area is measured by multiplying the peak height $h'$ by the base $\mu_i$ (triangle method) the accuracy of the measurement is affected by the shape of the curve and by the care with which the tangents are drawn. Obviously, this method should be used only when the sides of the peak are approximately rectilinear.

Assuming that the chromatographic peak is not very different from a normal gaussian curve, the following method for determining the peak area can be suggested[8]. The equation of this curve is of the form

$$y = \frac{Q}{\sqrt{2\pi}\,\mu_{st}} \times e^{-\frac{1}{2}\left(\frac{x}{\mu_{st}}\right)^2}. \qquad (1)$$

Here $y$ is the ordinate of the curve, measured at a distance $x$ from the ordinate at the maximum; $Q$ is the area of the peak; $\mu_{st}$ is the standard deviation. At the peak maximum, where $x = 0$, $y = h$.

Hence,

$$Q = 2\pi h\mu_{st} = 2.507h\mu_{st}. \qquad (2)$$

The height of the peak is measured directly, and the standard deviation can be determined from the width of the peak measured at various heights, thus:

$$\mu = \mu_{st} \quad \text{at } y = 0.882h,$$
$$\mu = 2\mu_{st} \quad \text{at } y = 0.607h,$$
$$\mu = 3\mu_{st} \quad \text{at } y = 0.324h,$$
$$\mu = 4\mu_{st} \quad \text{at } y = 0.134h, \text{ etc.}$$

Often the chromatographic peaks take the form of somewhat distorted gaussian curves. With asymmetric, biased peaks, for which the centres of the width lie on a straight line at all heights, the area can be calculated by Eqn. (2) just as though the peak were symmetrical[8].

It has been shown[8] that the standard deviation is a linear function of the retention time. Hence it is evident, see Eqn. (2), that the peak area can be measured[9] by using the peak height $h$ and the retention time $t_R$ (or the retention volume $V_R$). It can be readily shown[5] that the quantity $hV_R$ is proportional to the amount of the substance. The half-width of the band, expressed in units of volume, is known to be equal to

$$\omega_{0.5} = 3.33 \times \Gamma_0 \times S\sqrt{\frac{DLx}{\alpha}}, \qquad (3)$$

where $L$ and $S$ are the length and cross-section of the column respectively, $\varkappa$ is the fraction of free volume, $\alpha$ the linear velocity of the carrier gas calculated for the cross-section of the column, $D$ the effective coefficient of longitudinal diffusion, and $\Gamma_0$ the normal Henry coefficient. The retention volume is proportional to the length and cross-section of the column and to the Henry coefficient: $V_R = \Gamma_0 SL$. Cancelling $\Gamma_0 S$ from these two equations we find

$$V_R = \frac{\omega_{0.5}}{3.33}\sqrt{\frac{L\alpha}{D\varkappa}} = A\frac{\omega_{0.5}}{\sqrt{D}}, \quad (4)$$

where

$$A = \frac{\sqrt{L\frac{\alpha}{\varkappa}}}{3.33}.$$

It follows that

$$V_R \times h \sim \frac{Q}{\sqrt{D}}. \quad (5)$$

This method is to be preferred to the others, because it is simpler to measure a retention time than the width of a peak. Eqn. (5) shows that the relationship between $hV_R$ and the amount of a substance in the mixture varies from constituent to constituent due to difference in diffusion coefficient [10]. The method can be used successfully when high precision is not required. It should be noted that the method can be applied to overlapping peaks, whose area is often impossible to evaluate by any other method. All that is necessary in this case is to apply a correction to the peak height, depending on the extent of overlapping (see below for the calculation of the peak height correction).

Various integrating devices are used for measuring peak areas [11]. The mechanical integrator introduces errors into the measurement because it has a high inertia and gives few impulses per square millimetre of area, particularly with small areas and shallow peaks. The same disadvantages are found in the electromechanical integrator. The electronic integrator is much more accurate, but it cannot be used when the components of the mixture are not fully resolved. It should also be remembered that large errors may arise from drift of the base line.

Experimental tests of the various methods have been reported by many workers [4,7,11-15]. It has been shown that all methods give an appreciable error when the peak area is less than 50 mm² (15–25% for peak areas of the order of 25 mm²). The largest errors arise when planimeters or mechanical integrators are used, and the best results are obtained in calculations based on the peak height. When the peak area is about 50–100 mm², practically all the methods are liable to a 10% error, and the accuracy of the results can only be improved by averaging a large number of planimetric measurements. With peak areas above 100 mm² the error is 1–3%, irrespectively of the method.

## Determination of the Parameters of Incompletely Resolved Peaks

Incomplete resolution of the constituents of the mixture distorts the shape of the peaks and degrades the precision of quantitative analytical results. When resolution is not complete, allowance must be made for the presence of one component at the band maximum of another component. The total concentration, measured by the peak height on the chromatogram, is

$$C = C_{1,\max}\, e^{-\rho t_R^2} + C_{2,\max} e^{-\rho(\Delta t - t_R)^2}. \quad (6)$$

In this expression $\rho$ is a parameter which characterises the diffuseness of the band, $t_R$ is the retention time of the peak maximum of the second component, $\Delta t$ is the difference between the retention times of the maxima of the two components.

Starting from Eqn. (6), we can determine the true peak maxima of both components and evaluate the error which arises if the amount of a component is estimated from the apparent height of the peaks found on the chromatogram [16,17].

When the components of a mixture which give symmetrical chromatographic peaks are not fully resolved, the corrected peak heights can be calculated as a function of the extent of overlapping by the method of Stickler and Kovats [17]. Consider, for example, two peaks (Fig. 2) of height $h_1$ and $h_2$ whose maxima are a distance $\Delta l$ apart (measured in units of $\mu_{st}$). The ordinate $y$ of the curve for peak 1 at a distance $\Delta l$ from the maximum is

$$y = h_1 e^{-\frac{1}{2}\left(\frac{\Delta e}{\mu_{st_1}}\right)^2}, \quad \text{where } h_1 = \frac{Q}{\sqrt{2\pi}\,\mu_{st}}. \quad (7)$$

The corrected height of peak 2, allowing for the effect of peak 1, is given by

$$h_2 = \tilde{h}_2 - h_1 \times e^{-\frac{1}{2}\left(\frac{\Delta l}{\mu_{st_1}}\right)^2}, \quad (8)$$

where $\tilde{h}_2$ is the apparent height of the second peak. The area of peak 2 is then

$$Q = \sqrt{2\pi} h_2 \mu_{st_2} = 2.507 h_2 \mu_{st_2}.$$

In these expressions, $\mu_{st_1}$ and $\mu_{st_2}$ are the standard deviations of the first and the second peak respectively.

Usually the correction to the peak height is appreciable if $\Delta l$ is small, and becomes negligible when $\Delta l > 4\mu_{st}$.

When the overlapping peaks are asymmetrical the height correction is obtained as for the case of symmetrical peaks. In general, however, the calculation of the height correction becomes very complicated when asymmetry is present, and involves a number of approximations.

Bartlet and Smith [8] have shown that the two areas corresponding to the individual components can be evaluated with the help of Eqn. (1) even when two substances with similar

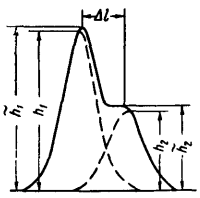



Fig. 2. Symmetrical, partially resolved peaks.

retention volumes give a single broad peak on the chromatogram. These authors used the method [18], and published a plot of the height correction as a function of the distance between the maxima of the overlapping peaks, measured in units of $\mu_{st}$.

Thus, Bartlet and Smith's method gives information on unresolved peaks without any need to choose conditions leading to complete resolution.

Polezzo and Taramasso [19] have proposed a similar method of calculation to give the area of unresolved peaks. They express the corrections to the heights of overlapping peaks in the form

$$a_1 = e^{-\frac{1}{2}\left(\frac{\Delta l}{\mu_{st_1}}\right)^2}, \quad a_2 = e^{-\frac{1}{2}\left(\frac{\Delta l}{\mu_{st_2}}\right)^2}, \tag{9}$$

the corrected peak heights being

$$h_1 = \tilde{h}_1 - h_2 a_2 \text{ and } \tilde{h}_2 = \frac{\tilde{h}_2 - a_1\tilde{h}_1}{1 - c_1 a_2}. \tag{10}$$

In this equation $\tilde{h}_1$ and $\tilde{h}_2$ are the quantities indicated in Fig. 2.

Since $\mu_{st}$ is not easy to measure in practice, it is more convenient to express the area of the peak in terms of other quantities.

We know that $\mu_{st} = 0.424\mu_{0.5}$. Hence

$$C_x = C_{max}\exp(-x^2/0.36\mu_{0.5}^2) \text{ or } C_{max} = \frac{C_x}{\exp(-x^2/0.36\mu_{0.5}^2)}, \tag{11}$$

so that the peak area is given by

$$Q = 1.064\, C_{max}\mu_{0.5} = \frac{1.064\, C_{max}\mu_{0.5}}{\exp(-x^2/0.36\mu_{0.5}^2)}. \tag{12}$$

Analogous formulae can be written in terms of $\mu_{0.75}$, $\mu_{0.9}$, etc.

An alternative method for calculating the areas of unresolved peaks, based on the assumption that the gaussian distribution applies in the case of linear sorption isotherms, was put forward by Zhukhovitskii and coworkers [20]. The area corresponding to a given amount of a component of a mixture is calculated using the equation

$$Q = K_\theta h \mu_{0.5}, \tag{13}$$

where $K_\theta$ is a coefficient, and $\mu_\theta$ is the width of the band at the height $\theta h$. For $\theta$ = 0.5, 0.75, and 0.9 the calculated values of the coefficient $K_\theta$ are 1.064, 1.650, and 2.710 respectively. According to the extent to which the components are separated, the value of $\theta$ should be chosen so that the width of the peak is unaffected by the neighbouring component. This method was tested, and it was shown that satisfactory results can be obtained at different $\theta$ values. However, errors are unavoidable at large $\theta$ because $\mu_{st}$ is small.

An interesting method of quantitative interpretation in the presence of partially resolved components is described by Serfas [21]. The outline of the chromatographic peak is linearised by using a probability scale as ordinate: the elution curve of two partially resolved peaks then consists of a line showing two rectilinear segments joined by a curve. The true outlines of the individual peaks of the two components are obtained by extrapolating the linear portions.

A theoretical method of calculation for unresolved peaks is given in a paper by Grant and Vaughan [22], in which an equation approximately describing the behaviour of three partly resolved peaks is presented. A method for the analysis of close-boiling compounds is based on this equation: the compounds were mostly isomeric, since compounds of similar boiling points but belonging to different classes can usually be separated by suitable choice of stationary phase. The method is used when the two components 1 and 2 give a single peak on the chromatogram, and their total concentration is known. A third substance is chosen such that the distance between the maximum of its chromatographic peak and the maximum of the peak for (1 + 2) is $\Delta l \simeq 3\mu_{st}$, and its peak area is the same as that of (1 + 2). The chromatogram of such a mixture gives a curve (Fig. 3) from which the quantity $h_{1,2,3(min)}/h_3$ can be evaluated: its value is substantially determined by all three components of the mixture. The concentrations of components 1 and 2 which correspond to this value are read off calibration curves constructed for mixtures of known composition.

Fredericks and Brooks [23] measured the areas of unresolved peaks by dropping a perpendicular from the minimum point to the base line and treating this line as the boundary between the two peaks. Their results were in agreement with the gravimetric composition of the mixture, but the method is unsuitable for asymmetric peaks and also for peaks of widely different size.

Bryce [4] has made an interesting study of the measurement of unresolved peak areas. He examined a mixture of benzene, toluene, and *p*-xylene in the ratio of 2 : 3 : 5, giving peaks of equal height on the chromatogram. Straightforward analysis gives complete separation of the peaks. The peaks of a given component were made to overlap by injecting a second sample, the degree of separation being controlled by the interval between the two sample injections. Perpendiculars dropped from the minimum point, and from the intersection of the tangents to the inner sides of the overlapping peaks, were treated as the peak boundary. The latter method of measuring peak areas gave the more accurate results. If, as a result of incomplete separation, one of the sides cannot be distinguished, the internal tangent is drawn symmetrically to the external tangent with respect to a perpendicular dropped from the peak "maximum" to the base line.

To obtain accurate results in the analysis of impurities whose peaks fall on the diffuse trailing edge of the peak of the main constituent, it is not advisable to use the peak height as a measure of concentration. In this case, the

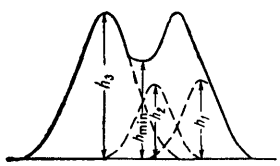



Fig. 3. Incomplete resolution of three components.

peak area is measured[4,24] by extrapolating the tail of the major peak and treating it as the base line of the impurity peak.

## III. METHODS FOR CALCULATING THE COMPOSITION OF A MIXTURE FROM THE CHROMATOGRAM PARAMETERS

The precision of the chromatographic method of analysis depends very much on choosing the most rational method for calculating the proportion of each constituent in the mixture for analysis. We showed in the previous Section how a differential chromatogram can be characterised quantitatively in terms of various peak parameters. By varying these parameters, and by choosing the most appropriate method of calculation, the percentage of any component of the mixture can be found.

The main methods of processing gas chromatograms are: the absolute calibration method, the internal normalisation method, and the internal standard method.

### The Absolute Calibration Method

In the analysis of trace constituents, quantitative interpretation is complicated by the special features of the chromatographic separation procedure. Absolute calibration is the most convenient and accurate method, in this case, for calculating the concentration of the components of interest. When using the absolute calibration method, either the height or the area of the peak can serve as the distinguishing parameters recorded on the chromatogram. The method presents rather stringent requirements as regards analytical procedure, and demands considerable skill and accuracy. The absolute calibration method consists in determining the relationship between the height or the area of the peak for a given component, and the amount of the latter, in a sample of given size[3,25-28]. Calibration is usually carried out by analysing a sample of known volume and accurately known composition. The experimental results are used to plot a graph of the peak height or area against the concentration of that component in the sample, and the concentration of the same component in the unknown mixture is obtained directly from the graph. When the calibration curves are straight lines, it is possible to calculate calibration coefficients which apply over wide limits, and the percentage of the compound can be calculated from the expressions

$$P_i = K\frac{Q_i}{g_i}\times 100 \qquad (14)$$

or

$$P_i = K\frac{h_i}{g_i}\times 100, \qquad (15)$$

where $Q_i$ and $h_i$ are the area and height of the peak, $g_i$ the weight of the component, and $K$ the calibration coefficient.

The accuracy of the quantitative results of the absolute calibration method depends first and foremost on the conditions under which the analysis is carried out and on the operating stability of the chromatographic apparatus. Reliable results are obtained only if the calibration and the analysis itself are carried out under identical conditions. Horn and coworkers[29] have given a detailed discussion of the problems arising from the influence of various factors on the height and area of the peak when calculating calibration coefficients. They showed that the correction factor for the peak height is a sensitive function of the amount of substance, whereas the correction factor for the peak area remains practically constant. In order to simplify the calculations, absolute calibration is often based on the height of the peaks, despite its great sensitivity to changes in experimental parameters. In particular, a one-degree change in the temperature of the column, detector, and connecting tubes can cause an error[24] of 2%. Sverak and Reiser[30], in their work on the determination of small quantities of ether in ethylene using a chromatograph with katharometric detection, allowed for a number of parameters in the formula used for quantitative calculations:

$$C_0 = \frac{KQV_\alpha}{v_n zE}, \qquad (16)$$

where $C_0$ is the concentration of ether (vol.%), $v_n$ the sample volume, $Q$ the peak area, $V_\alpha$ the flow rate of the carrier gas, $z$ the speed of the recorder chart, $E$ the sensitivity of the potentiometer, and $K$ the calibration factor.

It should be noted that calculations with allowance for correction coefficients are justified only as long as the detector response is linear in the concentration of the compound. When this is not true special corrections must be introduced.

### The Internal Normalisation Method

The internal normalisation method consists in bringing the sum of all the peak areas on the chromatogram to 100%. Instead of the peak areas, the product of the peak heights and the corresponding retention times of the components may be used. This method affords only the ratio between the amounts of the components whose peaks appear on the chromatogram, and is therefore valid only if all the constituents of the mixture for analysis are fully eluted. It is common practice to normalise corrected peak areas, that is, peak areas to which a correction for detector sensitivity has been applied. In some cases (for example, in the analysis of liquid hydrocarbons using a thermal conductivity detector with hydrogen or helium as the carrier gas, whose thermal conductivity is considerably higher than that of the substance to be analysed), correction coefficients can be ignored to a first approximation[7,31]. However, significantly higher precision is obtained by taking the correction coefficients into account. There is a wide range of publications[7,31-38] on the effect of various factors on peak areas and peak heights. Thus van de Craats[37] examined the problems associated with flow rate and sample size; Dimbat and coworkers[7] studied the effect of temperature and carrier-gas velocity on the parameters of the peak. The latter workers showed that the area of the peak is a function of the flow rate but does not vary with temperature, whereas the height of the peak depends on the temperature but is practically independent of flow rate. For temperature fluctuations of the order of one degree the relative error of peak area measurements is 0.3%. Ray[38] showed that the error caused by this same temperature variation can be as high as 2.4% when peak heights are used for the calculation. With streaming detectors of the flame ionisation type the height of the peak is very sensitive to the rate of flow of the carrier gas, but the area remains practically constant[39]. The time-constant (or inertia) of the system of detector, bridge, and recorder

must be considered when assessing the precision of the calculations. If the width of the peak is decreased by increasing the flow rate or by raising the temperature, the time-constant begins to have a significant effect and to distort the peak[39,40].

It follows from what has been said that the most satisfactory data on the quantitative composition of mixtures are obtained by using various correction coefficients, depending on the chosen method of detection.

In the internal normalisation method, the concentration (in percentage) of the $i$th component in the mixture to be analysed is calculated by the expression

$$P_i = \frac{K_i Q_i}{\sum_{i=1}^{n} K_i Q_i} \times 100. \qquad (17)$$

To speed up the calculations, some authors advise the use of nomograms[41], computing equipment[42], etc. According to the correction coefficient which was chosen, the concentration of a component found by formula (17) is expressed in weight or molar percentage. These aspects are discussed in greater detail below.

In practice one often has to deal with quite complicated organic mixtures which can only be separated by using multistage analytical procedures. It is obvious that the speed of the carrier gas changes when additional stages are inserted. If the calculation is based on concentration detectors, the corrected peak area should be obtained as the product of the area of the peak, of the correction coefficient, and of the velocity of the carrier gas during elution of the peak in question. Normalisation by multiplying the peak height by the retention time is not adequate in this case. In the analysis of complicated mixtures (petroleum spirit, pyrolysis tar, etc.) Vigdergauz and coworkers[43] used the method of double internal normalisation for quantitatively interpreting the chromatograms obtained at different stages. The first stage of their apparatus is intended to separate narrow fractions in the form of one or several peaks, which are then led to the column of the second stage for more detailed resolution. They showed that the corrected area of the peak of the $i$th component can be determined from the relationship

$$Q_{\text{corr},i} = \frac{KQ_i'' \sum_1^n Q_i'}{\sum_1^n Q_i''}, \qquad (18)$$

where $Q_i''$ is the area of the $i$th peak on the chromatogram of the second separation stage, and $\sum_1^n Q_i'$ and $\sum_1^n Q_i''$ are the sums of the peak areas corresponding to the fraction transferred to the second separation stage obtained on the chromatogram after the first and after the second stage respectively.

The percentage of the wanted component is calculated by the formula

$$P_i = \frac{Q_{\text{corr},i}}{\sum_1^n Q_{\text{corr},i}} \times 100. \qquad (19)$$

Conversion of the components at the detector inlet into carbon dioxide, hydrogen, or methane[44-46] is a very interesting method for the quantitative interpretation of gas chromatograms without previous calibration. The authors claim a number of advantages for this method over alternative methods of calculation, and they state that the precision and the reproducibility of the analytical results are higher.

When the gas-density balance (first described by Martin and James in 1956) is used as a detector, preliminary calibration or the experimental determinatin of correction coefficients are again unnecessary, since the signal of this detector depends only on the ratio of molecular weights of the substance being analysed and of the carrier gas[58]. In the analysis of the light fractions of crude oil (up to and including $C_7$) the measuring error was no more than 1% when a gas-density balance was used[55].

## The Internal Standard Method

The internal standard method, first proposed by Ray[38], relies on adding to the mixture for analysis a known amount of a suitable substance to act as a standard: the height or the area of the peak for the wanted component are then compared with those for the standard. This method is widely used both for major constituents and for the analysis of trace impurities[47,55]. The chosen standard should be a substance which is not contained in the mixture for analysis, which is thermally stable at the temperature of the experiment, and which cannot react with any of the constituents of the sample. At the same time, the standard peak should appear on the chromatogram as close as possible to the peaks of the mixture. The percentage of the $i$th component in the sample can be calculated from the formula

$$P_i = \frac{K_i Q_i}{K_s Q_s} R \times 100, \qquad (20)$$

where $K_i$ and $K_s$ are the correction coefficients for the peak area of the component and of the standard, determined by the sensitivity of the detector, $R$ is the ratio of the weight of internal standard to the weight of the mixture taken for analysis, and $Q_i$ and $Q_s$ are the peak areas of the component and of the standard.

An analogous expression applies to the peak heights. The calibration coefficients are determined by analysing binary mixtures of component and standard. Some workers prefer to plot calibration graphs for all the constituents of the mixture for analysis. Thus, Shlyakhov and coworkers[6], in their analysis of oxygenated hydrocarbons on a capillary column, plotted the ratio of the weight percentage of a given component to that of the standard (on the abscissa axis) against the ratio of the heights of the corresponding peaks (on the ordinate axis). The concentration of every component was determined from these calibration curves, with a mean relative error of 2%. When analysing multicomponent mixtures with a wide range of retention times, more accurate and reproducible results on the quantitative composition are obtained by using several internal standards. Lee and Oliver[56], using two internal standards, estimated small impurities (of the order of tenths of one per cent) of benzene, toluene, and styrene in ethylbenzene to a relative precision of 1–2%. Vlodavets and coworkers[57] used three internal standards for quantitative calculations when developing a method for the chromatographic estimation of acrolein and its dimerisation products.

It is evident from the above examples that the correct choice of method for calculating the composition of a mixture is the key to a successful quantitative analysis.

## IV. CALCULATION OF CORRECTION COEFFICIENTS IN QUANTITATIVE CHROMATOGRAPHIC ANALYSIS

The correct quantitative interpretation of chromatograms requires that the law relating the elution curve to the true ratio of components in the mixture should be known. A situation in which equal quantities of the substances to be separated correspond to equal values of the chosen parameter is exceptional in chromatographic practice. One usually has to apply correction coefficients, which make it possible to deal with the calculation as in the simplest case defined above. With these correction coefficients absolute calibration becomes unnecessary, and because of this many workers have examined the problem of evaluating the coefficients using both experimental and theoretical approaches.

The experimental determination of correction coefficients lags behind the rapidly growing number of substances to which chromatographic analysis is being applied. Furthermore, the experimental correction coefficients need to be critically scrutinised: different workers often report vastly different values which are due to subjective factors as well as to differences in the experimental conditions and procedures[31].

A more rational approach is to seek theoretical relationships between the signal of the detector and the physicochemical properties of the substances to be separated. An "ideal" method of processing the results of a chromatographic analysis would involve very complicated corrections for the distortions of the chromatogram introduced both by the column and by the detecting device.

The distortions introduced by the detector can be divided, on the whole, into two groups[59]: (1) those arising from non-linearity of the detector response as a function of the concentration of the wanted substance in the carrier gas, and (2) dynamical perturbations, caused by the rate of change of concentration in the carrier gas, affecting the sensitivity of the detector.

Obviously, correction coefficients can be tabulated for the entire range of concentrations of the wanted substances only if the calibration plot $y = f(c)$ is rectilinear, that is,

$$y = S_i c, \tag{21}$$

where $y$ is the deflection of the recorder pen, $c$ the concentration of the component in question, and $S_i$ the sensitivity of the detector towards that component.

For the first and the second group of distortions, Eqn. (21) becomes, respectively,

$$y = S_0 + S_1 c + S_2 c^2 + S_3 c^3 + \ldots \tag{22}$$

and

$$y = S_1 c + S_2 \frac{dc}{dt} + S_3 \frac{d^2c}{dt^2} + \ldots . \tag{23}$$

Since Eqn. (21) applies only to a limited range of concentrations (lying, as a rule, in the region of low values of $c$), it is always necessary in practice to estimate the order of magnitude of the error due to non-linearity[60].

A summary of published data on the upper limits of detector linearity is given in Kalmanovskii and Fesenko's paper[40] on detecting devices for gas chromatography.

Among the ways in which the separating part of the apparatus can distort the chromatogram we should list the increase in overall velocity of the flow occurring when the desired component emerges from the column, called the "surge effect" by van de Craats[37]. As a result of this effect, the peak area traced on the chromatogram is smaller than the area corresponding to the measured flow rate.

The author recommends the correction factor

$$f_1 = 1 + \frac{v_s c_s}{100\omega_u} \times \frac{V_2 - V_{gas}}{V_R}, \tag{24}$$

where $v_s$ is the sample size (ml), $c_s$ the concentration of the component in the sample (mole %), $\omega_u$ the width of the peak at the base obtained by drawing tangents (ml), $V_R$ the retention volume of the component (ml), and $V_{gas}$ the volume of gas in the column (ml). He also derives a more precise correction factor:

$$f_2 = 1 + 0.7\,\frac{c_{max}}{100 - c_{max}} \times \frac{V_R - V_{gas}}{V_R}, \tag{25}$$

where $c_{max}$ is the concentration corresponding to the peak maximum.

All these errors, most of which are effectively impossible to control, call for the application of corrections for every type of analytical procedure. However, in practical chromatography the corrections are usually confined to coefficients depending only on the principle of operation of the detector and on the nature of the carrier gas and of the wanted component.

We shall now discuss the methods of determining these correction coefficients, which, when multiplied by the peak areas, convert them into the appropriate gravimetric and molar amounts of substance injected into the column.

According to one school of thought[31], the correction coefficients should always convert the chromatographic results into percentage by weight. However, the present writers prefer to use molar correction coefficients in tabulations, because they reflect most clearly the relation between the signal corresponding to a substance and the chemical nature of the substance.

It is easy to show[43] that the molar correction factor for a given component can be readily converted into a gravimetric factor by the relation

$$\frac{K_w}{K_m} = \frac{M_i}{M_{st}}, \tag{26}$$

where $K_w$ is the gravimetric correction coefficient, $K_m$ the molar correction coefficient, $M_{st}$ the molecular weight of the standard (for which $K_w = K_m = 1$), and $M_i$ the molecular weight of the component.

As we have already pointed out, different substances have practically identical correction coefficients only in special cases. These occur, for example, in the analysis of members of a homologous series using katharometric detection and a light carrier gas (helium or hydrogen). The adequacy of this assumption depends, of course, on the analytical precision required. In every other case the correction coefficients are quite different.

Messner and coworkers[61] showed that for a katharometer detector and helium as the carrier gas a strictly linear relationship exists between the molecular weight and the value of $1/K_m$ for the individual members of homologous series of hydrocarbons, the slope of the resulting straight line decreasing as the degree of branching of the hydrocarbon increases. The following rules were established: $1/K_m$ is smaller for cyclic than for normal hydrocarbons; it is smaller for *ortho*-substituted isomers than

for the *meta*- and *para*-isomers; for normal paraffins $1/K_m$ is higher than for any functional derivatives.

Jamieson[62] has examined a large number of organic compounds, and he has confirmed the rule of Messner and coworkers according to which $1/K_m$ decreases as the branching of the hydrocarbon skeleton increases. He has also shown that this rule is not so strictly followed by polyfunctional derivatives (ethers, hydroxy-, alkoxy-, and ketoxy-ethers).

Jamieson, and also other workers[63,64], showed that with alcohols the relative molar correction varies with the square root of the molecular weight. Iogansen and coworkers[65] found that the correction coefficient for hydrocarbons varies with the 2/3 power of the molecular weight.

Nikelly[66] showed that the plot of correction factor against number of carbon atoms (for the case of a katharometer) is curved, the curvature decreasing in the sequence: alkanes, alkenes, alcohols. From the analytical results for a seven-component mixture of alkenes and alcohols, obtained with temperature programming and by using his own correction coefficients, he estimated an error of 2–4% for each of the components. In the same paper it is shown that the correction coefficients are independent of temperature variation during the analysis.

Similar observations are reported by Baumann and Olund[67], who determined the relation between molar corrections and the normal boiling points in a series of sulphides and thiols.

When a flame ionisation detector is used with hydrocarbons and their derivatives a strictly linear relationship is observed between the relative molar correction and the number of carbon atoms[68].

It should be noted that with many detectors there is no simple systematic relation between the signal and the nature of the substance. Typical of these is Grant's emissivity detector[69], for which the correction coefficients depend on the velocity of the carrier gas and on the absolute amount of substance for analysis. Another characteristic of this detector is that the signal depends very much on the class of compound, and is practically constant within a homologous series. Thus[22], the signal for paraffins and halogenated hydrocarbons relative to benzene is 0.14 and 0.15 respectively, whereas for naphthalene the signal is 2.0–3.0.

## Thermal Conductivity Detector

Most of the work on correction coefficients, both experimental and theoretical, relates to the thermal conductivity detector. The early workers[70,71] assumed that the results of chromatographic analysis are given in molar percentages: thus, Hausdorff[70] considered that when a katharometer is used in conjunction with a light carrier gas the area under the elution curve is proportional to the number of molecules of the substance, and therefore to its molar percentage.

The question of whether the area under the curve on the recorder gives a better approximation to the weight or to the molar percentage has been discussed in several papers[72–76].

More recent work has shown experimentally that in many cases, particularly in the analysis of hydrocarbon mixtures, the area of the peak of a component expressed as a fraction of the total area for all components gives a better approximation to the weight fraction of the component in the sample. However, in most cases the areas under the curve do not correspond either to weight or to molar percentages. This was clearly demonstrated by van de Craats[37], who measured the relative correction factors for the $C_1$–$C_4$ hydrocarbons.

Feish and Engel'gart[72] showed that the correction factors, defined as the peak areas for those hydrocarbons referred to the peak area of n-butane (for equal sample volumes), are equal to the ratio of molecular weights in the zeroth approximation, and to the 3/4 power of the ratio of molecular weights in the first approximation. The first approximation refers to a method in which the standard is chosen to have a molecular weight intermediate between those of the components in the mixture for analysis. In this case the coefficients, calculated as $(M_i/M_{st})^{3/4}$, are approximately the same as those found by van de Craats. At the same time, if the ratio of the areas is taken to the power 4/3 a better approximation to weight percentages is obtained.

The first papers on the determination of correction coefficients were those of Rosie and Grob[34] and Messner and coworkers[61]. Most of the workers who have examined the theoretical aspects of correction coefficients have checked their conclusions against the results of those papers.

Messner and coworkers[61] proposed that the relative molar correction should be expressed in the form

$$\frac{1}{K_M} = A + BM, \qquad (27)$$

where $A$ and $B$ are constants for a given homologous series, and $M$ is the molecular weight.

These workers calculated values of $A$ and $B$ for many classes of organic compounds. Some of their values are tabulated below:

| Series | A | B |
|---|---|---|
| n-Paraffins | 6.7 | 1.35 |
| Methylparaffins | 10.8 | 1.25 |
| α-Olefins | 13.0 | 1.20 |
| n-Alcohols, primary | 34.9 | 0.808 |
| n-Alcohols, secondary | 33.6 | 0.857 |
| n-Alcohols, tertiary | 34.9 | 0.808 |
| Acetates | 37.1 | 0.841 |
| Ketones | 35.9 | 0.881 |

These correction coefficients are independent of concentration over a wide range. A tenfold change (from 1.43 to 0.14) in the molar ratio of diisopropyl ether to benzene had practically no effect on the correction factor. In the same paper it is shown that the correction coefficients are independent of the type of katharometer used (thermistor, or hot wire). Furthermore, it was also established that the correction coefficients for helium and hydrogen are unaffected by change in temperature over a wide range. However, in the case of nitrogen, which shows a strong temperature variation of the correction coefficients, standardisation is particularly difficult. This is especially true of the $C_2$ hydrocarbons, to which the katharometer has practically no sensitivity between 50° and 80°.

As was to be expected, all the workers who studied correction coefficients for katharometers approached the problem by considering changes in thermal conductivity of

the carrier gas as a function of the concentration of the wanted component in the carrier. Keulemans[77] considers that at low concentrations, when the mole fraction ($x$) of the component in the carrier gas is less than $10^{-2}$, the thermal conductivity of the mixture is the sum of the thermal conductivities of the carrier and of the impurity multiplied by the appropriate mole fractions. Then

$$x = \frac{\lambda_1 - \lambda_{12}}{\lambda_1 - \lambda_2}, \quad (28)$$

where $\lambda_1$, $\lambda_2$, and $\lambda_{12}$ are the thermal conductivities of the carrier gas, of the wanted component, and of the mixture respectively. Thus, if the signal is proportional to the change in thermal conductivity ($\lambda_1$ - $\lambda_{12}$), the peak area should lead to an accurate value of the mole fraction when the correction factor $1/(\lambda_1 - \lambda_2)$ is used. However, this is inconsistent with the fact that the area under the elution curve usually corresponds to a weight percentage.

Iogansen[65] takes the same view, and suggests that the molar correction for light hydrocarbons should be calculated by the formula

$$\frac{1}{K_{M_i}} = \frac{\lambda_1 - \lambda_{12}}{\lambda_1 - \lambda_2} \times \sqrt[3]{(M_i/58)^2}, \quad (29)$$

where $M$ is the molecular weight of the wanted hydrocarbon, and 58 the molecular weight of n-butane (taken as standard).

Hinkle and Johnsen[36] propose a correction factor of $\rho^{-2/3}$ to the peak area, where $\rho$ is the vapour density, to give molar percentages. This agrees with Iogansen's conclusion, since

$$\rho = c\left(\frac{\mu c_p}{\lambda}\right)(M)(a)^{-1}, \quad (30)$$

where $c$ is a constant, $\mu$ the absolute viscosity, $\lambda$ the thermal conductivity, $c_p$ and $c_v$ are the specific heats at constant pressure and constant volume, $M$ is the molecular weight, and $a = c_p/c_v$.

Browning and Watts[32] proposed a correction to the peak areas on the basis of the thermal conductivity of the appropriate component. In principle, this correction relies on dividing the peak areas given by the analysis by the thermal conductivities of the corresponding substances, since large peak areas correspond to large thermal conductivities and conversely. Heft has shown[73] that with nitrogen as the carrier gas this correction only makes matters worse.

Littlewood[74], and more recently Mecke and Zirker[75], started from an expression for the thermal conductivity of a mixture derived from the theory of Chapman and Enskog.

Littlewood concluded that the thermal conductivity of the carrier gas, of the component being analysed, and of their mixtures ($\lambda_1$, $\lambda_2$, and $\lambda_{12}$ respectively), and also the mole fraction of the component in the carrier gas ($x_2$), are related to the average diameters of the molecules of the carrier ($\sigma_1$) and of the impurity ($\sigma_2$) by the expression

$$-\frac{1}{\lambda} \times \frac{d\lambda_{12}}{dx_2} = \frac{\sigma_{12}^2}{\sigma_1^2}, \quad (31)$$

where

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}.$$

To obtain the average molecular diameters needed for the calculation of correction coefficients this worker used some of Rosie and Grob's results on the cross-section of the methyl, methylene, methine, and phenyl groups, and also of the quaternary carbon atom and aromatic hydrogen. Littlewood, on the assumption that the molecular diameter is approximately equal to the sum of the diameters of the constituent elements, calculated correction coefficients (for helium) which were practically indistinguishable from some other results of Rosie and Grob:

| Compound | Relative molar correction | | Compound | Relative molar correction | |
|---|---|---|---|---|---|
| | Rosie and Grob | Littlewood | | Rosie and Grob | Littlewood |
| n-Heptane | 143 | 143 | Ethylbenzene | 129 | 135 |
| n-Octane | 160 | 162 | o-Xylene | 130 | 132 |
| 2-Methylpentane | 120 | 120 | p-Xylene | 131 | 132 |
| 3-Methylpentane | 119 | 120 | Mesitylene | 149 | 148 |

Mecke and Zirker, who also introduced a correction for the change in molecular diameter under the influence of molecular forces, arrived at the same conclusion.

In keeping with Littlewood's assumption, Mecke and Zirker showed (in the case of normal paraffins) that the ratio of the square of the increment in molecular diameter $\Delta d^2_{CH_2}$ to the increment in molecular weight $\Delta M_{CH_2}$ is a constant:

$$\frac{\Delta d^2_{CH_2}}{\Delta M_{CH_2}} = \text{const.} \quad (32)$$

Thus, for the homologous series $A-(CH_2)_n$, where $A$ is a functional group, the square of the average molecular diameter can be calculated by the formula

$$d^2 = d_A^2 + n d^2_{CH_2} = K(A + nM_{CH_2}). \quad (33)$$

The calculation of correction coefficients by the method of Littlewood and of Mecke and Zirker is made much easier by this relationship. The work of these authors is valuable also because it provides an explanation for the observed linear variation of the correction coefficients with molecular weight within a given homologous series, and for the slight deviation from linearity in the first few members (influence of $A$).

Schmauch and Dinerstein[78], and also Hoffman[79], arrived at their molecular correction coefficients from the classical kinetic theory of monatomic gases. According to the former, the sensitivity of the katharometer ($E_0$) is related to the thermal conductivity of the carrier gas ($\lambda_1$) and to that of the mixture ($\lambda_{12}$) by the following expression:

$$E_0 = c\sqrt{\lambda_1}\,\frac{\lambda_1 - \lambda_2}{\lambda_{12}}. \quad (34)$$

To calculate the thermal conductivity of the mixture they applied Vasil'eva's equation

$$\lambda_{12} = \frac{\lambda_1}{1 + A_{12}\left(\frac{1-x}{x}\right)} + \frac{\lambda_2}{1 + A_{21}\left(\frac{x}{1-x}\right)}, \quad (35)$$

where $x$ is the mole fraction, and $A_{12}$ and $A_{21}$ are constants. They conclude that the same correction coefficients can be used over a wide range of concentrations if the difference in thermal conductivity between the substance and the carrier gas is very large (for example, helium or hydrogen carriers, and organic compounds). In other systems, for example, when nitrogen is the carrier and the response is

not linear, a correction is needed for each concentration interval of the test substance.

Hoffman analyses the detector signal into four multiplicative terms: a cell factor, a carrier-gas factor, a molar thermal conductivity change factor, and a concentration factor. From Vasil'eva's equation for the change in molar thermal conductivity, Hoffman obtains

$$F=\frac{\lambda_1-\lambda_2}{\lambda_{12}\,x}=F_0+f_x\,(x\ll 1), \tag{36}$$

where

$$F_0=A_{12}-\frac{\lambda}{A_{12}} \text{ and } \lambda=\frac{\lambda_2}{\lambda_1},$$

$\lambda_1$ and $\lambda_2$ being the thermal conductivities of the pure carrier gas and of the component. Since $x \ll 1$, it follows that $F_0 \simeq F$. The quantity $F_0$ can be neglected in practice, but the quantity $F_{0i}/F_{0st}$, corresponding to the relative molar signal, can be calculated if the data needed to calculate the constants in Vasil'eva's equation are available.

The relative molar corrections obtained by Hoffman for nitrogen, helium, and hydrogen agree strikingly well with the corrections determined experimentally, and also with the results of Messner and coworkers[61], and others. Hoffman showed that the second term (effect of the carrier gas) accounts for only 4–13%. He ascribes the peak inversion which is observed when nitrogen is the carrier to negative $F_0$ values.

Heft[73] explains peak inversion by pointing out that the katharometer response is affected by changes in the specific heat of the mixture of carrier and substance for analysis as well as by thermal conductivity changes. For hydrogen and helium the ratio of these two effects is always much less than unity, whereas for nitrogen the specific heat effect can be much larger than the thermal conductivity effect. This causes cooling of the detector filament, and leads to peak inversion.

As a result of an interesting study of the influence of the specific heat of the components to be analysed on the detector signal, Heft concludes that when nitrogen is used as the carrier gas the areas of the peaks under the elution curve correspond to weight percentages only if one is dealing with members of a homologous series, or with substances having identical specific heats. In all other cases a correction is necessary.

## Gas-Density Balance

This detector, as stated above, is the most suitable for quantitative analysis. Phillips and Timms[58] found that the integral signal for the $i$th substance ($a_i$) depends on the molecular weight $M_i$ as indicated by the equation

$$Q_i=K\,g\left(\frac{M_i-M_0}{M_i}\right), \tag{37}$$

where $M_0$ is the molecular weight of the carrier gas, $g$ the amount of the substance, and $K$ an apparatus constant.

The relative correction coefficient is then

$$K_B=\frac{(M_{st}-M_0)\,M_i}{M_{st}(M_i-M_0)}. \tag{38}$$

Thus, for benzene as the standard and hydrogen as the carrier gas, the correction coefficient for the $i$th compound takes the value

$$K_B=\frac{M_i\times 76}{(M_i-2)\times 78}. \tag{39}$$

The main virtue of this detector is that it does not require tabulated and correction factors. When needed, the factors can always be calculated for any unknown substance provided that its molecular weight is known.

## Flame Ionisation Detector

At the present time, the flame ionisation detector is one of the most satisfactory devices for quantitative analysis by gas chromatography. It provides results which are independent of temperature and of carrier gas, and a large linear range of signals.

However, relatively little has been published on the use of the flame ionisation detector in the quantitative analysis of real mixtures. This is partly due to the fact that the signal depends very significantly on constructional details of the electrodes, burner geometry, flame temperature, etc.

The correction coefficients for the flame ionisation detector are far more sensitive to structural features of the compounds being analysed than are the coefficients for the katharometer[80]

As already pointed out, various authors have obtained a linear relation between the relative molar correction and the number of carbon atoms in the molecule. Altschuller and Clemons[28] showed that the signal of this detector is a linear function of the number of carbon atoms in aromatic hydrocarbons up to $C_{10}$.

One characteristic of the flame ionisation detector is that carbon atoms linked to oxygen or nitrogen contribute practically nothing to the signal given by the compound being examined[81–85]. This is because such a carbon atom does not take part in the combustion, which is the physicochemical basis of the operation of the flame ionisation detector.

Schomburg[68] found a molar correction coefficient (relative to $m$-xylene) varying only over the range 0.59–0.65 for a series of carbonate esters of molecular weight between 116 and 172.

Unfortunately, the special features of the flame ionisation detector limit (or even debar) its application in the analysis of some commercially important substances such as the inert gases, hydrogen, oxygen, carbon monoxide, carbon dioxide, and many others[86].

Schomburg warns[68] against the use of the flame ionisation detector in the analysis of substances whose combustion produces a solid deposit in the burner. For example, a solid residue of boron dioxide is formed in the analysis of alkylborons, and makes quantitative analysis impossible.

Ettre and coworkers[82] showed that the correction coefficients for the flame ionisation detector, like those for for the katharometer, can be calculated by Eqn. (27). Those workers, and also Desty and coworkers[87], obtained correction coefficients for very many organic compounds.

Bredel[88] states that the areas of hydrocarbon peaks are related to the retention times and to the number of carbon

atoms in the molecule by the expression

$$Q = t_R(A\,n + B), \tag{40}$$

where the coefficients $A$ and $B$ are different for different types of column. This author suggests that the peak areas should be corrected by dividing them by the product $t_R n$.

Ongkiehong[83] found that in many cases approximate correction coefficients can be calculated without appreciable loss of analytical precision from the formula

$$K_B = \frac{M_i n_{st}}{n_i M_{st}}, \tag{41}$$

where $M_i$ and $M_{st}$ are the molecular weight of the $i$th compound and that of the standard, and $n_i$ and $n_{st}$ the number of carbon atoms in the molecule of the $i$th compound and of the standard.

These approximate correction coefficients give particularly good results in the analysis of substances containing different functional groups (alcohols, acids, ether, etc.).

Sternberg and coworkers[89], and also Dewar[90], have correlated the detector signal with the structural properties of the substances being analysed.

### β-Ionisation Detector

This very sensitive detector can be used to analyse any compound whose ionisation potential is less than 11.7 eV. One of its characteristics is that the correction coefficients are relatively insensitive to changes in carrier-gas flow and in temperature, and also to the geometry of the apparatus. The integral signal of the β-ionisation detector is proportional to the molecular weight of the substance being analysed, but the recorder deflection is not linear in relation to concentration.

The theory of the β-ionisation detector was first investigated by Lovelock[91]. He showed, by analysing substances belonging to different classes, that the non-linearity of the correction coefficients (relative to pentan-1-ol) as a function of molecular weight varies for substances of different nature. Thus, with the methyl esters of primary fatty acids the correction coefficient decreases sharply with increase of molecular weight up to one hundred, after which it tends to a constant value. A similar behaviour is observed with n-primary alcohols, whereas with ethers and ketones the relative correction coefficient increases sharply over the whole interval of molecular weights (up to 200) which was examined. An increase in the weight correction coefficient with increase in molecular weight was found also in the analysis of non-esterified lower fatty acids[92]. When the molecular weight rises above one hundred the correction coefficient tends to a constant value.

By working with fully halogenated and nitrated hydrocarbons, Lovelock ascribed[93] these anomalies of the β-ionisation detector to the capture of free electrons by suitable groups, such as the carboxyl group, which also explains the results of Böttcher[92] and others.

The formula

$$1/K_M = 2.5 \log n - 1.41, \tag{42}$$

where $n$ is the number of carbon atoms in the molecule, has been suggested for calculating the relative correction factor (with respect to nonanoic acid).

TABLE 1. Molar correction coefficients $K_M$ for the $C_1$–$C_6$ hydrocarbons and light gases (relative to n-butane).

| Component | Carrier gas: hydrogen | | helium | | | nitrogen |
|---|---|---|---|---|---|---|
| | 31, 37* | 65 | 61, 102 | 103 | 104 | 65 |
| Hydrogen | — | — | 58.6 | — | 55.6[d] | — |
| Helium | 2.22 | — | — | — | — | — |
| Nitrogen | 1.764 | — | 2.02 | — | — | — |
| Oxygen | 1.955 | — | 2.12 | — | — | — |
| Carbon monoxide | 1.874 | — | 1.77 | — | — | — |
| Carbon dioxide | 1.548 | — | 2.02 | — | — | — |
| Hydrogen sulphide | — | — | 4.48 | — | — | — |
| Methane | 2.031 | 2.27 | 2.36 | — | 1.82[d] | — |
| Acetylene | 1.725 | 2.09 | — | — | — | — |
| Ethylene | 1.523 | — | 1.77 | — | 1.45[d] | 5.0 |
| Ethane | 1.436 | 1.45 | 1.66 | 1.663 | — | 5.3 |
| Allene | 1.295 | — | — | — | — | — |
| Cyclopropane | 1.225 | — | — | — | 1.33[d] | — |
| Methylacetylene | 1.265 | — | — | — | — | — |
| Propene | 1.236 | 1.37 | 1.35 | — | 1.32[d] | 1.43 |
| Propane | 1.169 | 1.23 | 1.31 | 1.284 | — | 1.5 |
| Isobutane | 1.030 | 1.12 | 1.03 | — | — | 1.03 |
| Isobutene | 1.044 | 1.02 | 1.03 | — | — | 0.91 |
| But-1-ene | 1.032 | 1.14 | 1.05 | — | — | 0.91 |
| Buta-1,3-diene | 1.085 | — | 1.06 | — | — | — |
| Buta-1,2-diene | 1.047 | — | — | — | — | — |
| n-Butane | 1.000[a] | 1.00 | 1.00[b] | 1.000[c] | 1.00 | 1.00 |
| *trans*-But-2-ene | 1.021 | — | 1.00 | — | — | 0.83 |
| *cis*-But-2-ene | 1.021 | — | 1.98 | — | — | 0.83 |
| Ethylacetylene | 1.074 | — | — | — | — | — |
| Neopentane | 0.922 | — | 0.85 | — | — | — |
| 3-Methylbut-1-ene | — | — | 0.86 | — | — | — |
| Isopentane | 0.915 | — | 0.83 | — | 0.79[d] | 0.78 |
| Pent-1-ene | 0.911 | — | 0.86 | — | — | 0.76 |
| 2-Methylbut-1-ene | — | — | 0.86 | — | — | 0.76 |
| n-Pentane | 0.888 | — | 0.80 | 0.825 | 0.78[d] | 0.76 |
| *trans*-Pent-2-ene | 0.911 | — | 0.81 | — | — | 0.76 |
| *cis*-Pent-2-ene | 0.911 | — | 0.86 | — | — | 0.76 |
| 2-Methylbut-2-ene | — | — | 0.88 | — | — | 0.76 |
| Cyclopentane | — | — | 0.87 | — | 0.81[e] | — |
| Penta-1,4-diene | — | — | 0.81 | — | — | — |
| Cyclopentene | — | — | — | — | 0.87[e] | — |
| Isoprene | 0.977 | — | — | — | — | — |
| Hexane | 0.809 | — | 0.70 | — | 0.57 | — |

a $K_M$ relative to benzene 1.000
b $K_M$ relative to benzene 1.177
c $K_M$ relative to benzene 1.173
d Measured in the temperature range −4–0°
e Measured at 52°

* These and the corresponding numerals in later Tables indicate literature references (Ed. of Translation).

The correction coefficients for the β-ionisation detector, with argon as the carrier gas, have been calculated by Simmons and coworkers[94] and by Durrett and coworkers[95].

Condon and coworkers[96] determined the weight correction factors (relative to n-butanol) for a number of alcohols.

When a gas not susceptible to metastable ionisation is used as the carrier, the sensitivity of this detector approaches that of the katharometer. Under these conditions the relative weight corrections are easily calculated by the formula

$$K_B = \frac{M_i(\sigma_{st} - \sigma_0)}{(\sigma_i - \sigma_0)M_{st}}, \tag{43}$$

where $\sigma_0$, $\sigma_i$, and $\sigma_{st}$ are the ionisation cross-sections of the carrier gas, the wanted compound, and the standard.

Otvos and Stevenson[97] showed that the ionisation cross-sections are additive, and can be calculated from the appropriate increments (which equal 4.16 and 1.00 for carbon and hydrogen respectively).

TABLE 2. Molar correction coefficients $K_M$ for hydrocarbons (relative to benzene).

| Component | Katharometer, carrier gas: hydrogen | helium | | nitrogen | | Flame ionisation detector | | Argon detector | Emissivity detector |
|---|---|---|---|---|---|---|---|---|---|
| | 79 | 79 | 34, 61 | 79 | 62 | 105 | 87 | 94 | 69 |
| n-Pentane | 0.931 | 0.953 | 0.95 | 1.960 | — | 1.130 | — | — | — |
| Cyclopentane | — | — | 1.03 | — | — | — | — | 0.644 | — |
| 2,2-Dimethylbutane | — | — | 0.863 | — | — | 0.920 | — | 0.456 | — |
| 2,3-Dimethylbutane | — | — | 0.863 | — | — | — | — | 0.498 | — |
| 2-Methylpentane | — | — | 0.834 | — | — | — | — | 0.535 | — |
| 2-Methylpent-1-ene | — | — | — | — | — | 0.980 | — | — | — |
| 3-Methylpentene | — | — | 0.841 | — | — | — | — | 0.529 | — |
| n-Hexane | 0.814 | 0.834 | 0.814 | 1.100 | 1.041 | 0.951 | 0.966 | 0.55 | 0.090 |
| Methylcyclopentane | — | — | 0.820 | — | — | — | — | 0.633 | — |
| Benzene | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Cyclohexane | 0.954 | 0.926 | 0.878 | 0.925 | — | — | 1.00 | 0.647 | 0.208 |
| 2,2-Dimethylpentane | — | — | 0.752 | — | — | — | — | 0.404 | — |
| 2,4-Dimethylpentane | — | — | 0.775 | — | — | — | — | 0.441 | — |
| 1,1-Dimethylcyclopentane | — | — | 0.808 | — | — | — | — | 0.517 | — |
| 2,3-Dimethylpentane | — | — | 0.741 | — | — | — | — | 0.399 | — |
| 2-Methylhexane | — | — | 0.736 | — | — | — | — | 0.441 | — |
| 2,2,3-Trimethylbutane | — | — | 0.775 | — | — | — | 0.825 | — | — |
| *cis*-1,3-Dimethylcyclopentane | — | — | — | — | — | — | — | 0.566 | — |
| *trans*-1,3-Dimethylcyclopentane | — | — | — | — | — | — | — | 0.561 | — |
| 3-Methylhexane | — | — | 0.753 | — | — | — | — | 0.402 | — |
| *trans*-1,2-Dimethylcyclopentane | — | — | — | — | — | — | — | 0.570 | — |
| 3-Ethylpentane | — | — | 0.764 | — | — | — | — | — | — |
| n-Heptane | 0.741 | 0.710 | 0.700 | 0.807 | 0.807 | 0.823 | 0.850 | 0.465 | 0.110 |
| *cis*-1,2-Dimethylcyclopentane | — | — | — | — | — | — | — | 0.507 | |
| Methylcyclohexane | — | — | 0.834 | — | — | 0.847 | 0.914 | 0.514 | 0.017 |
| Ethylcyclopentane | — | — | 0.794 | — | — | — | — | 0.471 | |
| Toluene | 0.863 | 0.863 | 0.863 | 0.863 | 0.827 | — | 0.966 | 1.012 | 1.100 |
| 2,2,4-Trimethylpentane | — | — | — | — | — | — | 0.685 | 0.35 | — |
| 1,1,3-Trimethylcyclopentane | — | — | — | — | — | — | — | 0.473 | — |
| 1,1,2-Trimethylcyclopentane | — | — | — | — | — | — | — | 0.382 | — |
| 2,5-Dimethylhexane | — | — | — | — | — | — | — | 0.338 | — |
| 1,2,4-Trimethylcyclopentane (*cis-trans-cis*) | — | — | 0.735 | — | — | — | — | 0.413 | — |
| 2,4-Dimethylhexane | — | — | — | — | — | — | — | 0.350 | — |
| 2,2,3-Trimethylheptane | — | — | — | — | — | — | — | 0.297 | — |
| 2,3,4-Trimethylpentane | — | — | — | — | — | 0.722 | — | 0.345 | — |
| 2,3,3-Trimethylpentane | — | — | — | — | — | — | — | 0.284 | — |
| 1,2,4-Trimethylcyclopentane (*cis-cis-trans*) | — | — | 0.700 | — | — | — | — | 0.403 | — |
| 2-Methylheptane | — | — | — | — | — | — | — | 0.348 | — |
| n-Octane | 0.657 | 0.614 | 0.626 | 0.654 | — | — | 0.76 | — | 0.089 |
| 1,2-Dimethylcyclohexane | — | — | — | — | — | — | — | — | 0.016 |
| 1,3,5-Trimethylbenzene | — | — | — | — | 0.600 | — | — | — | 0.830 |
| 1,2,4-Trimethylbenzene | — | — | 0.666 | — | 0.645 | — | — | — | 0.768 |
| t-Butylbenzene | — | — | — | — | 0.556 | — | — | — | — |
| s-Butylbenzene | — | — | 0.633 | — | 0.547 | — | — | — | — |
| 4-Isopropyl-1-methylbenzene | — | — | — | — | 0.556 | — | — | — | — |
| n-Butylbenzene | — | — | — | — | 0.518 | — | — | — | — |
| 1,2,4,5-Tetramethylbenzene | — | — | — | — | 0.553 | — | — | — | — |
| 1,2,3,5-Tetramethylbenzene | — | — | — | — | 0.556 | — | — | — | — |
| n-Decane | | | | | | | | | |
| Biphenyl | — | — | 0.503 | — | — | — | — | — | 0.092 |
| Naphthalene | — | — | — | — | — | — | — | — | 1.237 |
| 2-Methylnaphthalene | — | — | — | — | — | — | — | — | 1.714 |
| Camphene | — | — | — | — | — | — | — | — | 0.96 |
| α-Pinene | — | — | — | — | 0.70 | — | — | — | — |
| β-Pinene | — | — | — | — | 0.76 | — | — | — | — |
| Limonene | — | — | — | — | 0.77 | — | — | — | — |
| Myrcene | — | — | — | — | 0.67 | — | — | — | — |
| Ethylcyclohexane | — | — | — | — | 0.68 | — | — | — | — |
| Ethylbenzene | — | — | 0.690 | — | — | — | 0.817 | — | — |
| p-Xylene | — | — | 0.775 | — | 0.695 | 0.766 | 0.914 | — | — |
| m-Xylene | — | — | 0.764 | — | 0.690 | 0.766 | — | — | 0.800 |
| 2,2,5-Trimethylhexane | — | — | 0.764 | — | 0.700 | — | — | — | 0.760 |
| 2,2,4-Trimethylhexane | — | — | — | — | — | — | — | 0.319 | — |
| 2,3,5-Trimethylhexane | — | — | — | — | — | — | — | 0.323 | — |
| 2,2,3-Trimethylhexane | — | — | — | — | — | — | — | 0.327 | — |
| 2,3,3-Trimethylhexane | — | — | — | — | — | — | — | 0.323 | — |
| 2,2,3,3-Tetramethylpentane | — | — | — | — | — | — | — | 0.319 | — |
| | | | | | | | | 0.312 | — |
| n-Nonane | 0.542 | — | 0.565 | 0.486 | 0.550 | 0.65 | — | — | — |
| Isopropylbenzene | — | — | 0.705 | — | 0.620 | — | — | — | — |
| n-Propylbenzene | — | — | 0.690 | — | — | — | — | — | — |
| 4-Ethyl-1-methylbenzene | — | — | 0.666 | — | — | — | — | — | — |

## Combustion Tube

The quantitative interpretation of gas chromatograms is made easier if a combustion tube is provided as an attachment to the detector. When the components are converted into carbon dioxide or methane, the weight coefficients are readily calculated by formula (41):

$$K_B = \frac{M_i n_{st}}{n_i M_{st}},$$

where $n_i$ is the number of carbon atoms in the molecule of the $i$th component. For benzene as the standard,

$$K_B = \frac{M_i}{n_i} \times 0.077.$$

These correction coefficients are independent of the type of detector and of the nature of the carrier gas.

## Other Detectors

Information has been published on the correction coefficients of other detectors. Wirth[98] and Bredel[99] have shown that the relative molar correction coefficient for the flame temperature detector is the ratio of the heats of combustion. With other detectors there appears to be no simple systematic relationship between the signal and the nature of the substance for analysis[100,101].

TABLE 3. Molar correction coefficients $K_M$ for oxygenated compounds (relative to benzene). Katharometer detector.

| Component | Carrier gas: helium | | nitrogen | Component | Carrier gas: helium | | nitrogen |
|---|---|---|---|---|---|---|---|
| | 61 | 31 | 62 | | 61 | 31 | 62 |
| *Alcohols* | | | | Pentan-2-one | — | — | 1.03 |
| Water | 0.476 | 0.365 | — | Pentane-3-one | 0.909 | — | 1.02 |
| Methanol | 1.818 | 1.593 | 5.26 | 2-Methylpentan-4-one | — | — | 0.86 |
| Ethanol | 1.384 | 1.214 | 2.96 | 3,3-Dimethylbutan-2-one | 0.846 | — | 0.91 |
| Prop-2-en-1-ol | — | — | 2.00 | Hexan-2-one | — | — | 0.85 |
| Propan-2-ol | 1.174 | — | 2.04 | 2-Methylpent-2-en-4-one | — | — | 0.88 |
| Propan-1-ol | 1.200 | 1.048 | 1.75 | Heptan-2-one | 0.752 | — | 0.74 |
| Methylpropan-2-ol | 1.054 | — | — | Methylheptanone | — | — | 0.69 |
| Butan-2-ol | 1.033 | — | 1.39 | Octan-2-one | 0.679 | — | 0.62 |
| Methylpropan-1-ol | — | — | 1.25 | Methyl phenyl ketone | — | — | 0.69 |
| Butan-1-ol | 1.054 | 0.924 | 1.15 | Nonan-2-one | — | — | 0.55 |
| 2-Methylbutan-3-ol | 0.942 | — | — | Isophorone | — | — | 0.74 |
| Pentan-3-ol | 0.916 | — | — | Decan-2-one | — | — | 0.49 |
| Pentan-2-ol | 0.918 | — | — | Menthanone | — | — | 0.73 |
| 2-Methylbutan-4-ol | 0.933 | — | — | Camphor | — | — | 0.74 |
| Pentan-1-ol | 0.942 | 0.826 | 0.88 | Undecan-2-one | — | — | 0.44 |
| Hexan-1-ol | 0.849 | 0.744 | 0.73 | β-Ionone | — | — | 0.43 |
| Cyclohexanol | — | — | 1.09 | γ-Ionone | — | — | 0.40 |
| Heptan-1-ol | 0.773 | 0.678 | 0.60 | *Ethers* | | | |
| Phenylmethanol | — | — | 0.82 | Diethyl | 0.912 | — | 1.22 |
| Octan-1-ol | — | — | 0.52 | Butyl methyl | — | — | 0.98 |
| Nonan-1-ol | — | — | 0.46 | Diisopropyl | 0.768 | — | 0.86 |
| Decan-1-ol | — | — | 0.40 | Di-n-propyl | 0.761 | — | 0.78 |
| Citronellol | — | — | 0.47 | Butyl methyl | — | — | 0.99 |
| Geraniol | — | — | 0.48 | Butyl ethyl | 0.768 | — | 0.81 |
| Linalool | — | — | 0.49 | Butyl propyl | — | — | 0.68 |
| Menthol | — | — | 0.73 | Di-n-butyl | 0.625 | — | 0.59 |
| α-Terpineol | — | — | 0.68 | Dipentyl | 0.545 | — | — |
| Laurol | — | — | 0.40 | Furan | — | — | 1.30 |
| Myristol | — | — | 0.31 | Tetrahydrofuran | — | — | 1.04 |
| Stearol | — | — | 0.22 | 1,4-Dioxan | — | — | 0.99 |
| Palmitol | — | — | 0.26 | Tetrahydropyran | — | — | 0.96 |
| *Ketones* | | | | 2-Methylfuran | — | — | 1.02 |
| Propanone | 1.162 | — | 1.54 | 2,5-Dimethylfuran | — | — | 0.83 |
| Butanone | 1.020 | — | 1.25 | | | | |
| 2-Methylbutan-3-one | — | — | 1.05 | | | | |

TABLE 4. Molar correction coefficients $K_M$ for esters (with respect to benzene). Katharometer detector.

| Component | Carrier gas | | Component | Carrier gas |
|---|---|---|---|---|
| | helium 61 | nitrogen 62 | | nitrogen 62 |
| Methyl formate | – | 1.43 | n-Butyl propionate | 0.58 |
| Ethyl formate | – | 1.09 | Methyl 1-chloropropionate | 0.66 |
| Isopropyl formate | – | 0.94 | Methyl 2-chloropropionate | 0.60 |
| n-Propyl formate | – | 0.88 | Ethyl 1-chloropropionate | 0.59 |
| Allyl formate | – | 0.95 | Ethyl 2-chloropropionate | 0.52 |
| Isobutyl formate | – | 0.77 | Methyl pyruvate | 0.99 |
| s-Butyl formate | – | 0.79 | Ethyl pyruvate | 0.82 |
| n-Butyl formate | – | 0.74 | Methyl crotonate | 0.79 |
| 2-Chloroethyl formate | – | 0.72 | Ethyl crotonate | 0.67 |
| Ethyl acetate | 0.901 | 0.84 | Isopropyl crotonate | 0.61 |
| Isopropyl acetate | 0.826 | 0.75 | n-Propyl crotonate | 0.58 |
| n-Propyl acetate | 0.812 | 0.75 | Methyl isobutyrate | 0.77 |
| Allyl acetate | – | 0.78 | Ethyl isobutyrate | 0.67 |
| t-Butyl acetate | – | 0.72 | Isopropyl isobutyrate | 0.61 |
| Isobutyl acetate | 0.743 | 0.64 | n-Propyl isobutyrate | 0.59 |
| s-Butyl acetate | – | 0.68 | s-Butyl isobutyrate | 0.58 |
| Isopentyl acetate | 0.69 | 0.56 | Isobutyl isobutyrate | 0.55 |
| n-Hexyl acetate | – | 0.50 | n-Butyl isobutyrate | 0.54 |
| n-Heptyl acetate | 0.587 | 0.42 | Methyl n-butyrate | 0.74 |
| n-Octyl acetate | – | 0.36 | Ethyl n-butyrate | 0.65 |
| Decyl acetate | – | 0.31 | Allyl n-butyrate | 0.60 |
| Geranyl acetate | – | 0.33 | Isopropyl n-butyrate | 0.59 |
| Lauryl acetate | – | 0.27 | n-Propyl n-butyrate | 0.57 |
| Myristyl acetate | – | 0.23 | s-Butyl n-butyrate | 0.54 |
| Stearyl acetate | – | 0.19 | Isobutyl n-butyrate | 0.52 |
| Palmityl acetate | – | 0.21 | n-Butyl n-butyrate | 0.51 |
| 2-Acetoxyethanol | – | 1.00 | Methyl n-valerate | 0.63 |
| Methyl methoxyacetate | – | 0.82 | Ethyl n-valerate | 0.56 |
| Ethyl methoxyacetate | – | 0.69 | Methyl n-hexoate | 0.56 |
| Methyl ethoxyacetate | – | 0.68 | Methyl heptoate | 0.50 |
| 2-Methoxyethyl acetate | – | 0.66 | Methyl octoate | 0.42 |
| Ethyl ethoxyacetate | – | 0.59 | Methyl nonoate | 0.36 |
| 2-Ethoxyethyl acetate | – | 0.57 | Methyl decoate | 0.32 |
| Methyl acetoacetate | – | 0.69 | Methyl laurate | 0.28 |
| Ethyl acetoacetate | – | 0.61 | Methyl myristate | 0.25 |
| Methyl chloroacetate | – | 0.71 | Methyl palmitate | 0.22 |
| Ethyl chloroacetate | – | 0.60 | Methyl stearate | 0.20 |
| n-Propyl chloroacetate | – | 0.53 | Methyl eicosanoate | 0.18 |
| Methyl propionate | – | 0.88 | Ethyl glycollate | 1.04 |
| Ethyl propionate | – | 0.75 | Methyl lactate | 1.200 |
| Allyl propionate | – | 0.68 | Ethyl lactate | 0.93 |
| n-Propyl propionate | – | 0.64 | | |
| Isobutyl propionate | – | 0.58 | | |
| s-Butyl propionate | – | 0.60 | | |

TABLE 5. Molar correction coefficients $K_M$ for acetals (relative to benzene). Katharometer detector, nitrogen carrier [62].

| Component | $K_M$ | Component | $K_M$ |
|---|---|---|---|
| Dimethoxyethane | 1.28 | Diisopropoxyethane | 0.63 |
| Diethoxymethane | 0.94 | Di-n-butoxymethane | 0.52 |
| Dimethoxypropane | 0.96 | Diisobutoxymethane | 0.55 |
| Diethoxyethane | 0.80 | Di-n-propoxypropane | 0.51 |
| Di-n-propoxymethane | 0.68 | Diisopropoxypropane | 0.56 |
| Diisopropoxymethane | 0.74 | Di-n-butoxyethane | 0.47 |
| Diethoxypropane | 0.74 | Diisobutoxyethane | 0.49 |
| Di-n-propoxyethane | 0.59 | | |

TABLE 6. Molar correction coefficients $K_M$ for phenols and their ethers (relative to benzene). Katharometer detector, nitrogen carrier [62].

| Component | $K_M$ | Component | $K_M$ |
|---|---|---|---|
| Phenol | 1.16 | *o*-Chlorophenol | 0.67 |
| *o*-Cresol | 0.94 | *m*-Chlorophenol | 0.60 |
| *m*-Cresol | 0.86 | *p*-Chlorophenol | 0.60 |
| *p*-Cresol | 0.87 | 4-Chloro-2-methylphenol | 0.56 |
| 2-Ethylphenol | 0.73 | 4-Chloro-3-methylphenol | 0.55 |
| 4-Ethylphenol | 0.66 | Anisole | 0.84 |
| 2,6-Dimethylphenol | 0.73 | Phenetole | 0.66 |
| 2,4-Dimethylphenol | 0.68 | *o*-Cresyl methyl ether | 0.75 |
| 2,3-Dimethylphenol | 0.72 | *m*-Cresyl methyl ether | 0.67 |
| 2,5-Dimethylphenol | 0.69 | *p*-Cresyl methyl ether | 0.68 |
| 3,4-Dimethylphenol | 0.69 | *o*-Cresyl ethyl ether | 0.62 |
| 3,5-Dimethylphenol | 0.65 | *m*-Cresyl ethyl ether | 0.55 |
| 3-Methyl-5-ethylphenol | 0.53 | *p*-Cresyl ethyl ether | 0.54 |
| 2,4,5-Trimethylphenol | 0.60 | *o*-Chloroanisole | 0.55 |
| 2,3,5-Trimethylphenol | 0.60 | *m*-Chloroanisole | 0.49 |
| 2,4,6-Trimethylphenol | 0.60 | *p*-Chloroanisole | 0.49 |

TABLE 7. Molar correction coefficients $K_M$ for alcohols (relative to propan-1-ol). Katharometer detector, helium carrier [64].

| Component | $K_M$ | Component | $K_M$ |
|---|---|---|---|
| Methanol | 0.222 | 2-Methylbutan-1-ol | 0.756 |
| Ethanol | 0.135 | 3-Methylbutan-2-ol | 0.606 |
| Propan-2-ol | 0.962 | 2-Methylbutan-2-ol | 0.649 |
| Propan-1-ol | 1.00 | Pentan-3-ol | 0.725 |
| Methylpropan-2-ol | 0.787 | Pentan-2-ol | 0.641 |
| Butan-2-ol | 0.833 | Pentan-1-ol | 0.685 |
| Methylpropan-1-ol | 0.538 | 2-Methylpentan-2-ol | 0.629 |
| Butan-1-ol | 0.787 | Hexan-2-ol | 0.629 |

TABLE 8. Molar correction coefficients $K_M$ for aliphatic acids (relative to nonanoic acid). Argon detector [92].

| Component | $K_M$ |
|---|---|
| Butyric acid | 11.11 |
| Valeric acid | 2.86 |
| Hexanoic acid | 1.89 |
| Heptanoic acid | 1.35 |
| Octanoic acid | 1.16 |
| Nonanoic acid | 1.00 |
| Decanoic acid | 0.92 |

TABLE 9. Molar correction coefficients $K_M$ for alcohols (relative to butan-1-ol). Argon detector [80].

| Component | $K_M$ |
|---|---|
| Propan-1-ol | 1.86 |
| Methylpropan-2-ol | 2.17 |
| Butan-2-ol | 1.37 |
| Methylpropan-1-ol | 1.12 |
| Pentan-1-ol | 0.93 |
| Hexan-1-ol | 0.66 |

TABLE 10. Molar correction coefficients $K_M$ for phenols and pyridines (relative to benzene). Emissivity detector [31,69].

| Component | $K_M$ | Component | $K_M$ |
|---|---|---|---|
| Phenol | 0.656 | Pyridine | 0.306 |
| *o*-Cresol | 0.565 | 2-Methylpyridine | 0.344 |
| *m*-Cresol | 0.675 | 2,6-Dimethylpyridine | 0.313 |

TABLE 11. Molar correction coefficients $K_M$ for halogenated aromatic hydrocarbons, nitro-compounds[62], thiols, and sulphides[67] (relative to benzene). Katharometer detector.

| Component | Carrier gas: nitrogen | Component | Carrier gas: helium |
|---|---|---|---|
| *Halogen compounds* | | *Thiols* | |
| Chlorobenzene | 0.66 | Ethanethiol | 1.78 |
| *o*-Chlorotoluene | 0.58 | Propane-2-thiol | 1.64 |
| *m*-Chlorotoluene | 0.52 | Propane-1-thiol | 1.52 |
| *p*-Chlorotoluene | 0.52 | 2-Methylpropane-2-thiol | 1.42 |
| Benzyl chloride | 0.53 | 2-Methylpropane-1-thiol | 1.37 |
| Bromobenzene | 0.51 | Butane-2-thiol | 1.42 |
| *o*-Bromotoluene | 0.49 | Butane-1-thiol | 1.47 |
| *m*-Bromotoluene | 0.44 | Pentane-1-thiol | 1.51 |
| *p*-Bromotoluene | 0.43 | *Sulphides* | |
| *Nitro-compounds* | | Dimethyl sulphide | 1.14 |
| Nitromethane | 1.47 | Ethyl methyl sulphide | 0.99 |
| Nitroethane | 1.16 | Diethyl sulphide | 0.83 |
| Nitropropane | 0.93 | t-Butyl methyl sulphide | 0.82 |
| | | Ethyl isopropyl sulphide | 0.79 |
| | | Ethyl propyl sulphide | 0.91 |
| | | Thiacyclopentane | 0.94 |


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# THE USE OF ION-EXCHANGE CHROMATOGRAPHY FOR STUDYING THE STATE OF IONS OF HIGH-VALENCY ELEMENTS IN SOLUTION

B. I. Nabivanets

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## I. INTRODUCTION

Advances in the chemistry and technology of the rarer elements have set research workers a number of problems involving investigations into the state of ions from high-valency elements in solution. Generally, such ions cannot exist in the free state in aqueous solutions, owing to their relatively high ionic potential, and undergo hydrolysis or form complexes with various ligands; the formation of hydrolysed polymeric species is also characteristic of these ions.

The state of ions of high-valency elements greatly affects their reactivity with various reagents and the composition of the reaction products. This is of particular importance in analytical chemistry and in the hydrometallurgical processing of ores where one requires to separate metals, to isolate them from solution, and to obtain compounds or reaction products having a specific composition.

The nature of the reactions between complex ions [for example, $TiO_2^{2+}$, $Zr(OH)_x^{(4-x)+}$, $NbO_2^+$, $MoO_4^{2-}$, $WO_4^{2-}$, etc.] or polymeric species and various ligands, and thus the compositions and properties of the complexes formed, depends to a great extent on the state of the highly-charged ions in solution under given conditions; in addition, there may also be changes in the degree of hydrolysis or polymerisation of high-valency ions during the complex formation process [1].

To elucidate the formation mechanism and the true composition of complexes formed from highly-charged ions we must study the state of the latter under complex-forming conditions, as well as the changes which take place with highly-charged ions in the complex-forming process itself. Only by taking such data into account is it possible to determine that most important characteristic of complexes, their stability constants.

The principal characteristics of the states of high-valency ions in solutions are the sign and magnitude of the charge, the degree of hydrolysis, the polymerisation factor, and the composition and stability of complexes containing different ligands.

These characteristics can be determined by ion-exchange chromatography using ion exchangers having different chemical and physical properties.

## II. QUALITATIVE DETERMINATION OF THE FORM IN WHICH THE ELEMENT BEING STUDIED EXISTS IN SOLUTION

The absorption of the element under investigation by strongly acid cation exchangers is direct evidence of the existence of cationic species in a solution, but if the investigation is carried out in highly acid solutions then the presence of large amounts of foreign ions (for example, $H^+$) can lead to a shift in the equilibrium towards the displacement of ions of the element from the cation exchanger. For example, while it has been established in a number of investigations that $Ti^{IV}$, [2-6] $Zr^{IV}$, [2] and $Mo^{VI}$ [7] are hardly absorbed at all by cation exchangers in 1 *N* HCl, 3 *N* HCl, and 3 *N* $HNO_3$ respectively, electromigration experiments [8-10] have shown convincingly that Ti,[8] Zr,[9] and Mo [10] exist predominantly as cationic species in these media; the predominance of the cationic species $ZrCl^{3+}$, $ZrCl_2^{2+}$, and $ZrCl^+$ in 3 *N* HCl also depends on the stability constants of the zirconium chloro-complexes [11].

Account should be taken of the possibility of disturbing the equilibrium between the various ionic species during the absorption of the element by cation exchangers. For example, at pH 3–5 there is a marked absorption of sexivalent molybdenum ions by cation exchangers [10] although electromigration experiments [7], the determination of the isoelectric point of molybdic acid by a solubility method [7,12] as well as a calculation from the dissociation constants of molybdic acid [13] show that at this acidity practically all the Mo is present as hydrogen molybdate and molybdate ions or as isopolymolybdates [14-16].

Similar complications arise in the absorption by anion exchangers of the element being studied. For example, at pH > 12 $Mo^{VI}$, $Mo^V$, $Ta^V$, and $Ge^{IV}$ are not absorbed by anion exchangers due to competition from $OH^-$ ions although under these conditions these elements occur in solution as monomeric or polymeric anions of molybdic [10,14-16], niobic [17,18], tantalic [17,19,20], and germanic [21] acids. The competing effect of foreign ions can lead to false conclusions, particularly when studying low-stability complexes formed at high ligand concentrations, for under these conditions the ligand itself can be an ion displacer. For example, it has been established in a number of studies that an increase in sulphate ion concentration above a certain level leads to a reduction in the absorption of $Ti^{IV}$, [22] $Zr^{IV}$, [23] and $Nb^V$ [23] by anion exchangers, although electromigration experiments [8,24] show that under these conditions these elements are present in solution as anionic sulphato-complexes.

Similar equilibrium disturbances are found in anion exchange. For example, $Mo^{VI}$ is appreciably absorbed by anion exchangers in 0.2–1.0 *N* nitric acid [7] although molybdenyl cations predominate under these conditions [10].

Furthermore, anion exchangers containing $-NH_2$, =NH, or ≡N groups can absorb metal salt molecules to form complexes with the amino-groups of the resins. Such processes are characteristic of compounds of elements capable of coordinating with nitrogen atoms in various reagents. For example, it has been established that there is marked absorption of Cu, Co, Ni, Cd, and Zn by different types of anion exchangers from weakly acidic solutions, in which cationic species of these elements predominate [25]. The absorption under these conditions is due to the formation of complexes having the composition $[R_2M(H_2O)_2]X$, where R is an anion exchanger containing $-NH_2$, =NH, or ≡N, M a doubly-charged metal cation, and $X^-$ represents $Cl^-$ or $NO_3^-$.

The method of effluent curves is also used for making a qualitative determination of the form in which an element exists in solution [26]. Here one analyses successive individual portions of the test solution flowing from a column containing a cation or anion exchanger. If only ionic species are present in solution, then on passing a known volume of the solution through an ion-exchange column the ions under investigation are found to emerge in the filtrate, their concentration in individual portions of the filtrate increasing gradually and reaching a value equal to that in the initial solution. Such a curve has been obtained, for example, in the absorption of oxalato-complexes of Nb by EDE-10 anion-exchange resin† (curve *1*, Fig. 1) [26]; Nb is not absorbed under these conditions by KU-2 cation-exchange resin‡ (curve *2*, Fig. 1). If neutral molecules are present in solution the substance under investigation is not absorbed by ion exchangers, the effluent curve *2* in Fig. 1 being characteristic of this case. If colloidally dispersed particles predominate in the solution, however, then the adsorption is physical in nature, that is, it is independent of the charge sign of the active groups in the ion exchanger; in this case the effluent curves have the form of curves *3* and *4* in Fig. 1. Similar curves are obtained for colloidally dispersed particles of niobium hydroxide on an anion exchanger (curve *3*) and a cation exchanger (curve *4*) [26].

If there are several forms of the element in solution then it is impossible to detect the presence of the several different species from the first effluent curve, in which

† EDE-10 is a polyfunctional weakly or strongly basic anion-exchange resin prepared by the condensation of polyethylenepolyamines with epichlorohydrin, and contains secondary, tertiary, and quaternary nitrogen groups (Ed. of Translation).

‡ KU-2 is a monofunctional, strongly acid cation-exchange with $-SO_3H$ active groups, prepared by treating a swollen styrene-divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

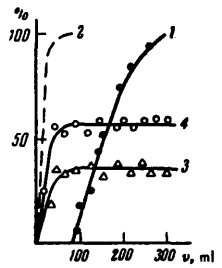



Fig.1. Relationship between the $Nb^V$ concentration in the filtrate and the volume of solution passed through the column (for microconcentrations of niobium)[26]:
1) effluent curve for EDE-10 anion-exchange resin;
2) on KU-2 cation-exchange resin in oxalate solution;
3) effluent curve for EDE-10 anion-exchange resin;
4) on KU-2 cation exchanger in $NaNO_3$ solution.

case "secondary" effluent curves are obtained. For this purpose the filtrate solutions remaining after recording the primary curve are passed through a cation or anion exchanger not containing the ions under investigation. For example, the primary and secondary effluent curves obtained on passing a solution of niobium in 1 *N* $HNO_3$ through an ion exchanger[26] are shown in Fig. 2; the nature of the curves indicates that under these conditions electrically neutral complexes of Nb which are hardly absorbed at all by the cation or anion exchanger (curves *c'*, *a'*, *c''*, *a''*, Fig. 2) and colloidal Nb species whose absorption is physical in nature (curves *c*, *a*, Fig. 2) are present in equilibrium in the solution.

Colloidal species of an element can only be detected by the effluent-curve method in microconcentrations, where the number of colloidal particles physically adsorbed on

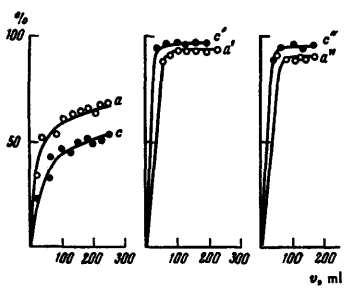



Fig.2. Effluent curves for micro-amounts of niobium in 1 *N* $HNO_3$:[26] *c*), *a*) are the first effluent curves on a cation exchanger (*c*) and an anion exchanger (*a*); *c'*), *a'*) are the secondary effluent curves after the cation exchanger on a cation exchanger (*c'*) and an anion exchanger (*a'*); *c''*), *a''*) are the secondary curves after the anion exchanger on a cation exchanger (*c''*) and an anion exchanger (*a''*).

the surface of the ion-exchanger granules represents an appreciable fraction of the total amount of the element concerned. For these reasons (equilibrium displacement, competition from foreign ions, etc.) the results of investigations by the effluent curve method can indicate only the presence of certain ionic species of the element under investigation in a given system; it is impossible, however, to show that these species predominate in the solution under the given conditions by this method.

## III. DETERMINATION OF THE MAGNITUDE OF THE IONIC CHARGE

Determining the magnitude of the ionic charge of complex ions formed by hydroxo-cations — $TiO^{2+}$, $Zr(OH)_x^{(4-x)+}$, $NbO_2^+$, etc. — can frequently serve as one of the principal methods of establishing the composition and formation mechanism of complex ions in solution.

Over the last 7–8 years the ion-exchange method has been used for determining the charge on the sulphato-complexes of uranyl[28], Ge,[29] Nb, and Ti;[30] the oxalato-complexes of Ge,[31] Zr, and Hf;[32] the chloro-complexes of Ru;[33] and the hydroxo-complexes of Ti,[34] germanate[21], isopolyvanadates[35], vanadyl[36], molybdenyl[7], Zr,[37] Pa,[38] and certain polynuclear complexes of Ru.[39]

The methods for determining the magnitude of the ionic charge can be divided into two groups, the first being based on the equivalence and reversibility of ion-exchange reactions and the second being based on the swelling of ion exchangers during the absorption of ions.

### 1. Methods Based on the Equivalence and Reversibility of Ion-Exchange Reactions

The absorption of the ions of an element under investigation $M^z$ by an ion exchanger loaded with ions $M_1^{z_1}$ having a known charge $z_1$ can be expressed by the equilibrium:

$$z_1 M^z + z\overline{R_{z_1}M_1} \rightleftarrows z_1\overline{R_z M} + z M_1^{z_1}. \quad (1)$$§

This equilibrium can pertain to both cation and anion exchange. Three methods are available for determining the required charge magnitude $z$.

The first method is based on determining the exchange capacity of the ion exchanger for the element being studied $M^z$. For this we must know the total exchange capacity of the ion exchanger for an ion $M_1^{z_1}$ having a known charge $z_1$ and then completely displace the equilibrium (1) to the right by saturating the ion exchanger with the ions being studied $M^z$. The charge $z$ is found from the relationship

$$z = \frac{Q}{G}, \quad (2)$$

where $Q$ is the capacity of a given weight of ion exchanger expressed in g-equiv. of absorbed $M_1^{z_1}$ ions, and $G$ the amount of the element $M^z$ in g-moles absorbed by the same weight of ion exchanger.

This method of determining the charge magnitude can involve substantial errors for a number of reasons, the chief ones being as follows. When determining the exchange capacity of an ion exchanger, $H^+$, $Na^+$, or $Ca^{2+}$ ions (for cation exchangers) and $Cl^-$ ions (for anion

§ Both here and subsequently the bar lines indicate the ion-exchanger phase.

exchangers) are usually used as $M_1^{z_1}$. These ions have relatively small radii and therefore readily penetrate into the pores of the ion exchanger to occupy practically all the active sites. In the absorption of high-valency ions or complex ions and polymeric species, however, which have larger ionic radii, these do not always succeed in occupying all the active sites of the ion exchanger. Furthermore, owing to the absorption of $M^z$ ions the concentration of $M_1^{z_1}$ in solution is increased, which prevents the displacement of equilibrium (1) to the right. All of this can lead to excessively high results in the determination of $z$. Finally, a shift in equilibrium (1) towards ion-exchanger saturation by $M^z$ ions is only possible with a substantial increase in the concentration (or absolute quantity) of the latter; this makes it difficult to determine the charge magnitude at low concentrations of the element.

Thus, a determination of the charge by using the total exchange capacity of an ion exchanger is not always reliable. For example, when using this method to find the charge on the cations of quadrivalent zirconium in perchloric acid solutions it was found[40] that the charge on the zirconium ions is increased on lowering the concentration of $HClO_4$, which contradicts the results obtained[41] by using the stability constants of zirconium hydroxo-complexes[42].

The second method is based on the relationship between the number of $M_1^{z_1}$ ions displaced and the charge magnitude $z$ of the absorbed $M^z$ ions. Experimentally this method is carried out by determining concentration changes for the ions under investigation ($\Delta M^z$) and the displaced ions ($\Delta M_1^{z_1}$) on bringing the solution into contact with an ion exchanger $\overline{R_{z_1}M_1}$. The specific charge is calculated from the relationship

$$z = \frac{\Delta M_1^{z_1}}{\Delta M^z}. \qquad (3)$$

where $\Delta M_1^{z_1}$ is expressed in g-equiv. and $\Delta M^z$ in g-moles.

A necessary condition for obtaining reliable results is sufficient sensitivity in determining $\Delta M^z$ and $\Delta M_1^{z_1}$. Most analytical methods enable element concentrations of $10^{-4}$–$10^{-5}$ M and above to be determined in solution. Frequently, however, the charge magnitude has to be determined in the presence of foreign electrolytes whose concentration considerably exceeds the concentration of the element under investigation. In such cases the ion exchanger must first be saturated with ions of the foreign electrolyte. Consequently, while the element ($M^z$) is being absorbed it dislodges from the ion exchanger the foreign electrolyte ions ($M_1^{z_1}$), whose concentration even before absorption was appreciable. Thus, $\Delta M_1^{z_1}$ must be determined at a substantial concentration of $M_1^{z_1}$, which is only possible if the concentration of $M^z$ ions being absorbed is fairly high. A reliable determination of $\Delta M_1^{z_1}$, is possible by changing the concentration of $M_1^{z_1}$ by at least 10%; therefore in determining the charge magnitude from relationship (3) the concentration of the element being studied should be not less than 10% of the concentration of foreign electrolyte (calculated per g-equiv.).

Table 1 shows the results of charge determinations for $Ti^{IV}$ cations at various pH.[34] The values of $z$ show that at pH < 1.17 doubly-charged titanyl cations $TiO^{2+}$ predominate in solution and on raising the pH hydrolysis occurs to form singly-charged cations¶

$$TiO^{2+} + H_2O \rightleftarrows TiO(OH)^+ + H^+. \qquad (4)$$

¶ The absence of titanium poly-ions in solution under these conditions has been proved by a study of the ion-exchange kinetics and by dialysis[43].

TABLE 1. Magnitude of the charge on $Ti^{IV}$ cations*.

| Initial solution | | | Equilibrium solution | | | $z$ |
|---|---|---|---|---|---|---|
| $pH_1$ | $[H^+]_1$ | $[Ti]$ | $pH_2$ | $[H^+]_2$ | $[Ti]$ | |
| 0.50 | $3.16\cdot10^{-1}$ | $4.95\cdot10^{-2}$ | 0.40 | $3.98\cdot10^{-1}$ | $1.25\cdot10^{-2}$ | 2.21 |
| 1.17 | $6.76\cdot10^{-2}$ | $9.46\cdot10^{-2}$ | 1.05 | $8.91\cdot10^{-2}$ | 0 | 2.24 |
| 1.40 | $3.98\cdot10^{-2}$ | $1.20\cdot10^{-2}$ | 1.33 | $4.68\cdot10^{-2}$ | $5.27\cdot10^{-2}$ | 0.99 |
| 5.75 | $1.78\cdot10^{-6}$ | — | 3.50 | $3.16\cdot10^{-4}$ | — | — |

* All concentrations are molar.

A similar principle is used for determining the charge of anions by using anion exchangers. For example, a study of the absorption of germanate ions by IRA-400 anion-exchange resin in the $OH^-$ and $Cl^-$ forms showed[21] that at pH ≃ 9 the absorption of 2.5 moles Ge leads to the displacement of one g-equiv. of $OH^-$ or $Cl^-$ ions. Thus, under these conditions Ge is present in solution as pentagermanate ions $Ge_5O_{11}^{2-}$ (according to these results).

The third method is based on displacing the equilibrium of reaction (1) [27,28] and consists of studying the effect of varying concentrations of $M_1^{z_1}$ on the absorption of the ions being studied, under the conditions $[\overline{R_{z_1}M_1}] \simeq$ const. In this case the equilibrium constant of (1) is

$$K = \frac{[\overline{R_zM}]^{z_1}\,[M_1^{z_1}]^z}{[M^z]^{z_1}} = (K_d)^{z_1}\,[M_1^{z_1}]^z. \qquad (5)$$

Here $K_d$ is the coefficient for the distribution of element $M^z$ between the ion exchanger and the solution, determined from the relationship

$$K_d = \frac{a}{100-a} \times \frac{v}{m}, \qquad (6)$$

where $a$ is the amount of absorbed element in the equilibrium state (%), $v$ is the volume of solution (ml), and $m$ is the weight of ion exchanger (g).

Eqn. (5) supposes that the ratio of the activity coefficients of $M^z$ ions in solution and in the ion-exchanger phase remains constant over a certain range of concentration. Putting Eqn. (5) in logarithmic form we obtain

$$\log K_d = -\frac{z}{z_1}\log[M_1^{z_1}] + \frac{1}{z_1}\log K. \qquad (7)$$

The ratio $z/z_1$ and thus the charge magnitude $z$, can be found from the slope of the curve of $\log K_d$ against $(-\log[M_1^{z_1}])$.

It was indicated above that the condition $[R_{z_1}M_1] \simeq$ const. must be observed while carrying out this method. This means that the amount of ion exchanger taken for each experiment should be fairly high, so that the absorption of $M^z$ is hardly reflected at all in the amount of ion exchanger in the $[\overline{R_{z_1}M_1}]$ form. A determination of the charge magnitude using Eqn. (7) gives reliable results if the amount of $[\overline{R_{z_1}M_1}]$ is changed by not more than 1–2% during the absorption of $M^z$.

This condition can be written in the following form

$$mQ \geqslant v[M^z]z \times 50, \text{ or}$$

$$[M^z] \leqslant \frac{Q}{50z\ v/m}. \qquad (8)$$

Here $[M^z]$ is the molar concentration of $M^z$ in the solution under investigation prior to contacting it with the ion exchanger, $Q$ is the total exchange capacity of the ion exchanger (mg-equiv. $g^{-1}$), $z$ the expected value of the

charge†, $m$ the mass of ion exchanger (g), and $v$ the volume of solution (ml).

To avoid a substantial change in the volume of the solution, arising from the swelling of the ion exchanger, the experiments are usually carried out by observing the relationship

$$\frac{v}{m} \geqslant 50. \qquad (9)$$

Taking condition (9) into account, the concentration of $M^z$ can be readily calculated from Eqn. (8), which ensures that the determination of $z$ by using Eqn. (7) is reliable.

By way of example, the results of charge determinations on $Ti^{IV}$ cations in perchloric acid solutions[34] are shown in Fig. 3. In this case $M_1^{z_1} = H^+$ ($z_1 = 1$), so that the slope of the curve in Fig. 3 relative to the abscissa axis gives the value of $z$ directly. According to Fig. 3, doubly-charged cations predominate in solution at pH < 1, these clearly being titanyl ions $TiO^{2+}$. At higher pH values hydrolysis occurs to form singly-charged $TiO(OH)^+$ cations, which agrees with the data in Table 1.

It is convenient to use the equivalence of ion exchange to determine the charge magnitude for relatively high concentrations of the ions under investigation (of the order of $10^{-2}$ M and above); at lower concentrations (of the order of $10^{-3}$ M and below) we generally employ the equilibrium displacement method.

## 2. Methods Based on the Swelling of Ion Exchangers

In an investigation of ion exchange on swelling ion exchangers it was found[37] that the exchange selectivity of ions having different valency depends very greatly on the swelling power of the ion exchanger. Therefore the amounts of ions absorbed can be expressed in the exchange isotherm equation as equivalent concentrations by including the specific volume of the swollen resin ($V$) in the equation:

$$\frac{g_1^{1/z_1} V^{1/z_1} \bar{f}_1^{1/z_1}}{g_2^{1/z_2} V^{1/z_2} \bar{f}_2^{1/z_2}} = K \frac{C_1^{1/z_1} f_1^{1/z_1}}{C_2^{1/z_2} f_2^{1/z_2}}. \qquad (10)$$

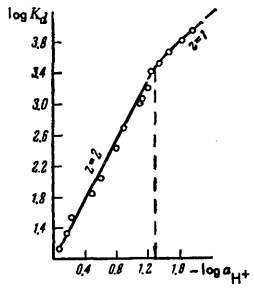



Fig. 3. Effect of the activities of hydrogen ions on the absorption of titanium by KU-2 cation-exchange resin[34]. Initial titanium concentration $2 \times 10^{-4}$ M.

† Usually $z \leqslant 4$ in aqueous solutions.

Here $g_1$, $g_2$ and $\bar{f}_1$, $\bar{f}_2$ are the equivalent amounts of ions absorbed by the ion exchanger and their activity coefficients in the ion-exchanger phase respectively; $C_1$, $C_2$ and $f_1$, $f_2$ are the concentrations and activity coefficients of the exchanging ions in solution respectively; $z_1$ and $z_2$ are the ionic charges.

If one of the exchanging ions is a microcomponent ($g_1$), then the specific capacity of the ion exchanger for the macrocomponent ($g_2$) is equal to the total specific capacity of the resin and the concentration of macrocomponent in solution ($C_2$) will be the constant total concentration of the solution. In this case the activity coefficients of the ions in solution remain constant.

The distribution of microcomponent under investigation between the solution and resin is given by the coefficient:

$$K_{d_1} = \frac{g_1}{C_1} = K' \frac{g^{z_1/z_2} \bar{f}_2^{z_1/z_2}}{C^{z_1/z_2} \bar{f}_1 V^{z_1 - z_2/z_2}}. \qquad (11)$$

Eqn. (11) shows how the distribution coefficient of the element under investigation depends on the specific capacity of the resin ($g$), the total concentration of the solution ($C$), the specific volume of the resin ($V$), and the activity coefficients of the ions in the ion-exchanger phase. It follows from this equation that for $z_1 = z_2$ the distribution coefficient of the element is independent of the swelling power of the resin.

The selectivity in the absorption of the element under investigation on to two resin samples having different swelling powers can be expressed by the relative exchange selectivity coefficient $\beta_1$:

$$\beta_1 = \frac{K_{d_1}^{\mathrm{I}}}{K_{d_1}^{\mathrm{II}}} = \left(\frac{g^{\mathrm{I}}}{g^{\mathrm{II}}}\right)^{z_1/z_2} \left(\frac{V^{\mathrm{II}}}{V^{\mathrm{I}}}\right)^{z_1 - z_2/z_2} \left(\frac{\bar{f}_2^{\mathrm{I}}}{\bar{f}_2^{\mathrm{II}}}\right)^{z_1/z_2} \left(\frac{\bar{f}_1^{\mathrm{II}}}{\bar{f}_1^{\mathrm{I}}}\right). \qquad (12)$$

In this equation the indices I and II relate to resin samples having different swelling powers. It has been found experimentally that the activity coefficients of ions in the resin phase are independent of its swelling power, so that the ratio of the activity coefficients in Eqn. (12) is unity. For investigations in which resins having different swelling powers and the same total specific capacity ($g^{\mathrm{I}} = g^{\mathrm{II}}$) are used, Eqn. (12) assumes the form

$$\frac{K_{d_1}^{\mathrm{I}}}{K_{d_1}^{\mathrm{II}}} = \left(\frac{V^{\mathrm{II}}}{V^{\mathrm{I}}}\right)^{z_1 - z_2/z_2}. \qquad (13)$$

Using univalent ions as the macrocomponent ($z_2 = 1$) the equation for determining the charge has the form:

$$z = \frac{\log \dfrac{K_d^{\mathrm{I}}}{K_d^{\mathrm{II}}}}{\log \dfrac{V^{\mathrm{II}}}{V^{\mathrm{I}}}} + 1. \qquad (14)$$

To determine $z$ we must have two resin samples of different swelling powers and the same specific capacity. In essence the experiment consists of determining the distribution coefficients $K_d^{\mathrm{I}}$ and $K_d^{\mathrm{II}}$ for the element under investigation on the two resin samples under strictly identical conditions; the specific volumes $V^{\mathrm{I}}$ and $V^{\mathrm{II}}$ of the swollen resins are determined pyknometrically under the same conditions. The concentration of the element should be at least 100 times less than the concentration of macrocomponent ions, in order to obtain reliable results.

As an example, the results of charge magnitude determinations for $Zr^{IV}$ ions in nitric acid solutions[37] are presented in Table 2. They show that quadruply-charged $Zr^{4+}$

TABLE 2. Determination of the magnitude of the charge on $Zr^{IV}$ ions as a function of nitric acid concentration[37].

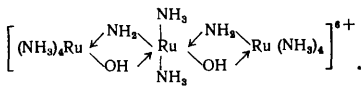
| $[HNO_3]$, $N$ | pH | $K_d^I$ on a resin containing 12% divinylbenzene | $K_d^{II}$ on a resin containing 2% divinylbenzene | $V^I$ ml $g^{-1}$ | $V^{II}$ ml $g^{-1}$ | $z$ |
|---|---|---|---|---|---|---|
| 5.0 | — | 6.4 | 4.5 | 0.578 | 0.775 | +2.21 |
| 3.0 | — | 10.8 | 6.8 | 0.623 | 0.820 | +2.70 |
| 2.5 | — | 40.0 | 19 | 0.630 | 0.835 | +3.66 |
| 2.0 | — | 72.5 | 30 | 0.637 | 0.855 | +3.99 |
| 1.5 | — | 140 | 82 | 0.645 | 0.905 | +2.66 |
| 1.0 | — | 383 | 292 | 0.655 | 0.940 | +1.83 |
| 0.5 | — | 397 | 373 | 0.670 | 0.997 | +1.19 |
| 0.3 | — | 517 | 490 | 0.710 | 1.08 | +1.13 |
| 0.1 | 1.0 | 535 | 535 | 0.720 | 1.09 | +1.00 |
| — | 1.2 | 602 | 602 | 0.720 | 1.13 | +1.00 |
| — | 1.5 | 760 | 685 | 0.720 | 1.16 | +1.21 |
| — | 1.8 | 805 | 710 | 0.720 | 1.19 | +1.12 |

ions are formed only over a narrow range of acid concentrations (2–2.5 $N$); the charge is reduced at higher $NHO_3$ concentrations owing to the formation of nitrato-complexes of Zr, and at lower acid concentrations due to the hydrolysis of Zr cations.

### 3. Some Special Aspects of Determining the Charge Magnitude of High-Valency Ions.

High-valency ions generally exhibit a strong tendency towards complex-forming reactions. Therefore, in certain cases, as was indicated earlier, they may be absorbed by ion exchangers by a molecular mechanism, which makes it impossible to determine their charge. To avoid such complications when determining the magnitude of the ionic charge it is necessary to use strongly acid cation exchangers containing active $-SO_3H$ groups (KU-2 or Dowex 50) and strongly basic anion exchangers containing active $\equiv\overset{+}{N}-OH$ groups (AV-17‡ or Dowex 1). These ion exchangers absorb high-valency ions virtually only by an ion-exchange mechanism.

In determining the charge magnitude of poly-ions the treatment of the results obtained by any of the methods described above depends on the method by which the amount of element absorbed by the ion exchanger is determined. If the total amount of absorbed element is determined in g-atoms then the result obtained is the value of the specific charge, that is, the charge attached to one atom of the element concerned in the poly-ion. The determination of the charge magnitude of polygermanate ions[21] mentioned above may be quoted as an example. However, if we determine the amount of absorbed poly-ions of the element under investigation by some method then we obtain the value of the effective (overall) charge of the poly-ion§. This quantity was obtained, for example, in a determination of the charge on the polynuclear complex Ru ion[39].



‡ AV-17 is a strongly basic anion-exchange resin containing quaternary nitrogen groups. It is based on styrene and trimethylamine (Ed. of Translation).

§ In the absence of poly-ions the specific charge is also the effective charge of the complex ion.

In this case the change in the concentration of the polynuclear complex in solution during absorption by a cation exchanger was determined spectrophotometrically from the characteristic maximum in the absorption spectrum of the polynuclear complex.

When low-stability complexes are formed in solution the degree of bonding of a highly-valent element in the complex depends on the excess concentration of ligand (in the case of hydroxo-complexes, on the pH). At the same time the ligand concentration in solution can differ considerably from that in the ion-exchanger phase[45]. For example, it has been found experimentally[46] that for the cation exchanger Dowex 50, with 1–2 $N$ HCl in the aqueous phase, the concentration of HCl in the ion-exchanger phase was 0.09 and 0.2 $N$ respectively. This gives reason to suppose that the state of highly-valent elements in the ion-exchanger phase may differ from that in the solution.

Nevertheless, under certain experimental conditions it is possible to obtain results which will yield the charge magnitude of the ions in solution. Let us suppose that in the absorption of a polymeric action $M_p(OH)_x^{(pq-x)+}$ by a cation exchanger the poly-ion dissociates and there is a change in the degree of hydrolysis, which leads to the formation of a cation $M(OH)_{\frac{x}{p}+y}^{\left(q-\frac{x}{p}-y\right)+}$ in the ion-exchanger phase ($q$ is the valency of the central metal). This process can be represented by the equilibrium

$$M_p(OH)_x^{(pq-x)+} + p\left(q-\frac{x}{p}-y\right)\overline{RH} + py\,H_2O \rightleftarrows \rightleftarrows p\,\overline{R_{q-\frac{x}{p}-y}M(OH)_{\frac{x}{p}+y}} + z\,H^+. \quad (15)$$

A similar equation can be written for any change in the polymerisation factor $p$ or for the similar case of only monomeric ions ($p$ = 1) being present in solution.

The absorption of the complex $M_pA_x^{(pq-x)-}$ by an anion exchanger to form a complex $MA_{\frac{x}{p}+y}^{\left(q-\frac{x}{p}-y\right)-}$ in the ion-exchanger phase can be expressed by the equilibrium

$$M_pA_x^{(pq-x)-} + p\left(q-\frac{x}{p}-y\right)\overline{RA} \rightleftarrows p\,\overline{R_{q-\frac{x}{p}-y}MA_{\frac{x}{p}+y}} + z\,A^-. \quad (16)$$

A similar equation can be written for any change in the polymerisation factor $p$ and the ratio M : A. It is readily seen that in Eqns. (15) and (16) $z = pq - x$, that is, the number of cations or anions displaced by ion exchange is equivalent to the charge in solution of the ions under investigation.

Eqns. (15) and (16) show that to determine the magnitude of the charge on ions present in solution it is necessary to use ion exchangers loaded with ions which are present in the complex ion being studied, or are connected by a chemical equation with ions present in it. In Eqn. (16) these are the $A^-$ ions, in Eqn. (15) they are the $H^+$ ions connected with $OH^-$ ions by the chemical equation $H^+ + OH^- \rightleftharpoons H_2O$.

This condition is not guaranteed when determining the charge on complex ions having high stability, whose composition cannot be changed with differences in ligand concentration in solution and in the ion-exchanger phase.

When determining the charge magnitude of ions one frequently has to deal with solutions containing ions having

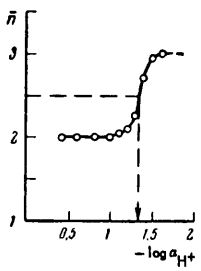



Fig.4. Relationship between $\bar{n}$ and the acidity of the medium in the formation of the hydroxotitanyl complex (calculated from the curve in Fig.3)[34].

different charge magnitudes in equilibrium. On contacting such a solution with an ion exchanger, ions having the higher charge will be absorbed first, and this can lead to a considerable disturbance in the equilibrium between the various ionic species. However, this disturbance in equilibrium is equivalent to the change in the composition of the ions in the ion-exchanger phase, so that by observing the conditions given above we obtain the mean charge magnitude of the ions in solution prior to absorption at given concentration conditions.

The results of charge magnitude determinations for ions can, in certain cases, be used to calculate the instability constants of the complexes. It follows from Eqn. (7) that

$$z = z_1 \frac{\Delta \log K_d}{\Delta \log [M_1^{z_1}]}. \qquad (17)$$

In complex formation involving a metal cation $M^{q+}$ ($q$ being the valency of the metal) the relationship between the Bjerrum formation constant $\bar{n}$ and the charge of the complex ion is expressed by the equation

$$\bar{n} = q - z = q - z_1 \frac{\Delta \log K_d}{\Delta \log [M_1^{z_1}]}. \qquad (18)$$

If a ligand or another ion, whose concentration is proportional to the ligand concentration, is taken as $M_1^{z_1}$ then it is possible to determine the composition of the complexes formed and their instability constants from the relationship

$$\bar{n} = f([M_1^{z_1}]).$$

This method has been used[34] to determine the instability constants of the hydroxotitanyl complex $TiO(OH)^+$. The variation of $K_d$Ti with pH on KU-2 cation-exchange resin in the hydrogen form was studied, that is, the $OH^-$ ion, whose concentration is connected with the $H^+$ concentration by the ionic product of water was taken as $M_1^{z_1}$. The relationship $\bar{n} = f(\text{pH})$ is shown in Fig. 4; the instability constant of the hydroxotitanyl complex, which is numerically equal to the $OH^-$ concentration at $\bar{n} = 2.5$, was found graphically from this curve:

$$K_{\text{instab}} = \frac{[TiO^{2+}][OH^-]}{[TiO(OH)^+]} = 1.5 \times 10^{-3} \text{ at } 18°.$$

A similar result has been obtained by the solubility method[34].

## IV. DETERMINATION OF THE POLYMERISATION FACTOR

Two methods can be used for determining the polymerisation factor by using ion exchangers. The first is based on the fact that ion-exchange processes on synthetic ion exchangers obey the law of mass action[47,48], thus making it possible to use the equilibrium displacement method, which enables the coefficients in the chemical equations to be determined. The second method[48] is based on the rate of diffusion of ions within the cation exchanger being a function of their sizes[49] a study of the ion-exchange kinetics thus enabling one to determine the conditions under which the polymeric species exist in solution and, in certain cases, to judge approximately the polymerisation factor of the ions under investigation.

### 1. The Equilibrium Displacement Method

It has been shown in studies of the polymerisation processes of Zr, Nb, Ta ions[17,50,51] that the polymeric species dissociate during the formation of stable complexes. Synthetic ion exchangers may be considered as macromolecular insoluble reagents[52]; with a fairly stable bond between the element under investigation and the ion exchanger (a high $K_d$ value) it may be assumed that the polymeric species will dissociate in the ion-exchanger phase. In this case the ion-exchange reaction can be expressed by the equation

$$pz\overline{RM_1} + M_p^z \rightleftarrows p\overline{R_zM} + pzM_1, \qquad (19)$$

where $M_1$ is a singly-charged ion and $p$ is the polymerisation factor.

It follows from Eqn. (19) that for $[\overline{RM_1}] \simeq$ const and $[M_1] \simeq$ const the distribution coefficient for the element under investigation ($K_d$) between the solution and the ion exchanger depends on the concentration of $M_p^z$. This enables the polymerisation factor $p$ to be determined from the change in total concentration of the element.

Under these conditions the distribution coefficient assumes the form

$$K_d = \frac{G^p}{[M_p^z]} \times \frac{v}{m}. \qquad (20)$$

Here $G$ is the amount of the element, in g-atoms, absorbed by the ion exchanger under the given conditions, $[M_p^z]$ the equilibrium concentration of poly-ions in solution, $v$ the volume of the solution under investigation (ml), and $m$ the mass of ion exchanger (g).

Eqn. (20) shows that $K_d$ depends on the polymerisation factor $p$; a definite value of the distribution coefficient corresponds to each polymeric species, this remaining constant in a series of experiments in which the concentration of the element under investigation varies, if $p$ is not altered.

The equilibrium concentration of polymeric species in solution can be expressed in terms of the total analytical concentration $C$:

$$[M_p^z] = \frac{1}{p} \times C. \qquad (21)$$

Combining Eqns. (20) and (21) we obtain:

$$K_d = \frac{G^p}{\frac{1}{p} \times C} \times \frac{v}{m}. \qquad (22)$$

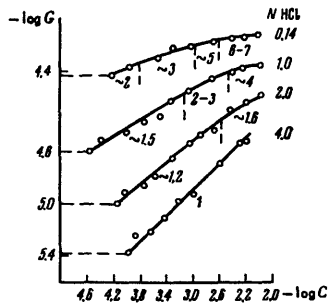



Fig.5. Relationship between the amount of Zr absorbed by KU-1 cation-exchange resin and its equilibrium concentration[48]. The figures under the curves denote the polymerisation factor $p$.

$G$ and $C$ are found experimentally and the ratio $v/m$ is constant in a given series of experiments. Expressing Eqn. (22) in logarithmic form we obtain:

$$p \log G = \log C + \log \frac{1}{p} + \log K'_d. \qquad (23)$$

For a definite constant polymerisation factor ($p$ = const, $K'_d$ = const), Eqn. (23) assumes the form

$$p \log G = \log C + \text{const}. \qquad (24)$$

On plotting $\log G$ against $\log C$ the polymerisation factor $p$ can be determined from the slope of the curve relative to the ordinate axis. If $p$ alters with a change in the concentration ($C$) of $M^z$, then the slope of the curve reflecting the relationship $\log G = f(\log C)$ will alter accordingly.

The results of experiments for $Zr^{IV}$ in perchloric acid solutions[48] are shown in Fig. 5. $H^+$ ions were used as the $M_1$ ions having constant concentration. The experiments were carried out under static conditions using a sulphonated KU-1 cation-exchange resin¶ in the hydrogen form†. The slope of the curves in Fig. 5 relative to the ordinate axis shows that in 4 $N$ $HClO_4$ at zirconium concentrations of $1 \times 10^{-4}$–$1 \times 10^{-2}$ M there are only monomeric species in solution; the polymerisation factor is increased by lowering the acid concentration or increasing the zirconium concentration. Similar results have been obtained by a dialysis method[50].

## 2. Ion-Exchange Kinetics.

Ion-exchange kinetics curves have a varying steepness depending on the rate at which equilibrium is established. A convenient way of comparing the kinetic curves is to determine graphically the time over which half the element being studied is absorbed, compared with the equilibrium state[48]. It has been proposed to call this time the half-equilibrium time and to represent it by $\tau_{\frac{1}{2}}$. Various types of kinetic curves are shown in Fig. 6. Curve *1* corresponds to the absorption by a cation exchanger of $Co^{2+}$ ions, which do not form polymeric species, and curves *2* and *3* to the absorption of zirconium cations for various polymerisation factors. If the transition to the horizontal section on the ion-exchange-kinetics curve occurs over a long interval of time (curve *3*, Fig. 6) then it is necessary to determine the percentage absorption in the equilibrium state ($A$), to read off half this value ($B$) from the ordinate axis and to find the corresponding value of $\tau_{\frac{1}{2}}$ (curve *3*).

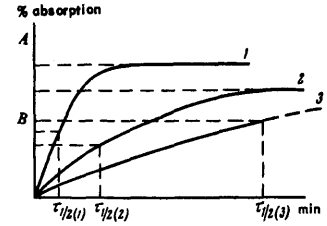



Fig.6. Graphical determination of the half-equilibrium time $\tau_{\frac{1}{2}}$.[48]

TABLE 3. Variation in the polymerisation factor* and the rate of ion exchange of zirconium in perchloric acid solutions[48]. The calculated data obtained from the approximate formula $\tau'_{\frac{1}{2}} p \simeq \tau_{\frac{1}{2}} p'$ are in parentheses.

| $[HClO_4]$, M | Zirconium concentration, M | | | | | |
|---|---|---|---|---|---|---|
| | $1 \times 10^{-2}$ | | $1 \times 10^{-3}$ | | $1 \times 10^{-4}$ | |
| | $\tau_{\frac{1}{2}}$ (min) | $p$ | $\tau_{\frac{1}{2}}$ (min) | $p$ | $\tau_{\frac{1}{2}}$ (min) | $p$ |
| 0.14 | 95 | 8 | 40 | 4 | 22 | 2 |
| 0.50 | 70 | (6) | — | — | 19 | (1.8) |
| 1.0 | 36 | 4 | 28 | 2 | 14 | 1.5 |
| 2.0 | — | 1.6 | 14 | 1.2 | 11 | 1.1 |

* The values of $p$ are taken from Fig.5.

As an illustration, the results of studies on the rate of ion exchange of zirconium cations in perchlorate solutions of KU-1 cation exchanger[48] are shown in Table 3. The data show that the polymerisation factor $p$ and the half-equilibrium time $\tau_{\frac{1}{2}}$ are directly proportional. A similar method has been used in a study of the state of $Ti^{IV}$ in hydrochloric acid solutions[43].

A calculation using the energy characteristics for ion interactions indicates that polyhydroxo-cations are ring-like structures[54]. Therefore it is to be expected that the plot of $\tau_{\frac{1}{2}}$ against $p$ will be a straight line for the formation of polyhydroxo-cations in solution (for example, see Table 3). It is possible that this enables the kinetic method to be used not only for determining the conditions under which poly-ions exist in solution, but also for estimating approximately the mean polymerisation factor of polyhydroxo-cations.

¶ KU-1 is a difunctional, strongly acid cation-exchange resin with $-SO_3H$ and $-OH$ active groups, prepared by the condensation of $p$-phenolsulphonic acid with formaldehyde in acid (Ed. of Translation).

† Zirconium forms fairly stable sulphato-complexes[53], during which the polymeric species dissociate[24]. Therefore it may be assumed that polymeric cations of zirconium dissociate during absorption by a cation exchanger containing active sulphonate groups.

## V. DETERMINATION OF THE COMPOSITION AND STABILITY OF COMPLEXES IN SOLUTION

Ion exchange has been widely used for determining the composition and stability constants of the complexes of many elements, including high-valency elements. For example, it has been used to study the chloro-[11], nitrato-[11,55], sulphato-[56], and oxalato-complexes[57] of $Zr^{IV}$ and $Hf^{IV}$, the complexes of these elements with certain hydroxy-acids[58,59], the chloro-complexes of $Ru^{IV}$,[60] the oxalato-complexes of $Pu^{IV}$,[57] and the nitrato-complexes of $Th^{IV}$.[61]

The theory and practice of studying complex formation under static conditions using cation exchangers[59,62-66] and anion exchangers[66-69], as well as the study of complex formation under dynamic conditions[70-72], are described in sufficient detail in the literature. In this review we shall restrict ourselves merely to setting out the principles of carrying out an experiment and the basic formulae for the methods of Schubert[62-64], Fronaeus[65], and Paramonova[66], which have been most widely used.

Schubert's method[62,63] is used for studying systems in which only one complex, which is not absorbed by a cation exchanger, is formed. An indication of the formation of a single complex over a certain range of ligand concentration is a linear relationship for $1/K_d = f([A^{y-}])$, where $K_d$ is the distribution coefficient of the element under investigation between the cation exchanger and the solution, and $[A^{y-}]$ is the equilibrium ligand concentration. It can be shown[64] that when working with microconcentrations of the element under investigation in the presence of a macroconcentration of singly-charged ions, the stability constant of a complex formed by the reaction $M + nA \rightleftharpoons MA_n$ can be calculated from the formula

$$\beta_n = \frac{[MA_n]}{[M][A]^n} = \frac{K_{d_0}/K_d - 1}{[A]^n}. \quad (25)$$

Here $K_{d_0}$ and $K_d$ are, respectively, the distribution coefficients of the element in the absence of the ligand A and in the presence of different concentrations of it. Putting Eqn. (25) into logarithmic form, we obtain

$$\log(K_{d_0}/K_d - 1) = n\log[A] + \log\beta_n. \quad (26)$$

A graphical plot of relationship (26) enables $n$ to be determined from the slope of the curve relative to the abscissa; the stability constant of the complex is calculated from Eqn. (25).

Fronaeus' method[59,65] is used to study systems in which several complexes are formed, including positively charged complexes which are absorbed by a cation exchanger. An indication of the formation of several complexes over a given range of ligand concentrations is a non-linearity for the relationship $1/K_d = f([A^{y-}])$.

For a reaction between a central ion $M^{q+}$ and a ligand $A^{y-}$ to form the complexes $MA^{(q-y)+}$, $MA_2^{(q-2y)}$, and $MA_3^{(q-3y)}$, of which the first is markedly absorbed by the cation exchanger, the stability constants are calculated from the following equations:

$$\varphi = \frac{K_{d_0}/K_d - 1}{[A]} = \frac{\beta_1 - l + \beta_2[A] + \beta_3[A]^2}{1 + l[A]}, \quad (27)$$

$$f = \frac{K_{d_0}/K_d\{(\beta_1 - l)[A] - 1\} + 1}{[A]^2} = \beta_1\varphi - x, \quad (28)$$

$$x = \beta_2 + \beta_3[A], \quad (29)$$

$$\frac{\Delta f}{\Delta[A]} = \beta_1\frac{\Delta\varphi}{\Delta[A]} - \beta_3. \quad (30)$$

In these equations $K_{d_0}$ and $K_d$ are the distribution coefficients of the element under investigation between the cation exchanger and the solution in the absence and presence of the ligand respectively, [A] is the equilibrium ligand concentration, $\beta_n$ are the cumulative stability constants of the complexes, $l$ is a quantity which takes account of the absorption of the complex $MA^{(q-y)+}$, $\varphi$ and $f$ are the Fronaeus functions, $\Delta\varphi = \varphi - \varphi_0$, $\Delta f = f - f_0$. Experimentally one determines the values of $K_d$ and $K_{d_0}$‡ for a constant ionic strength of the solution observing the condition $[M]_{total} \ll [A^{y-}]$§.

It follows from Eqn. (27) that

$$\lim_{[A]\to 0}\varphi = \beta_1 - l = \varphi_0.$$

Substituting the value of $\beta_1$-$l$ obtained in formula (28) enables the function $f$ to be calculated at different ligand concentrations. The value of $f_0$ is found graphically by extrapolating relationship (28) to zero ligand concentration. By having a number of values of $\varphi$ and $f$ for different ligand concentrations, $\beta_1$ and $\beta_3$ can be determined from Eqn. (30):

$$\lim_{\frac{\Delta\varphi}{\Delta[A]}\to 0}\frac{\Delta f}{\Delta[A]} = -\beta_3, \qquad \frac{\Delta f}{\Delta[A]}\Big/\frac{\Delta\varphi}{\Delta[A]} = \beta_1.$$

$\beta_2$ is calculated from Eqns. (28) and (29).

It is also possible to use the Fronaeus method for calculating stability constants in the more complicated case where four complexes are formed in the system concerned. An example of such a calculation may be found in a paper dealing with the chloro-complexes of $Zr^{IV}$.[11]

Paramonova's absorption curve method[66] provides for the use of both cation and anion exchangers for studying complex formation processes, the method leading to a way of expressing the experimental results which enables data obtained for both types of resin to be compared. In this method one studies the absorption of micro- or semimicro-concentrations of an element by cation and anion exchangers from solutions having constant ionic strength and constant salt composition, but differing from each other in ligand concentration. The experimental results are expressed in relative units of absorption of the element by the cation exchanger $\gamma_+ = g_M/g_M^\circ$ and the anion exchanger $\gamma_- = g_{MA}/g_{MA}^\circ$, where $g_M^\circ$ is the maximal absorption of the element M by the cation exchanger in the absence of ligand A, $g_M$ is the absorption of M by the cation exchanger in the presence of A, $g_{MA}$ is the absorption of M by the anion exchanger from the solution under investigation, and $g_{MA}^\circ$ is the absorption of M by the anion exchanger from a solution in which the concentration of A is so high that the further addition of ligand does not lead to an increase in the absorption of M, since it is already present completely in the form of a coordinatively saturated anionic complex.

‡ $K_{d_0}$ can be determined graphically by extrapolating the relationship $K_d = f([A^{y-}])$ to zero ligand concentration.

§ The total molar concentration of M in the equilibrium solution should not exceed 1–2% of the total molar concentration of $[A^{y-}]$. Furthermore, the concentration of the element under investigation should be considerably less than the concentration of the exchanging ions.

The latter circumstance somewhat limits the range of application of anionic exchange. For low-stability complexes the anionic species are formed only at appreciable ligand concentrations, in which case the ligand may displace anionic complexes of the element under investigation from the anionic exchanger, thus making it difficult to determine $\gamma_-$. In this case, for approximate calculations, the maximum absorption of M attained by the anion exchanger on increasing the concentration of A may be used for $g^{\circ}_{MA}$.

If the concentration of the element under investigation is considerably lower than the concentration of the exchanging ion then it can be shown that $\gamma_+$ and $\gamma_-$ express the fraction of cationic and complex anion species of the element in a given solution. The fraction of the element present in solution in the form of an electrically neutral complex is equal to:

$$\gamma_0 = 1 - \gamma_+ - \gamma_-.$$

When working under static conditions $\gamma_+$ and $\gamma_-$ are calculated from the formula

$$\gamma = \frac{(C_{init} - C)\, C_0}{(C_{init} - C_0)\, C}.$$

Here $C_{init}$ is the concentration of the initial solution, $C$ is the total concentration of M in the equilibrium solution in the presence of the ligand, $C_0$ in the calculation of $\gamma_+$ is the total concentration of M in the solution in equilibrium with the cation exchanger in the absence of the ligand; $C_0$, when calculating $\gamma_-$, is the total concentration of M in the solution in equilibrium with the anion exchanger at that ligand concentration at which all of the element is combined in anionic complexes (or a maximal absorption of M by the anion exchanger is observed).

As an example we present for the simplest cases the formulae for calculating the stability constants of complexes from the experimentally found $\gamma_+$ and $\gamma_-$.

(a) Complex formation taking place according to the equation $M^{z+} + A^{y-} \rightleftharpoons MA^0$. In this case

$$\beta = \frac{[MA^0]}{[M^{z+}][A^{y-}]} = \frac{1-\gamma_+}{\gamma_+[A^{y-}]}. \qquad (31)$$

It follows from Eqn. (31) that the stability constant is numerically equal to $1/[A^{y-}]$ at $\gamma_+ = 0.5$.

(b) Complex formation proceeding according to the scheme $M^{z+} + Ay^- \rightleftharpoons MA^{x-}$ $(y > z)$. In this case

$$\beta = \frac{[MA^{x-}]}{[M^{z+}][A^{y-}]} = \frac{\gamma_-}{\gamma_+[A^{y-}]}. \qquad (32)$$

It follows from Eqn. (32) that $\beta = 1/[A^{y-}]$ at $\gamma_- = \gamma_+$.

(c) Two complexes being formed according to the scheme $M^{z+} + A^{y-} \rightleftharpoons MA^0$, $MA^0 + A^{y-} \rightleftharpoons MA_2^{y-}$. For this system $\beta_1$ is found as in case (a) at those ligand concentrations where there is no anionic complex. The overall stability constant is calculated from the formula

$$\beta_2 = \frac{[MA_2^{y-}]}{[M^{z+}][A^{y-}]^2} = \frac{\gamma_-}{\gamma_+[A^{y-}]^2}. \qquad (33)$$

It follows from Eqn. (33) that $\beta_2 = 1/[A^{y-}]^2$ at $\gamma_- = \gamma_+$.

The methods described above enable the stability constants to be determined for cases where the state of the central ion $M^{q+}$ and the ligand $A^{y-}$ does not change during the complex formation, that is, the reaction between them takes place according to the scheme

$$M^{q+} + nA^{y-} \rightleftarrows MA_n^{(q-yn)}.$$

For complex formation in which hydrolysed cations $M(OH)_x^{(q-x)+}$ participate, the state of the latter may change during complex formation

$$M(OH)_x^{(q-x)+} + nA^{y-} \leftrightarrows M(OH)_{x-n}A_n^{(q+n-yn)} + nOH^-.$$

In this case the above methods only make it possible to determine the equilibrium constants at a given pH.

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Arising from certain specific properties of ion exchangers (equivalence of ion exchange, swelling, the diffusion kinetics of exchange) the ion-exchange method can be successfully applied to studying the states of high-valency ions in solution. At the present time ion exchange is the only method which enables the magnitude of the charge on ions in solution to be determined directly by experiment. Ion exchange enables us to study the polymerisation of inorganic compounds in solution in addition to other methods available. In conjunction with other methods ion exchange is a powerful means of studying the complexes of high-valency elements and it enables us to determine the quantitative characteristics of complex formation processes in solution.


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# COMPOUNDS OF ELEMENTS OF GROUP 0

A. B. Neiding

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## I. INTRODUCTION

In a brief review published a short while ago[1] the first papers on compounds of elements of Group 0 of Mendeleev's Periodic System were considered. The production of a complex of xenon and platinum hexafluoride, $XePtF_6$,[2] of xenon tetrafluoride $XeF_4$,[3-5] and of a radon fluoride of unknown composition[6] was described. Brief mention was also made of the production of xenon difluoride $XeF_2$ [7,8] and xenon hexafluoride $XeF_6$,[9,10] some information was given about the chemical and physical properties of these substances, and the first attempts at a theoretical explanation of the formation of chemical bonds by the atoms of the Group 0 elements[11,12] were discussed.

The first successful investigation stimulated a further, quite intensive development of work in this direction, and in a comparatively short time the experimental and theoretical material has become so voluminous that it seems opportune to attempt to give a more complete review of the present state of the investigations in the field of compounds of the Group 0 elements.

In both the Russian and foreign press a series of articles has appeared already, devoted to complete or partial reviews, sometimes popular in nature[13-31]; however, these articles do not illuminate in sufficient detail all the available material.

The present review covers the literature available to the author up to 1 October 1964. It is expedient to start by considering the compounds of xenon, since the overwhelming majority of studies are devoted to them and at present they are the most thoroughly investigated.

## II. COMPOUNDS OF XENON

### A. Fluorides

1. Xenon difluoride. Several methods for obtaining xenon difluoride $XeF_2$ have been described. Smith[8] synthesised $XeF_2$ by the reaction of gaseous xenon (partial pressure 60 mmHg) and fluorine (240 mmHg) in a nickel circulating system at 400° or above. Weeks and coworkers[32] obtained $XeF_2$ by irradiation of a mixture of fluorine and xenon with ultraviolet light from a high-pressure mercury lamp. Mixtures with $F_2$ : Xe molar ratios from 0.91 to 5.20 were used, circulated in a nickel apparatus with sapphire

windows at room temperature and a pressure of 890–1030 mmHg. The xenon difluoride was condensed in a trap at -78°C; under these conditions pure $XeF_2$ is obtained, but without a trap $XeF_4$ is also formed[33]. Further photochemical reaction of fluorine with $XeF_2$ leads to the formation of $XeF_4$. The quantum yield of $XeF_2$ is 0.3–0.7 but is somewhat less if the pressure is raised, especially the fluorine pressure. The following mechanism is proposed[33] for the photochemical formation of $XeF_2$:

$$F_2+h\nu \rightarrow 2F,$$
$$2F+F_2 \rightarrow 2F_2,$$
$$2F+Xe \rightarrow F_2+Xe,$$
$$F+Xe+F_2 \rightarrow XeF+F_2,$$
$$F+Xe+Xe \rightarrow XeF+Xe,$$
$$XeF+F \rightarrow XeF_2,$$
$$XeF+XeF \rightarrow XeF_2+Xe,$$
$$XeF+XeF \rightarrow 2Xe+F_2.$$

Xenon difluoride is also formed in the irradiation of xenon–fluorine mixtures by $\gamma$-rays from $^{60}Co$ or by high-energy electrons in nickel apparatus[34]. At room temperature and above, mixtures of $XeF_2$ and $XeF_4$ are formed, but at -35°C only $XeF_2$ is obtained.

A method by which pure $XeF_2$ can be obtained in yields of ~ 100 mg $h^{-1}$ was described in detail by Hoppe and coworkers[35]. They passed an electric discharge from an induction coil through mixtures of xenon and fluorine with $Xe : F_2$ molar ratios from 1 : 1 to 1 : 3, at room temperature; $XeF_2$ was condensed on a cold finger at -78°C. The apparatus used is shown schematically in Fig. 1. Xenon from cylinder *1* and fluorine, vaporised from container *2* containing thoroughly purified liquid fluorine, is admitted into reaction vessel *3*, into which pass electrodes from the induction coil, through ground joints. The $XeF_2$ formed in the reaction is condensed on cold finger *4*, cooled by a mixture of alcohol and solid carbon dioxide, and occasionally shaken off into ampoule *5* for weighing.

Khutoretskii and Shpanskii[36] proposed a simple method of synthesising $XeF_2$; they showed that it is formed from the elements at ordinary temperature and increased pressure, with liberation of heat (~ 40–60 kcal $mole^{-1}$) and sometimes even explosively. The experiments were made in nickel, stainless steel, or Monel vessels; fluorine was introduced first into the reactor to a pressure of 18 atm, then xenon was added to a pressure of 35 atm; reaction was almost instantaneous.

A somewhat different method, not employing elemental fluorine, was used by Milligan and Sears[37], who obtained pure $XeF_2$ by passing a high-potential discharge through an

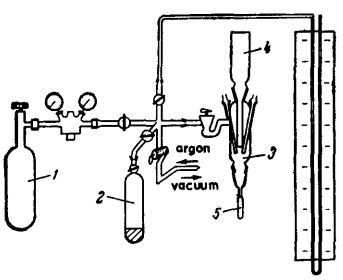



Fig. 1. Apparatus for preparing xenon difluoride[35].



Fig. 2. Crystals of xenon difluoride (a millimetre scale is shown below).

approximately equimolar mixture of xenon and carbon tetrafluoride in a Pyrex glass vessel cooled with a mixture of solid carbon dioxide and acetone, then distilling and recrystallising the reaction products.

The $XeF_2$ in the experiments described above was identified mass-spectrometrically and by chemical analysis.

Xenon difluoride is a colourless solid with vapour pressure 3.8 mmHg at 25°C and 318 mmHg at 100°C.[8,38] It forms excellent gleaming crystals, which grow in a few hours to millimetre dimensions (Fig. 2). The crystals exhibit double refraction. Solid $XeF_2$ melts at ~ 140°C and can be supercooled to 50°C without solidification[38]. At room temperature $XeF_2$ is stable and can be kept in nickel or quartz vessels for a few months[8]. In sealed glass ampoules, $XeF_2$ can be kept at the temperature of solid carbon dioxide for a long time, but at room temperature, even in the dark, it slowly decomposes, possibly as a result of reaction with the glass[35].

Xenon difluoride has a sharp nauseating odour[35]. It reacts vigorously with methanol and slowly with water[35]. It decomposes in solutions of alkalis (NaOH) and dilute acids ($H_2SO_4$) but the reactions are not particularly violent. Iodine is liberated by the action of $XeF_2$ on an acidified solution of potassium iodide or on moist potassium iodide–starch paper. Decomposition of $XeF_2$ takes place even in kerosene, redistilled and dried over metallic sodium[35]. $XeF_2$ dissolves in anhydrous hydrogen fluoride without decomposition; the solubility at 25°C is ~ 10 moles $XeF_2$ in 1000 g HF.[39] Hydrogen at 400°C completely reduces $XeF_2$ to elemental xenon and hydrogen fluoride[15].

Appelman and Malm[40] investigated the chemical properties of aqueous solutions of $XeF_2$ and the ultraviolet absorption spectra of such solutions. Xenon difluoride forms colourless, slowly hydrolysed aqueous solutions in which the $XeF_2$ is probably present as undissociated molecules, which do not form complex anions with fluoride ions. This, follows, firstly, from the low solubility of $XeF_2$ in water (~ 0.15 M at 0°C), and secondly, from the similarity of the spectra shown in Fig. 3 for an aqueous solution of $XeF_2$ at ~ 5°C and for gaseous $XeF_2$ at 30°C.[40,41]

The distribution coefficient of $XeF_2$ between water and carbon tetrachloride is 2.3 and does not change significantly in 1 M $HClO_4$ or in 4 M $KHF_2$. $XeF_2$ solution is a strong oxidant, which rapidly oxidises HCl to $Cl_2$, iodate to periodate, $Ce^{III}$ to $Ce^{IV}$, $Co^{II}$ to $Co^{III}$, and $Ag^{I}$ to $Ag^{II}$. The redox potential of the $Xe-XeF_2$ system in an acid medium is 2.2 V. The half-decomposition life of $XeF_2$ dissolved in water is ~ 7 h at 0°C, in 1 M $HClO_4$ it falls to ~ 5 h, and in 30% HF to ~ 3 h. When $XeF_2$ solution is made alkaline, it rapidly becomes yellow and the solution decomposes; it was suggested[40] that the yellowing is due to the formation of an oxygen compound of xenon(II).

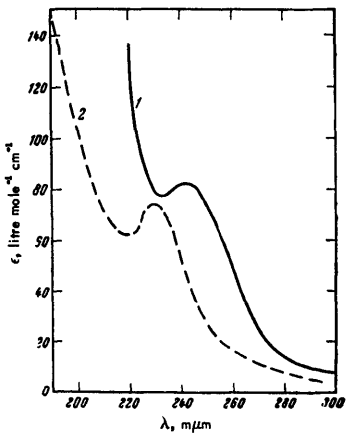



Fig. 3. Ultraviolet absorption spectrum of xenon difluoride: 1) aqueous solution at ~5°C;[40] 2) gas at 30°C.[41]

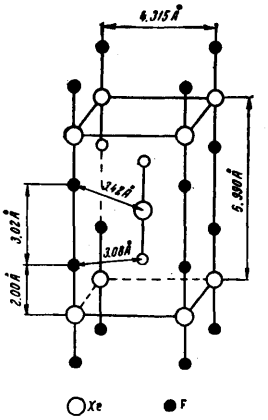



Fig. 4. Crystal structure of xenon difluoride according to neutron diffraction analysis[46].

Xenon difluoride is diamagnetic[35]; its molar magnetic susceptibility is $\chi_M = (40-50) \times 10^{-6}$. The heat of sublimation of crystalline $XeF_2$ is 12.3 ± 0.2 kcal mole$^{-1}$,[42] and was determined from the temperature dependence of the intensity of the spectral bands in the vacuum ultraviolet region of gaseous $XeF_2$ in thermal equilibrium with the crystals[43]. The standard heat of formation of gaseous $XeF_2$, calculated from mass-spectroscopic data, is 37 ± 10 kcal × × mole$^{-1}$,[44] which gives a mean energy of 39 ± 10 kcal × × mole$^{-1}$ for the Xe–F bond in $XeF_2$.

The structure of $XeF_2$ has been studied by X-ray diffraction[45] and neutron diffraction[46] methods. The X-ray studies indicated that $XeF_2$ is tetragonal and has space group $I4/mmm$; the lattice parameters are: $a$ = 4.315 ± ± 0.003, $c$ = 6.990 ± 0.004 Å. The density calculated for two formula units in the unit cell is 4.32 g cm$^{-3}$. The molecule has a linear configuration F–Xe–F and the Xe–F distance is 2.14 ± 0.14 Å.

The neutron diffraction results confirmed these facts, by showing that $XeF_2$ has a body-centred tetragonal lattice (space group $I4/mmm$) of parallel, linear, symmetrical F–Xe–F molecules (Fig. 4). The Xe–F distance is 2.00 ± ± 0.01 Å. Each fluorine atom is associated with another fluorine atom at a distance of 3.02 Å and four fluorines at a distance of 3.08 Å. The least intermolecular Xe–F distance is 3.64 Å.

The infrared spectrum of gaseous $XeF_2$ [8,38] shows two intense bands: at 555 and 213.2 cm$^{-1}$. The first, without a $Q$-branch, relates to the antisymmetric stretching vibration $\nu_3$, and the second, with a distinct $Q$-branch, to the $\nu_2$ bending vibration. A third band, at 1070 cm$^{-1}$, is considered to be a weak $\nu_1 + \nu_3$ combination, including the infrared-inactive band of symmetrical stretching vibrations, $\nu_1$ = 515 cm$^{-1}$.

The $XeF_2$ spectrum is characteristic of a symmetrical linear molecule. The Xe–F interatomic distance, calculated from the $P$–$R$ spacing for $\nu_3$ of 16 cm$^{-1}$ (the maxima of the $P$- and $R$-branches are at 566 and 550 cm$^{-1}$, respectively), is ~1.7 Å. The force constants have been determined: $k_r$ (the constant for the principal stretching vibration) is 2.85, $k_{rr}$ (the constant of stretching interaction) 0.11, and $k_\delta/l^2$ (the constant of bending vibrations)

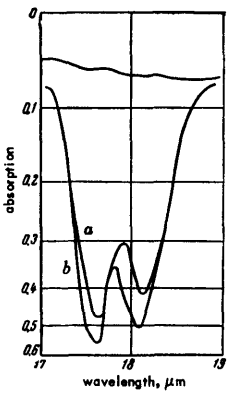



Fig. 5. Infrared spectrum of gaseous xenon difluoride[47]: *a*) pure $XeF_2$; *b*) $XeF_2 + F_2$ (~0.7 kgf cm$^{-2}$).

0.19 mdyn Å$^{-1}$; these values enabled the structure of the $XeF_2$ molecule to be settled (see p. 419).

The main points of the above picture were confirmed by Milligan and Sears[37], who also observed a very weak band at 520 cm$^{-1}$, probably $\nu_1$.

An investigation of the effect of fluorine pressure on the infrared spectrum of $XeF_2$ [47] gave a slightly more accurate $P$–$R$ spacing, 14.2 ± 0.2 cm$^{-1}$, which corresponds to the Xe–F distance of 1.9 Å. The more accurate force constants $k_r$ and $k_{rr}$ are 2.82 and 0.15 mdyn Å$^{-1}$ respectively. Fig. 5 shows the infrared spectrum of gaseous $XeF_2$, according to Smith[47].

The Raman spectrum of solid $XeF_2$ [38] has lines at 108 and 497 cm$^{-1}$. The first is probably a libration frequency, but the second is $\nu_1$. Lines at 548 and 509 cm$^{-1}$ are evidently due to the impurity $XeF_4$.

Investigation of the spectrum of gaseous $XeF_2$ in the far ultraviolet region[43] gave information about the excited electronic levels of the molecule and this was used in

deciding the structure of the $XeF_2$ molecule (see p. 420). Kuznetsov and coworkers[48] investigated the spectrum from a high-frequency discharge through $XeF_2$ vapour; the bands found belonged to $XeF_2$ and XeF molecules.

Nuclear magnetic resonance has also been used in studying $XeF_2$, the investigation being made in anhydrous hydrogen fluoride[49,50] and in the solid state[50]. At room temperature $XeF_2$ enters into exchange with the solvent, but at -19.5°C this exchange is so slow that the measurements are completely feasible. Fig. 6 shows the magnetic resonance spectrum[49] of $XeF_2$ in HF at -20°C and at a frequency of 56.422 MHz. The chemical shift of $^{19}F$ in $XeF_2$ (for a solution in anhydrous HF) is 629 parts per million relative to $F_2$ [50] and 2.3 parts per million relative to HF[50]; the latter quantity at -20°C is also reported[49] to be 3.3 parts per million. The $^{129}Xe-^{19}F$ coupling constant for $XeF_2$ in HF is 5600 Hz [50] or 5690 Hz.[49] The impossibility of observing the $^{131}Xe-^{19}F$ coupling follows from the electrical asymmetry of the $XeF_2$ structure. The results of the nuclear magnetic resonance investigation of $XeF_2$ in HF confirmed that the $XeF_2$ is present in solution mainly as undissociated molecules.

The shielding constant for solid $XeF_2$ is 612 parts per million (relative to $F_2$) and the width of the resonance line is ~ 6.0 G.[50] The results of the nuclear magnetic resonance studies enable a number of views about the electron density distribution in the $XeF_2$ molecule and about the structure of this molecule to be ruled out. The Mössbauer effect in solid $XeF_2$ has also been studied[51,52].

2. Xenon tetrafluoride. A detailed description of the preparation of xenon tetrafluoride by heating a mixture of xenon and fluorine[3,5] was given in the previous review[1], which also included some information about the physical and chemical properties of $XeF_4$.

Another method, which also looks quite promising for the future preparative studies in the field of Group 0 compounds (see pp. 413 and 417) was employed by Kirshenbaum and his coworkers[53,54], who subjected a mixture of xenon and fluorine to the action of an electric discharge. They used an apparatus similar to that employed earlier for the synthesis of the oxygen fluorides $O_3F_2$ and $O_4F_2$ [55-57] (Fig. 7). The diameter of the reactor was 6.5 cm and the distance between the electrodes (dia. 2 cm) 7.5 cm. The mixture of gases with $Xe : F_2 = 1 : 2$ (by volume) was passed at a rate of 136 $cm^3\ h^{-1}$ (under standard conditions) into the reaction vessel cooled to -78°C, and was quantitatively converted into $XeF_4$. The discharge was varied from

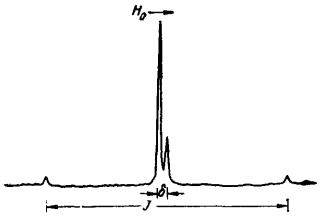



Fig. 6. Magnetic resonance spectrum with high resolution of $^{19}F$ in xenon difluoride at -20°C and frequency 56.422 MHz.[49] The chemical shift of $^{19}F$ relative to $H^{19}F$ is denoted by δ and the spin–spin coupling constant of $^{19}F-^{129}Xe$ is denoted *J*.

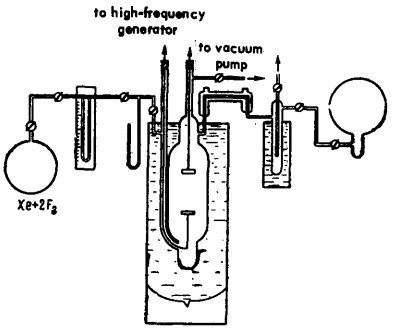



Fig. 7. Apparatus for preparing the fluorides of the Group 0 elements by the electric discharge method[54].

1100 V and 31 mA to 2800 V, 15 mA. In addition to the well-known methods for analysing the reaction products, a new method of determining xenon was employed, based on the quantitative reaction of xenon tetrafluoride with an excess of mercury:

$$XeF_4+4Hg\rightarrow Xe+2Hg_2F_2.$$

Schumacher and Schaefer[58] obtained $XeF_4$ in 97% yield (on Xe) from a mixture of $Xe + 3F_2$, which was circulated in an apparatus (Fig. 8) having a main section heated to 560°C and consisting of a Monel tube furnace packed with pieces of nickel sheet. Up to 20 g $XeF_4$ were obtained in 2 h.

A radiation method has also been used to synthesis $XeF_4$.[59] A mixture of xenon and fluorine in a stainless steel reactor was irradiated with a beam of electrons of energy 1.6 MeV and the reaction products were identified by their infrared spectra, which showed that $XeF_4$ and $XeF_2$ were formed.

The formation of $XeF_4$ (and xenon oxide fluorides) was observed in the reaction of xenon with $OF_2$ in an electric discharge at pressures of 3–62 mmHg and in a nickel tube at 400°C and initial pressure ~ 3.5 atm.[60]

In addition to the chemical properties of xenon tetrafluoride reviewed earlier[1] qualitative investigations[58] have

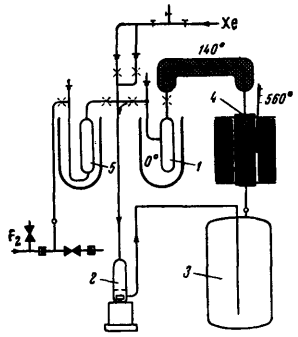



Fig. 8. Apparatus for preparing xenon tetrafluoride by a circulation method[58]:
1) trap at 0°C; 2) Teflon pump; 3) cylinder capacity 4.4 litres; 4) Monel tube furnace packed with nickel sheet; 5) trap.

shown that $XeF_4$ slowly attacks glass with formation of $SiF_4$ and $O_2$; when enclosed in aluminium foil it does not detonate under impact, although mixtures of $XeF_4$ with sugar or sulphur explode like mixtures of these substances with $KClO_3$. On being put on paper or cotton wool, dry $XeF_4$ explodes on heating; $XeF_4$ moistened in air instantly chars paper, which often also ignites spontaneously. Xenon tetrafluoride oxidises, on heating, metallic platinum to $PtF_4$, and possibly to $PtF_6$. $XeF_4$ dissolves in water, glacial acetic acid, concentrated nitric and sulphuric acids, and reacts with these solvents in doing so. In the reaction of $XeF_4$ with $CH_3CO_2H$ or $(CH_3CO)_2O$, a crystalline substance is formed, which the authors[58] think may by xenon acetate. Cyclopentadiene, tetrahydrofuran, dioxan, and ethanol ignite under the action of $XeF_4$; the mixture of vapours often explodes. Acetone does not react immediately with $XeF_4$, but after some time the mixture froths up and the $XeF_4$ dissolves. Petroleum slowly dissolves $XeF_4$, with darkening. In carbon disulphide, carbon tetrachloride, dimethylformamide, diethyl ether, and cyclohexane, $XeF_4$ is insoluble, and it does not react with these substances. $XeF_4$ fumes in air, being hydrolysed to $Xe(OH)_4$. The formation of this compound, which vigorously explodes on being heated to 30–40°C in a vacuum, was noted a little earlier by Bartlett and Rao[61]; according to these authors $Xe(OH)_4$ (or $XeO_2.2H_2O$) is obtained in the hydrolysis of $XeF_4$ by water in an evacuated quartz vessel.

Xenon tetrafluoride dissolves rapidly in potassium iodide solution, with quantitative liberation of xenon[5]:

$$XeF_4+4I^- \rightarrow Xe+2I_2+4F^-.$$

The results of an investigation of the hydrolysis of $XeF_4$ in acid, alkali, and neutral media are not completely reproducible owing to the heterogeneous nature of this reaction. The experimental $Xe:O_2$ ratio found in the reaction products is not 1 : 1, thus indicating a departure from the simple reaction:

$$XeF_4+2H_2O \rightarrow Xe+4HF+O_2.$$

In the hydrolysis of $XeF_4$ in acid and neutral media the yields of xenon and oxygen do not exceed 50 and 70% respectively[62,63]; in 6 M NaOH the yield in each instance is almost quantitative, but the results in 1 M NaOH are the same as in acid and neutral media[63]. Evidently $XeF_4$ disproportionates in solution with the formation of xenon and a soluble compound of xenon(VI). Evaporation of the solution formed by the acid hydrolysis of $XeF_4$ led to the formation of the oxide $XeO_3$ [62] (see p. 414).

The reaction of $XeF_4$ with $SF_4$ leads to the formation of $SF_6$ and elemental xenon; with $O_2F_2$, $XeF_6$ is formed[58]. The reactions of $XeF_4$ with $SbF_5$ and $TaF_5$ give the compounds $XeF_2.2SbF_5$ and $XeF_2.2TaF_5$ [64] (see p. 411); the same compounds are formed in the reaction of $XeF_2$ with the corresponding pentabromides. Xenon tetrafluoride does not react with $BF_3$, NaF, or KF, up to 200°C.[64,65] However, according to Schumacher and Schaefer[58], $XeF_4$ and $BF_3$ form a violet addition product, stable below -100°C.

Xenon tetrafluoride is diamagnetic: the molar magnetic susceptibility at room temperature is $-50.6\times10^{-6}$, but below 240°K the diamagnetism of $XeF_4$ begins, according to Slivnik and coworkers[66], to decrease with fall in temperature. A very close value for the susceptibility, $(-56\pm5)\times10^{-6}$ was found by other authors[67]. Careful measurements of the susceptibility of pure specimens of $XeF_4$ between 77° and 293°K showed, however, that the diamagnetism of $XeF_4$ is independent of temperature in this range; the molar susceptibility of xenon tetrafluoride is $(-53\pm5)\times10^{-6}$; the deviation does not exceed the limits of experimental error[68].

Boudreaux[69] made a theoretical calculation of the magnetic susceptibility of $XeF_4$ in the MO–LCAO approximation, paying special attention to the high-frequency elements of the paramagnetic part of the susceptibility and obtained results which agreed with the experimental data and also confirmed his assumptions concerning the scheme of molecular orbitals[79] (see p. 420).

The problem of the thermodynamic properties of xenon tetrafluoride has received much attention. $XeF_4$ has a high melting point, ~114°C.[15] The heat of sublimation of solid $XeF_4$, determined (just as that for $XeF_2$) from the temperature dependence of the intensity of the spectral bands in the vacuum ultraviolet region of gaseous $XeF_4$ in thermal equilibrium with crystals[43], was found to be $15.3\pm0.2$ kcal mole$^{-1}$.[42]

The heat of formation of solid $XeF_4$ was calculated from the calorimetrically measured heat of reaction of $XeF_4$ with an acidified aqueous solution of potassium iodide[71]. The value found for the standard heat of formation of crystalline $XeF_4$ was -60 kcal mole$^{-1}$, from which the calculated mean energy of the Xe–F bond is 30 kcal. Using the method of reducing $XeF_4$ with hydrogen by the reaction:

$$XeF_4(gas)+2H_2(gas) \rightarrow Xe(gas)+4HF(gas),$$

in an isothermal calorimeter at 120–130°C, preliminary values were found for the heat of formation of gaseous $XeF_4$ and the Xe–F bond energy, -55 kcal mole$^{-1}$ and +32 kcal respectively[72]. The standard heat of formation of gaseous $XeF_4$, calculated from the mass spectrometric result, is $-53\pm5$ kcal mole$^{-1}$,[44] which gives $32\pm2$ kcal for the mean energy of the Xe–F bond.

The heat capacity of solid $XeF_4$ was measured in the temperature range from 20°K to room temperature in an adiabatic calorimeter[73,74]. The preliminary value found for the standard entropy of formation of $XeF_4$ was $\Delta S^\circ = -102.5$ e.u., which, together with the heat of formation[71], gives $\Delta G^\circ = -29.4$ kcal mole$^{-1}$.

The form of the curve of the temperature dependence of heat capacity of $XeF_4$ (Fig. 9) is the same as for molecular crystals, for example, $C_6H_6$, $CO_2$, or $CH_4$. The heat capacity of $XeF_4$ at 298°K is ~28 cal mole$^{-1}$ deg$^{-1}$; the theoretical heat capacity of a molecular crystal of five atoms with six degrees of freedom is ~30 cal mole$^{-1}$deg$^{-1}$.

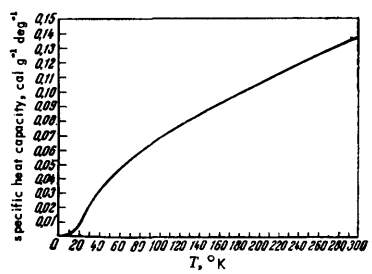



Fig. 9. Curve for the temperature dependence of the specific heat capacity of xenon tetrafluoride[74].



Fig. 10. Crystals of xenon tetrafluoride.

Judging from the heat capacity curve, $XeF_4$ does not undergo phase transformations in the temperature range studied.

From the results on vibrational spectra and structure of $XeF_4$, the thermodynamic functions of $XeF_4$ have been calculated for the range from 50° to 2000°K.[75]

Structural investigations on xenon tetrafluoride have employed X-ray diffraction[45,76-78] and neutron diffraction[79] with single crystals of $XeF_4$ (Fig. 10). The X-ray study[77] showed that $XeF_4$ is monoclinic, space group $P2_1/n$. The lattice parameters of $XeF_4$ are: $a = 5.050$, $b = 5.922$, $c = 5.771$ Å, $\beta = 99.6°$. The density calculated for two formula units in the unit cell is 4.04 g cm$^{-3}$; this agrees with the pyknometric determination[80].

The Xe–F distances are 1.90 and 1.92 Å, the F–Xe–F valency angles are 89.7° and 90.3°. The $XeF_4$ molecule has a square planar configuration with F–F distances of 2.69 and 2.71 Å. The shortest distance between two neighbouring molecules is 3.02 Å.

Neutron diffraction investigation[79] confirmed and somewhat refined the X-ray data. According to the neutron diffraction results, the Xe–F(1) and Xe–F(2) distances are 1.951 and 1.954 Å respectively; the F(1)–Xe–F(2) angle is 90.0 ± 0.1° (Fig. 11). Fig. 12 shows the position of the $XeF_4$ molecules in the crystal.

In a preliminary X-ray structural investigation of $XeF_4$ the existence of yet another polymorphic modification of

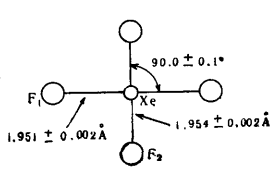



Fig. 11. Crystal structure of xenon tetrafluoride[79].

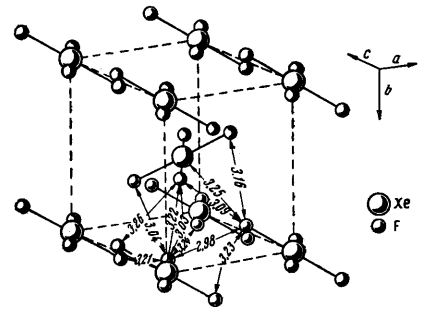



Fig. 12. Crystal structure of xenon tetrafluoride[79].

$XeF_4$ was suggested[76]. Subsequently it was shown[81,82] that this "modification" was really a molecular compound, $XeF_2.XeF_4$. The following parameters were found for this compound, which has the space group $P2_1/c$: $a = 6.64$, $b = 7.33$, $c = 6.40$ Å, $\beta = 92°40'$; for four formula units in the unit cell the density is 4.02 g cm$^{-3}$. In this compound the $XeF_2$ and $XeF_4$ molecules almost completely retain their usual configuration. The least intermolecular Xe–F distance is close to the distances in the $XeF_2$ and $XeF_4$ structures and the least intermolecular F–F distance (2.87 Å), although somewhat less than in these structures, nevertheless corresponds to the uncombined fluorine atoms. The absence of structural indications of the existence of strong bonds between the molecules supports the treatment of $XeF_2.XeF_4$ as a molecular compound.

Gaseous $XeF_4$ has been studied by electron diffraction[83]. The results showed that in the gaseous state the $XeF_4$ molecule has a square planar configuration with Xe–F distance of 1.94 Å.

The vibrational spectra of $XeF_4$ (the infrared spectrum of the gas and the Raman spectrum of the solid) were studied in detail by Claassen and coworkers[84], Figs. 13 and 14 show the spectra and a comparison of the frequencies is given in Table 1.

The results obtained show — in agreement with the structural data — that the $XeF_4$ molecule has a square planar configuration (symmetry $D_{4h}$). From the $Q$–$R$ spacing for $\nu_2$, 11 ± 1 cm$^{-1}$, the Xe–F interatomic distance was evaluated, 1.85 ± 0.2 Å. The force constants were determined: stretching vibrations, 3.00 mdyn Å$^{-1}$; stretching interaction between bonds at right angles,

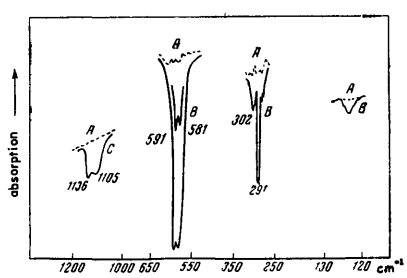



Fig. 13. Infrared spectrum of gaseous xenon tetrafluoride[84]: *A*) background; *B*) optical path 10 cm; *C*) optical path 60 cm.

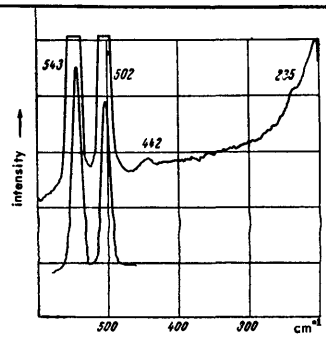



Fig. 14. Raman spectrum of solid xenon tetrafluoride[84].

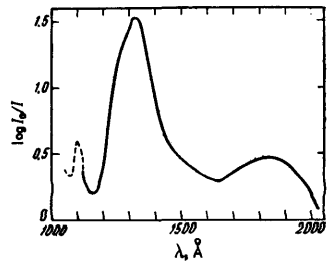



Fig. 15. Spectrum of xenon tetrafluoride in the far ultraviolet region[86].

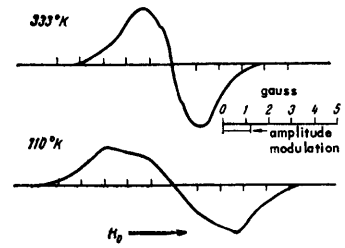



Fig. 16. Nuclear magnetic resonance spectrum of fluorine in xenon tetrafluoride at the frequency 29 MHz.[88]

TABLE 1. Assignment of the frequencies in the vibrational spectra of $XeF_4$.[84]

| | | | | |
|---|---|---|---|---|
| | $a_{1g}$ | $\nu_1$ | RS | 543 $cm^{-1}$ (v.s.) |
| | $a_{2u}$ | $\nu_2$ | IR | 291 $cm^{-1}$ (s.) |
| | $b_{1g}$ | $\nu_3$ | RS | 235 $cm^{-1}$ (w.) |
| | $b_{1u}$ | $\nu_4$ | inactive | 221 $cm^{-1}$ (?) |
| | $b_{2g}$ | $\nu_5$ | RS | 502 $cm^{-1}$ (v.s.) |
| | $e_u$ | $\nu_6$ | IR | 586 $cm^{-1}$ (v.s.) |
| | $e_u$ | $\nu_7$ | IR | 123 $cm^{-1}$ (?) |
| | | $\nu_5+\nu_6$ | IR | 1105 $cm^{-1}$ (w.) |
| | | $\nu_1+\nu_6$ | IR | 1136 $cm^{-1}$ (w.) |

Note. The following abbreviations are used in the table: IR = infrared spectrum of gaseous $XeF_4$; RS = Raman spectrum of solid $XeF_4$; v.s. = very strong; s. = strong; w. = weak intensity of band.

The 442 $cm^{-1}$ band in the Raman spectrum is considered as comprising $2\nu_4$; hence the value 221 $cm^{-1}$ is taken for $\nu_4$.

0.12 mdyn $Å^{-1}$; stretching interaction between oppositely situated bonds, ~0.06 mdyn $Å^{-1}$; the values found were comparable with the corresponding quantities for the $XeF_2$ [8,38] and $PuF_6$ [85] molecules.

The investigation of the spectrum of gaseous $XeF_4$ in the far ultraviolet region[86] made it possible to obtain information about the excited electronic levels of the molecule and these results could be used for assigning the structure of $XeF_4$ (see p. 420). Fig. 15 gives the spectrum.

Nuclear magnetic resonance has also been used for investigating $XeF_4$. The first measurements of the resonance of $^{19}F$ in solid $XeF_4$, made over a wide range of temperatures[87] showed — in accordance with static magnetic measurements[66], a change in the form of the spectrum near 273°K. However, somewhat later these authors refuted their own results[88] and showed that the form of the line was unchanged throughout the whole temperature range investigated (Fig. 16). The asymmetry of the $XeF_4$ spectra is ascribed to the anisotropy of the chemical shift of fluorine[66], and this problem received detailed study[88-93]. The shielding constant for solid $XeF_4$ was 482 parts per million (relative to $F_2$) and the line width ~3.8 G.[50]

Measurements of the magnetic resonance of $^{19}F$ in $XeF_4$ were also made in anhydrous HF.[49,50,94] In the spectrum there was a strong central line with a chemical shift of 175 parts per million relative to HF[49,94] and 454 parts per million relative to $F_2$.[50] Two weak lines on either side of the main line relate to the $^{129}Xe-^{19}F$ coupling. The coupling constant is 3860 Hz. As also in the case of $XeF_2$, the $^{131}Xe-^{19}F$ coupling does not appear in the spectrum; this shows the asymmetry surrounding the xenon nucleus and provides a basis for assuming[50] that the square planar structure of the $XeF_4$ molecule is also retained in solution. As for $XeF_2$, the xenon tetrafluoride is present in solution in HF mainly as undissociated molecules[50].

The information obtained from nuclear magnetic resonance spectra enabled some conclusions to be drawn about the electron density distribution and the structure of the $XeF_4$ molecule. The Mössbauer effect for solid $XeF_4$ was also investigated[51,52]. $^{131}XeF_4$ shows the Szillard-Chalmers effect[95], unlike the clathrate compounds of xenon, in which it is known that xenon does not form chemical bonds. In $\gamma$-irradiation at 77°K with single-crystal $XeF_4$, electron paramagnetic resonance studies showed the existence of an entrapped XeF radical; the spectrum of this radical was interpreted[96,97].

3. Xenon hexafluoride. To prepare xenon hexafluoride $XeF_6$ mixtures of xenon with a large excess of fluorine (Xe : $F_2$ ratios from 1 : 4 to 1 : 20) were heated to 300–700°C

at pressures up to 200 atm in nickel or stainless steel reactors[9,10,98,99]. Xenon hexafluoride is also formed on passing an electric discharge[54] through a 1 : 3 $Xe : F_2$ mixture at -78°C. The specimens of $XeF_6$ obtained by these methods were not completely pure and contained more or less appreciable amounts of $XeF_4$, $XeF_2$, and $XeOF_4$ impurities. Sheft and coworkers[100] proposed a method for obtaining pure crystals of $XeF_6$ based on the fact that unlike the other xenon fluorides and oxide fluorides $XeF_6$ forms a molecular compound with sodium fluoride; this offers the possibility of effectively separating the impurities.

Xenon hexafluoride at room temperature is a colourless crystalline material, m.p. 47.7° ± 0.2°C.[100] Solid $XeF_6$ becomes yellow at 43–43.5°C, and on melting it gives a yellow liquid, but on cooling and solidifying it becomes colourless again[9,100]. The vapour pressure of solid $XeF_6$ is ~ 7 mmHg at 0°C and 30 mmHg at 25°C; $XeF_6$ vapour is pale yellow-grey. $XeF_6$ dissolves in anhydrous HF, the solubility being ~ 10 moles $XeF_6$ in 1000 g HF at 25°C; the yellow solutions are decolorised on cooling[39]. Unlike the analogous solutions of $XeF_2$ and $XeF_4$, solutions of $XeF_6$ in HF exhibit high electrical conductivity (for example, the molar conductance of 0.02 M $XeF_6$ is 147 $\Omega^{-1}$ $cm^{-1}$)[39]; it has been suggested that on dissociation $XeF_5^+$ and $HF_2^-$ ions are formed[15].

With hydrogen at room or slightly higher temperatures, $XeF_6$ is reduced to elemental xenon[9]; mercury at 100°C has the same effect[10]. $XeF_6$ can be kept for a long period in nickel or poly(chlorotrifluoroethylene) vessels but it reacts with quartz at room temperature to form xenon oxide tetrafluoride $XeOF_4$.[9,101] The reaction of $XeF_6$ with $BF_3$ or $AsF_5$ at room temperature leads to the formation of the addition products $XeF_6.BF_3$ and $XeF_6.AsF_5$[102] (see p. 412).

Several important results were obtained in studying the hydrolysis of $XeF_6$. Dudley and coworkers[99] showed that when $XeF_6$ reacts with water a solution exhibiting strong oxidising properties is formed. The reaction of this solution with KI solution leads to the quantitative release of xenon. On this basis it was concluded[99] that xenic acid $Xe(OH)_6$ is formed in the solution. The alkaline hydrolysis of $XeF_6$ leads to the formation of pale yellow solutions, from which stable precipitates of salts of xenic acid are deposited[63,103-106] (see p. 415). Xenon trioxide $XeO_3$ (see p. 414) was obtained by the slow hydrolysis of $XeF_6$ with water vapour at room temperature[107] and $XeOF_4$ is formed in incomplete hydrolysis[108] (see p. 412).

Sheft and Hyman[109] studied the exchange of $^{19}F$ between $XeF_6$ and gaseous fluorine: the rate of exchange (at $XeF_6$ concentration of 0.02 M and 150°C) is a linear function of the fluorine concentration, and on extrapolation the straight line passes through the origin. The results were interpreted as showing the association of $XeF_6$ with a molecule of $F_2$.

Xenon hexafluoride is thermodynamically stable. The reduction of $XeF_6$ by hydrogen according to the reaction:

$$XeF_6(gas) + 3H_2(gas) \rightarrow Xe(gas) + 6HF(gas),$$

in an isothermal calorimeter at 120–130°C was used to find preliminary values of the heat of formation of $XeF_6$ and the energy of the Xe–F bond, -79 kcal $mole^{-1}$ and 31 kcal respectively[72]. Experimental results on the vapour pressure of solid $XeF_6$ were used to derive the vapour pressure equation:

$$\log P_{mm} = 8.155 - 1900/T,$$

from whence the heat of sublimation of $XeF_6$ is found to be 9.15 kcal $mole^{-1}$.[54]

The crystal structure and configuration of the $XeF_6$ molecule have not yet been established. The X-ray and electron diffraction studies are hindered by the relatively high vapour pressure of $XeF_6$ and its reactivity with ordinary capillary materials. Possibly X-ray diffraction studies at low temperatures have a better prospect. Preliminary electron diffraction data[110] are incompatible with the symmetry of the structure of the gaseous molecule.

No light has been cast on the problem of the structure of $XeF_6$ by the investigation of its vibrational spectra[9,10,47,111], which could not be sufficiently fully studied owing to experimental difficulties. In the infrared spectra of $XeF_6$ vapour there are bands at 520, 565, 612, 1100, and 1230 $cm^{-1}$, and in the Raman spectrum of solid $XeF_6$ lines at 582, 635, and 655 $cm^{-1}$. A solution of $XeF_6$ in anhydrous HF showed Raman lines at 620 $cm^{-1}$. The bands of the infrared spectrum have an unusual shape and are anomalously broad. The lines of the Raman spectrum lie in the stretching vibration region.

In view of the impossibility of a reliable allocation of frequencies, the $XeF_6$ spectra do not offer sufficient basis for establishing the structure of the molecule. The principal question under discussion is whether the $XeF_6$ structure is a right octahedron with symmetry $O_h$, similar to other hexafluorides[112], or whether it exhibits lower symmetry. This problem is not devoid of theoretical interest also (see p. 420).

The nuclear magnetic resonance of fluorine in $XeF_6$ was investigated in anhydrous hydrogen fluoride[49,50], and also in the solid and liquid states[50]. In anhydrous HF the rate of exchange of $XeF_6$ with the solvent is so high that only a single broad line is observed in the spectrum. The value of the chemical shift depends considerably on the $XeF_6$ concentration in the solution. On reducing the temperature from 25°C to -13°C the width of the resonance line decreases by ~ 40%. An attempt to resolve the lines of $XeF_6$ and HF by cooling to solid carbon dioxide temperature did not succeed; attempts to find a solvent with which $XeF_6$ would not react were equally unsuccessful[50].

The shielding constant for solid $XeF_6$ is 310 parts per million (relative to $F_2$) and for the liquid, 309 parts per million. The width of the resonance lines of solid and

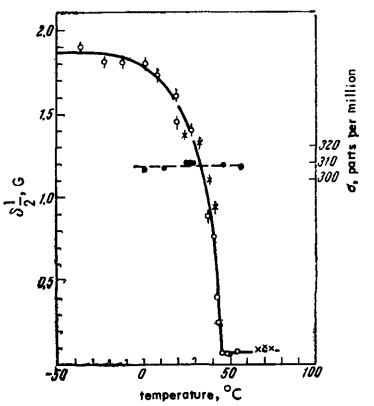



Fig. 17. Effect of temperature on the nuclear magnetic resonance spectrum of $^{19}F$ in solid xenon hexafluoride[50].

liquid $XeF_6$ are ~ 1.9 and ~ 0.14 G respectively. The temperature dependence of the shielding constant and of the line width in the nuclear magnetic resonance spectrum of $^{19}F$ in solid $XeF_6$ is shown in Fig. 17.

4. Other xenon fluorides. By heating a gaseous mixture with the molar ratio $Xe : F_2 = 1 : 16$ at 620°C and 200 atm a yellow substance was obtained whose analysis showed a higher concentration of fluorine than that corresponding to the formula $XeF_6$.[113,114]

After cooling to -78°C the excess of fluorine was evacuated through a trap at liquid nitrogen temperature. In the trap there condensed a yellow substance with a vapour pressure considerably less than that of fluorine, since it remained in the trap even after prolonged evacuation with a mercury diffusion pump.

Analysis of the material, by direct determination of fluorine and finding the xenon by difference, gave an atomic ratio of F : Xe equal to 7.9 ± 0.3 and 8.1 ± 0.1, which closely corresponds to xenon octafluoride $XeF_8$.

In order to trace in greater detail the path of the synthesis the pressure of a reaction mixture with $Xe : F_2 = 1 : 20$ was measured continuously on heating it from 20° to 620°C. The measurements showed clearly that the quantity of combined fluorine exceeds that required for the formation of $XeF_6$. The F : Xe ratio calculated from the pressure measurements was 6.5; the authors[113,114] assume that a mixture of 75% $XeF_6$ + 25% $XeF_8$ was formed.

At room temperature in a sealed glass ampoule the substance obtained is a pale yellow gas which is decolorised in ~ 5 min and attacks the glass. At liquid nitrogen temperature the pale yellow gas is condensed with formation of a yellow solid. In a dilute sodium hydroxide solution the substance is hydrolysed with formation of a yellow solution; the colour is stable for a few hours.

Mass spectrometric studies did not enable the product to be identified although it was suggested earlier[115] that the mass spectrograms obtained indicate the existence of higher fluorides of xenon up to $XeF_8$.

It is interesting to compare the above results with those obtained in investigating the kinetics of the exchange of $^{19}F$ between $XeF_6$ and gaseous fluorine[109]. As noted above (see p. 410), these results show the association of $XeF_6$ with a molecule of $F_2$. A careful study of equilibrium in the xenon–fluorine system[116] gave no indication of the formation of xenon fluorides higher than $XeF_6$.

The same investigation enabled the authors[116] to propose the existence of xenon pentafluoride $XeF_5$. A band at 520 $cm^{-1}$ in the infrared spectrum of $XeF_6$ was also initially ascribed to $XeF_5$; however, this band was observed in the spectrum of pure $XeF_6$.

As noted above, when $XeF_4$ single crystals are irradiated with $^{60}Co$ $\gamma$-rays at -195°C, there is a blue coloration. The electron paramagnetic resonance spectrum of the irradiated crystal has a hyperfine structure, indicating that the xenon atom is bonded with only one fluorine atom, and consequently that the radical XeF is formed[96,97].

In the mass-spectrometric study of $XeF_2$ and $XeF_4$[117,118] a series of fragments ($XeF^+$, $Xe_2F^+$, $Xe_2F_2^+$, $Xe_2F_3^+$, $Xe_2F_5^+$, $Xe_2F_7^+$) were observed, evidently formed in the spectrometer as a result of ionic-molecular association.

Experiments on the reaction of xenon with strong oxidants[119] are also of interest; they lead mainly to the formation of $XeF_2$, but give no indication of the production of any other fluorides.

5. Complex fluorides of xenon. As is well-known[1], the first chemical compound of xenon which was prepared was the complex $XePtF_6$.[2] Subsequently similar compounds were obtained with ruthenium[3] and rhodium[120,121].

A more detailed study of the reactions of xenon with $PtF_6$,[120] made in glass, quartz, and nickel vessels, showed that the products obtained have the composition $Xe(PtF_6)_x$, where $x$ is between 1 and 2. The infrared spectra of these compounds have bands at 652 and 550 $cm^{-1}$, and the spectra for different composition cannot be distinguished.

The complexes of xenon with $PtF_6$ are yellow in thin layers and dark red in bulk. On heating to 115°C the solid becomes vitreous but does not melt below 165°C, at which temperature it decomposes, with formation of $XeF_4$ and a brick-red diamagnetic powder with a composition close to $XePt_2F_{10}$.[120] The X-ray diagrams of a product of composition $XePtF_6$ do not give a diffraction picture and products with greater values of $x$ give complex X-ray diagrams.

The reaction of $XePtF_6$ with rubidium fluoride in iodine pentafluoride gave $RbPtF_6$ containing platinum(V) but reaction of $Xe(PtF_6)_2$ with caesium fluoride under the same conditions gave $CsPtF_6$. These reactions were thought[120] to confirm that $XePtF_6$ and $Xe(PtF_6)_2$ contain platinum(V) and that consequently the first compound should be formulated as $Xe^+[PtF_6]^-$ (this also agrees with the similarity of the infrared spectra of $XePtF_6$, $KPtF_6$ and $O_2PtF_6$) and the second as either a mixture of $XePtF_6$ and $PtF_5$, formed by the reaction:

$$Xe + 2PtF_6 \rightarrow XeF_2 + PtF_5,$$

or as a complex containing platinum(V) and xenon(II).

As for the compound $XePt_2F_{10}$ formed in the pyrolysis of $Xe(PtF_6)_{1.8}$, its reaction with CsF in iodine pentafluoride gives $Cs_2PtF_6$, with platinum(IV). The X-ray diagram of $XePt_2F_{10}$ is complex but does not contain lines which can be ascribed to xenon tetrafluoride, therefore this substance cannot be considered a mixture of $XePtF_6$ and $XeF_4$.

The complex of xenon with $RhF_6$ is characterised by a much closer approach to the 1 : 1 stoichiometric ratio than for that with $PtF_6$.

The formation of products close in composition to $Xe(PtF_6)_2$ in the explosion produced on passing a current through a platinum wire in an atmosphere of fluorine and xenon has been established[122,123].

When $XeF_4$ is dissolved in liquid antimony(V) fluoride, a gas is evolved and a greenish solution is formed, from which a precipitate of a yellow diamagnetic complex $XeF_2 . 2SbF_5$, m.p. 63°C, separates; it sublimes in a vacuum at 60°C. The same compound is formed in the reaction between $XeF_2$ and $SbF_5$. A straw-yellow complex, $XeF_2 . 2TaF_5$, m.p. 81°C is obtained by the action of $TaF_5$ on $XeF_4$; the X-ray powder diagrams of the two complexes indicate their structural similarity. The diamagnetism of $XeF_2 . 2SbF_5$ indicates the formation of a covalent compound of xenon(II) of the type $F_5SbFXeFSbF_5$.[64] $XeF_4$ does not react with $BF_3$ even on heating to 200°C,[64,65] however, from other results[58], $XeF_4$ and $BF_3$ form a violet addition product, stable at a temperature below -100°C.

The action of a glow discharge (6500–7000 V) on a mixture of gaseous xenon and fluorine (molar ratio 2 : 1) in a

glass vessel at -78°C and a pressure below 10 mmHg leads to the formation on the walls of the vessel of a white crystalline substance, stable at -78°C, but decomposing on warming to room temperature, with formation of Xe and $SiF_4$.[124] Analysis of the substance showed the composition $Xe_{2.3}SiF_{5.8}$. Similar experiments with a mixture of xenon with fluorine and $SiF_4$ in the molar ratio 2 : 1 : 1 gave a product with the atomic ratio Xe : Si = 2.2 : 1. It was concluded from these results that a complex $Xe_2SiF_6$ is formed, whose structure can be expressed by the formula $(Xe^+)_2SiF_6^{2-}$.

The analogous reaction of xenon with platinum pentafluoride and fluorine gives a solid which is white to yellow, unstable at room temperature and containing — according to the mass spectrometric and infrared spectroscopic analyses of the decomposition products — xenon and platinum pentafluoride [124].

By heating 0.153 moles $SbF_5$, 0.0435 moles Xe, and 0.0410 moles $F_2$ in a nickel bomb at 250°C for 12 h, a pale yellow solid was obtained which reacts vigorously with water, xenon being liberated. This compound, which is given the composition $XeSbF_6$ [124] does not sublime below 100°C, unlike the other complex with $SbF_5$.

Selig [102] established the formation of addition products of $XeF_6$ and $BF_3$ and of $XeF_6$ and $AsF_5$. At room temperature, $BF_3$ and $XeF_6$ give the compound $XeF_6.BF_3$, which is a white solid, melting at 90°C to a pale yellow viscous liquid. At 20°C the vapour pressure of this addition compound is less than 1 mmHg, but it can be sublimed at this temperature and pressure. The infrared spectrum of solid $XeF_6.BF_3$ at -195°C is complex, but has a broad band with centre close to 1025 $cm^{-1}$, characteristic for the $BF_4^-$ ion. The infrared spectrum of the vapour of the addition compound has bands characteristic of $BF_3$ and $XeF_6$; this signifies partial dissociation in the vapour phase.

The reaction of $XeF_6$ and $AsF_5$ at room temperature also gives a 1 : 1 addition compound — a white solid which does not sublime in a vacuum at room temperature. The Raman spectra of solid $XeF_6.BF_3$ and $XeF_6.AsF_5$ have maxima at 612 and 620 $cm^{-1}$ respectively; it is interesting to note that a solution of $XeF_6$ in anhydrous hydrogen fluoride also gives a maximum in the Raman spectrum at 620 $cm^{-1}$.[39]

The reactivity of the addition products of $XeF_6$ is comparable with that of $XeF_6$ itself. These substances are extremely hygroscopic and although they can be stored in nickel vessels, they react with Pyrex glass. By analogy with the complex $XeF_2.2SbF_5$ (see p. 411), a covalent structure has been proposed for $XeF_6.BF_3$ and $XeF_6.AsF_5$, although an ionic structure of the type $(XeF_5)^+(AsF_6)^-$ cannot be ruled out.

## B. Oxide Fluorides

1. Xenon oxide tetrafluoride. The first indications of the possible existence of xenon oxide tetrafluoride $XeOF_4$ were obtained in the mass-spectrometric investigation of $XeF_4$.[115,117] Then the formation of $XeOF_4$ was established in the reaction of $XeF_6$ with quartz [9,101] and as a result of the slow hydrolysis of $XeF_6$.[101,108]

For the preparation of $XeOF_4$ by the first method [101], $XeF_6$ was condensed in a quartz vessel, this was sealed and then heated to ~50°C. The liquid $XeF_6$ reacted with the $SiO_2$ thus:

$$2\,XeF_6+SiO_2 \rightarrow 2\,XeOF_4+SiF_4.$$

The vessel was cooled to -78°C and the $SiF_4$ evacuated, leaving a colourless liquid in the vessel. In prolonged reaction, a white crystalline precipitate was formed in addition to the liquid; the precipitate was subsequently identified as $XeO_3$.[107] Evidently the reaction proceeds stepwise:

$$2\,XeOF_4+SiO_2 \rightarrow 2XeO_2F_2+SiF_4,$$

$$2XeO_2F_2+SiO_2 \rightarrow 2XeO_3+SiF_4.$$

Smith [108] obtained $XeOF_4$ in the circulating system which he employed for the synthesis of $XeF_2$ (without the heater zone) by the action of air saturated with water vapour, on $XeF_6$ at room temperature. After removing unreacted $XeF_6$ and hydrogen fluoride the yield of $XeOF_4$ was ~80%. In a somewhat different method [101] a known weight of $XeF_6$ was hydrolysed with the accurately calculated quantity of water in accordance with the equation:

$$XeF_6+H_2O \rightarrow XeOF_4+2HF$$

Xenon hexafluoride was condensed in a small nickel vessel at liquid nitrogen temperature, and water in a glass vessel. The two vessels were evacuated to a pressure of $10^{-4}$ mmHg, the water was transferred into a nickel vessel and the latter warmed to room temperature; during this the $XeF_6$ and $H_2O$ were completely converted into the vapour phase and under these conditions there was hydrolysis. After purifying the $XeOF_4$, it was analysed, using the method of reduction by hydrogen:

$$XeOF_4+3H_2 \rightarrow Xe+H_2O+4HF.$$

An analysis was also made by mass spectroscopy.

Xenon oxide tetrafluoride is a colourless liquid stable at room temperature and can be kept in a nickel vessel for several days. It freezes at -41°C.[108] It is reported [101] that its melting point, measured in a sealed quartz capillary, is -28°C. The vapour pressure of $XeOF_4$ is ~8 mmHg at 0°C and ~29 mmHg at 23°C.[101]

The infrared spectrum of $XeOF_4$ vapour and the Raman spectrum of liquid $XeOF_4$ were studied by Smith [47,108] and by Claassen and coworkers [125]. The spectra are shown in Figs. 18 and 19, and the allocation of the frequencies according to Claassen and coworkers [125] in Table 2 (Smith's results [47,108] are only slightly different).

These results support a $XeOF_4$ structure with symmetry $C_{4v}$. The vibrational spectra of $XeOF_4$ and $BrF_5$ [126]

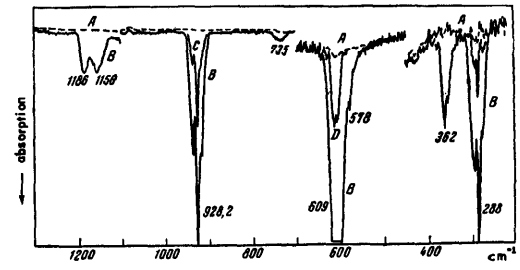



Fig. 18. Infrared spectrum of gaseous $XeOF_4$.[125] Optical path 10 cm: *A*) background; *B*) pressure of 30 mmHg; *C*) pressure of 2 mmHg; *D*) pressure of 1 mmHg.

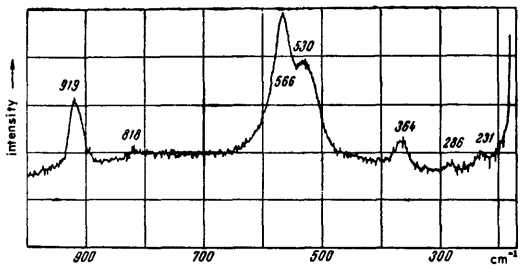
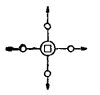
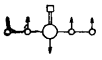
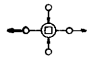
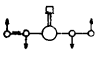
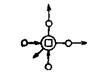
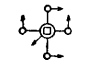



Fig. 19. Raman spectrum of liquid $XeOF_4$.[125]

TABLE 2. Assignment of the frequencies in the vibrational spectra of $XeOF_4$.[125]

| | | | | |
|---|---|---|---|---|
|  | $a_1$ | $\nu_1$ | RS, p<br>IR | 919 $cm^{-1}$ (s.)<br>928 $cm^{-1}$ (s.) |
|  | $a_1$ | $\nu_2$ | RS, p<br>IR | 566 $cm^{-1}$ (v.s.)<br>578 $cm^{-1}$ (v.s.)? |
|  | $a_1$ | $\nu_3$ | RS<br>IR | 286 $cm^{-1}$ (v.s.)<br>288 $cm^{-1}$ (s.) |
|  | $b_1$ | $\nu_4$ | RS | 231 $cm^{-1}$ (w.) |
|  | $b_2$ | $\nu_5$ | RS | 530 $cm^{-1}$ (s.) |
|  | $b_2$ | $\nu_6$ | RS | not observed |
|  | $e$ | $\nu_7$ | RS<br>IR | not observed<br>609 $cm^{-1}$ (v.s.) |
|  | $e$ | $\nu_8$ | RS<br>IR | 364 $cm^{-1}$ (w.)<br>362 $cm^{-1}$ (s.) |
|  | $c$ | $\nu_9$ | RS<br>IR | 161 $cm^{-1}$ (v.w.)<br>not observed |
| | | $\nu_3+\nu_7$ | IR | 1186 $cm^{-1}$ (w.) |
| | | $2\nu_3$ | IR | 1156 $cm^{-1}$ (w.) |
| | | $2\nu_9$ and/or $\nu_7+\nu_9$ and/or $\nu_5+\nu_6$ | IR | 735 $cm^{-1}$ (w.) |
| | | $\nu_3+\nu_5$ | RS | 818 $cm^{-1}$ (w.) |

Note. The following abbreviations are used in the table: IR = infrared spectrum of gaseous $XeOF_4$; RS = Raman spectrum of liquid $XeOF_4$; p. = polarised; v.s. = very strong; s. = strong; w. = weak; v.w. = very weak intensity of band.

are very similar, and on this basis it was concluded[47,108] that the structures of these compounds are similar; consequently $XeOF_4$ has been given[47,108] the structure of a square pyramid with an atom of oxygen at the apex and the xenon atom is close to the plane of the four fluorine atoms.

The force constants for $XeOF_4$ were calculated[47,108] for idealised valency angles of 90°, and the values found (mdyn $Å^{-1}$) were: Xe–F stretching vibration, 3.20; Xe–O stretching vibration, 7.10; stretching interaction for Xe–F bonds at right angles, 0.12; stretching interaction for Xe–F bonds at 180°, 0.15. The high value of the constant for the stretching vibration of the Xe–O bond indicates that it possesses appreciable double-bond character.

The nuclear magnetic resonance spectra of $^{19}F$ and $^{129}Xe$ in $XeOF_4$ were investigated for liquid $XeOF_4$ [50] and for solutions of $XeOF_4$ in anhydrous hydrogen fluoride[49,127]. The triplet structure of the spectrum of liquid $XeOF_4$, consisting of a central line and a symmetrical doublet, agrees with the structure proposed on the basis of the spectral results. The doublet corresponds to the $^{129}Xe-^{19}F$ interaction; the coupling constant of which is 1086 Hz. The shielding constant is 326 parts per million (relative to $F_2$).[50] The double resonance spectra of $^{19}F$ and $^{129}Xe$ in a solution in anhydrous hydrogen fluoride has been recorded; as for liquid $XeOF_4$, the $^{19}F$ spectrum confirms the views about the equivalency of the four fluorine atoms. The chemical shift of $^{19}F$ is 292 parts per million and that of $^{129}Xe$ is 5511 parts per million (relative to HF). The constant of the $^{129}Xe-^{19}F$ interaction is 1163 Hz.[49,127]

2. Other oxide fluorides. Mass spectrometric investigations[117,118] showed the possibility of the existence of other oxide fluorides of xenon in addition to $XeOF_4$. The oxide fluoride $XeO_2F_2$ was obtained by slow, controlled hydrolysis of $XeF_6$ with subsequent careful separation of the reaction products[118]. The compound was identified mass-spectrometrically[118]. The authors[118] suggested that the hydrolysis of $XeF_6$ proceeds thus:

$$XeF_6+H_2O \rightarrow XeOF_4+2HF,$$
$$XeOF_4+H_2O \rightarrow XeO_2F_2+2HF,$$
$$XeO_2F_2+H_2O \rightarrow XeO_3+2HF.$$

The action of fluorine on xenon at 250–400°C in a flow system, using oxygen or air as carrier gas gave $XeF_2$ plus a little of a more volatile fraction with m.p. 90°C, b.p. ~115°C; in preliminary experiments this fraction was identified as $XeOF_2$.[64]

The oxide fluoride $XeOF_2$ was also prepared by passing an electric discharge through a 1 : 1 mixture of xenon and $OF_2$ at 195°K.[54] Fig. 7 (p. 406) shows the apparatus in which the experiments were made, the pressure in the reaction vessel was 3–62 mmHg and the discharge current was varied between 12 and 32 mA, and the potential between 1200 and 3600 V. The colourless crystals, whose analysis led to the formula $XeOF_2$, were stable at room temperature.

Heating a 1 : 1 mixture of xenon and $OF_2$ at 300–400°C led to the formation of colourless transparent crystals stable at room temperature and which readily sublime and grow to more than 2 mm. Analysis of the crystals gave the empirical formula $Xe_{1.2}O_{1.1}F_{3.0}$, close to the formula $XeOF_3$.[54] It is not clear whether this substance is an individual compound.

C. Oxygen compounds

1. Xenon trioxide. Xenon trioxide $XeO_3$, as noted above, is formed as a result of the neutral or acid hydrolysis of $XeF_4$,[62,128] in the prolonged action of $XeF_6$ on quartz[107] and in the slow hydrolysis of $XeF_6$ by water vapour[107].

The hydrolysis of $XeF_4$ in alkaline, neutral, and acid media was studied by Williamson and Koch[128], who showed that in the last two stages hydrated $XeO_3$ (the degree of

hydration was not found) is formed in the solution and on evaporating the solution at room temperature over barium oxide, colourless crystals are deposited. Analysis of these crystals, carried out by determining the atomic ratio O : Xe in their decomposition products, led to the formula $XeO_3$. The hydrolysis evidently proceeds according to the equation [104]:

$$3XeF_4+6H_2O\rightarrow XeO_3+2Xe+1{,}5O_2+12HF.$$

The mechanism of this reaction can be represented thus [63,104]:

$$2XeF_4+6H_2O \rightarrow 2XeO+XeO_4+12HF,$$
$$2XeO \rightarrow 2Xe+O_2,$$
$$XeO_4 \rightarrow XeO_3+0.5O_2.$$

No one has yet succeeded in establishing the existence of XeO, although a band spectrum observed in the electric discharge was ascribed to this molecule [129]. As regards $XeO_4$, this compound has been obtained and identified [130,131] (see next section).

As a result of the slow hydrolysis of $XeF_6$ at room temperature in the vapour phase, carried out analogously to that described above for $XeOF_4$ (see p. 412), colourless acicular crystals of $XeO_3$ were formed directly [107]. The hydrolysis follows the equation:

$$XeF_6+3H_2O \rightarrow XeO_3+6HF.$$

Xenon trioxide is a colourless involatile crystalline substance. Crystals of $XeO_3$ are strongly hygroscopic and so explosive that there is a great hazard in working with them. $XeO_3$ explodes on rubbing, compression, even on slight heating, and also in contact with cellulose-containing materials; explosions also occur near aqueous solutions. Crystals of $XeO_3$ are considerably less stable under conditions of even very slight humidity than in a dry atmosphere. Because of the risk of explosion ($XeO_3$ is comparable with trinitrotoluene as regards the force of explosion), working with quantities of $XeO_3$ exceeding 50 mg is not recommended [107]. A few hundred milligrammes of $XeO_3$ are sufficient to blow a hole in a Teflon plate 1 cm thick, or to rupture a desiccator [128]. It was noted [128] that preparations of $XeO_3$ obtained by hydrolysis of $XeF_4$ are more stable as regards detonation if the hydrolysis is performed with distilled water in the presence of traces of sulphuric acid (for example, 10 ml $H_2O$ + 4 $\mu$l 1 M $H_2SO_4$ per 1 g $XeF_4$).

The chemical properties of solid $XeO_3$ have been little studied [107]. At a humidity greater than 25% crystals of $XeO_3$ start to deliquesce, bubbles appear in the liquid formed, and the $XeO_3$ is decomposed. When the deliquescing crystals of $XeO_3$ are in contact with copper, the liquid becomes pink and after drying a little dark residue is left. With nickel, a green residue remains. On adding $XeO_3$ to dilute ammonia and drying the solution a precipitate soluble in water is formed, whose infrared spectrum shows the presence of the $NH_4^+$ ion and of another ion absorbing at 790 $cm^{-1}$. This observation could be reproduced only once since usually $XeO_3$ exploded even in direct proximity to the solution.

Aqueous solutions of $XeO_3$ were investigated by Willamson and Koch [128,132] and also by Appelman and Malm [104,106]. The solubility of $XeO_3$ in water exceeds 2 M. [104] Measurements of Raman spectra of such solutions provide a basis for assuming that the dissolved substance is present in solution mainly as the molecule $XeO_3$, [104] but the degree and character of hydration were not established. The chemistry of aqueous solutions of xenon(VI) and xenon(VIII) compounds are considered in detail in the section dealing with xenic acids and their salts (see p. 415).

To determine the heat of formation of $XeO_3$ we measured the heat of explosion of $XeO_3$ calorimetrically [133]. The standard heat of formation of $XeO_3$ was found to be 96 ± 2 kcal $mole^{-1}$. The energy of the Xe–O bond in $XeO_3$ can be evaluated only approximately [143]; it is evidently considerably less than the energy of the Xe–F bond.

The crystal structure of $XeO_3$ was investigated by X-ray diffraction on single crystals [134,135]. Xenon trioxide is orthorhombic with parameters $a$ = 6.163 ± 0.008, $b$ = 8.115 ± ± 0.010, $c$ = 5.234 ± 0.008 Å; space group $P2_12_12_1$; the density calculated for four formulae units in the unit cell is 4.55 g $cm^{-3}$. The $XeO_3$ molecule has the trigonal pyramid configuration; the distances and valency angles are shown in Fig. 20. The least O–O distance between different $XeO_3$ molecules is 2.91 Å, the remaining distances exceed 3.02 Å. Each xenon atom has, as well as the nearest atoms of oxygen, three neighbouring oxygen atoms of adjacent molecules at distances of 2.80, 2.89, and 2.90 Å. It was noted that the crystal structure of $XeO_3$ closely resembles that of $HIO_3$.

The explosibility of $XeO_3$ did not permit the Raman spectrum of this molecule to be investigated. Only the infrared spectrum of a thin film of $XeO_3$ in polyethylene could be recorded [47]. Absorption bands were observed in the 800 and 300 $cm^{-1}$ regions and the principal frequencies were assigned by analogy with $ClO_3^-$, $BrO_3^-$, and $IO_3^-$ ions: $\nu_1(a)$ 770 $cm^{-1}$, $\nu_2(a)$ 311 $cm^{-1}$, $\nu_3(e)$ 820 $cm^{-1}$, and $\nu_4(e)$ 298 $cm^{-1}$. The force constant of the principal stretching vibration (5.66 mdyn $Å^{-1}$) shows the considerable degree of double-bond character of the xenon–oxygen bond in $XeO_3$.

2. Xenon tetroxide. The existence of xenon tetroxide $XeO_4$ was first established by the mass-spectrometric analysis of the gas liberated during the reaction of sodium perxenate with concentrated sulphuric acid [130]. Then $XeO_4$ was obtained in quantities up to 100 mg by the reaction of sulphuric acid with sodium or barium perxenate in a glass U-tube [131]. As a result of the reaction a pale yellow substance condensed in a glass trap cooled by liquid nitrogen, and after its purification by sublimation its analysis indicated the formula $XeO_4$. It was analysed by determining the Xe : $O_2$ ratio in the decomposition products; these were identified by mass spectrometry.

Better yields of $XeO_4$ (34%) were obtained when the reaction was slow; the most satisfactory results were given by

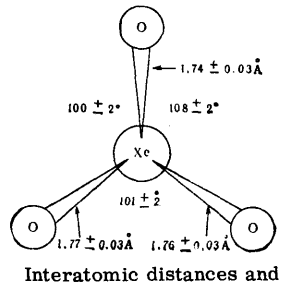



Fig. 20. Interatomic distances and valence angles of the $XeO_3$ molecule according to the X-ray diffraction data [134].

slow addition of the salt (preferably barium perxenate) to the acid cooled to -5°C.

The vapour pressure of $XeO_4$ is 3 mmHg at -35°, 10 mmHg at -16°, and 25 mmHg at 0°C. The specimen could be heated to 0°C only in rare instances; usually the substance decomposed (sometimes with explosion) before reaching this temperature, xenon and oxygen being formed.

Gaseous $XeO_4$ is relatively stable at room temperature also. This enabled its infrared spectrum to be studied (Fig. 21). The two intense bands were found to belong to $XeO_4$ and the weaker bands (marked X in Fig. 21) are obviously due to impurities. The frequencies corresponding to the maxima of the *P*-, *Q*-, and *R*-branches are: 298, 305.7, 314, and 870, 877, 885 $cm^{-1}$. In the infrared spectrum of $XeO_4$ only two frequencies are active: 877 ($\nu_3$) and 305.7 ($\nu_4$); the frequencies $\nu_1$ and $\nu_2$ are inactive. This circumstance and also the triplet structure of both bands, equally also the close similarity of the spectra of $XeO_4$ and $IO_4^-$ provide a basis for assuming that the $XeO_4$ molecule has a tetrahedral structure and symmetry $T_d$, which had been predicted[136] even before the discovery of this compound. From the *Q*–*R* spacing, 16 $cm^{-1}$, the approximate length of the Xe–O bond in $XeO_4$ was found to be 1.6 Å.

3. Xenic acids, xenates, and perxenates. On the basis of the results of studies of the hydrolysis of $XeF_4$ and $XeF_6$ in acid, neutral, and alkaline media, conclusions have been drawn concerning the existence in solution under known conditions of unstable xenic acids: $H_6XeO_6$ with sexivalent xenon, and $H_4XeO_6$ with octovalent xenon. The salts of these acids were separated and named respectively xenates ($Xe^{VI}$) and perxenates ($Xe^{VIII}$).

Closely connected with the work on the isolation and study of salts of xenic acids is the investigation of the chemistry of aqueous solutions of $Xe^{VI}$ and $Xe^{VIII}$ compounds. Study of the chemical properties of solutions of $XeO_3$ showed[128] that even dilute solutions exhibit strong oxidising properties. Table 3 gives some qualitative results.

Koch and Williamson[132] investigated the kinetics of the reaction of aqueous $XeO_3$ with bromide and iodide ions. The reaction follows the equation:

$$XeO_3 \cdot aq + 6H^+ + 9X^- \rightarrow Xe + 3H_2O + 3X_3^- \ (X = Br, I).$$

From the experimental results curves were constructed of the dependence of the optical density on time, the order of the reaction was determined, and the activation energy was found.

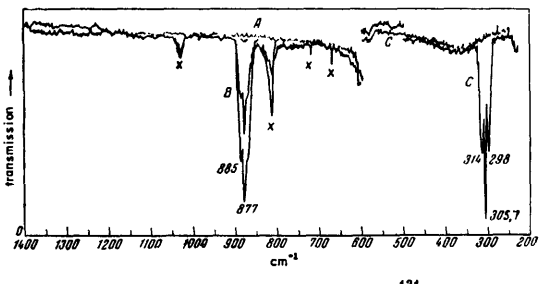



Fig. 21. Infrared spectrum of gaseous $XeO_4$:[131] *A*) background; *B*) optical path 10 cm, pressure unknown; *C*) optical path 10 cm, pressure 8 mmHg.

TABLE 3. Chemical reactions of $XeO_3$.aq.[128]

| Reagent | pH | Product | |
|---|---|---|---|
| $NH_3$ | 6 M $NH_4OH$ | presumably $N_2$ | very vigorous |
| Excess of $I^-$ | 7 or less | $I_3^-$ | rapid |
| 3% $H_2O_2$ | neutral | $O_2$ | very vigorous |
| Excess of $Br^-$ | 1 or less | $Br_2$ | slow |
| $Fe^{2+}$ | neutral | $Fe^{3+}$ | rapid |
| Hg | 1 M $H_2SO_4$ | $Hg_2SO_4$ | rapid |

Appelman and Malm[104], and also Appelman[106] made detailed studies of the chemical properties of solutions of compounds of xenon(VI) and xenon(VIII) using chemical analysis, cryoscopy, conductometry, pH measurement, and spectrophotometry in the ultraviolet region. During this investigation they isolated and characterised several salts of xenic acids.

Solutions of $Xe^{VI}$ are strong oxidants, and there is simultaneous reduction of xenon to the elemental form. Iodide is oxidised by a $Xe^{VI}$ solution to iodine very rapidly in acid solution, but rather slowly at pH > 7, and bromide is rapidly converted into bromine in 1 M HBr, but considerably more slowly at lower $H^+$ and $Br^-$ concentrations. The $Cl^-$ ion is oxidised to $Cl_2$ slowly in 2 M HCl, more rapidly in 3 M HCl, and very rapidly in 6 M HCl. Acid solutions of $Mn^{2+}$ are oxidised to $MnO_2$ in a few hours and after 1–2 d $MnO_4^-$ is formed. In 2 M $HClO_4$, iodine is very slowly converted into iodate. The rate of this reaction is considerably greater in 6 M $HClO_4$; at this concentration of the acid $XeO_3$.aq very slowly oxidises bromine to bromate.

The ultraviolet absorption spectra of $Xe^{VI}$ solutions, according to Appelman and Malm's results[104], differ considerably from those given by Williamson and Koch[128]; the reason for the difference is not clear. On the basis of the pH dependence of the ultraviolet spectra and also the pH titration of $XeO_3$ solutions by alkali, it was concluded[104] that there is the equilibrium:

$$HXeO_4^- \rightleftarrows XeO_3 + OH^-.$$

with an equilibrium constant of $(6.7 \pm 0.5) \times 10^{-4}$ at 25°C. Possibly, however, ions of the type $H_5XeO_6^-$ are formed and also unchanged $XeO_3$ molecules with attached $OH^-$ ions, for example, $XeO_3.OH^-$.[104] $XeO_3$ does not exhibit noticeable basic properties[104].

In the hydrolysis of $XeF_6$ by the action of 2.5 M sodium hydroxide, a solution of $Xe^{VI}$ is formed instantaneously, which then undergoes slow disproportionation accompanied by deposition of a perxenate precipitate; the overall equation is:

$$2XeF_6 + 4Na^+ + 16OH^- \rightarrow Na_4XeO_6 + Xe + O_2 + 12F^- + 8H_2O.$$

The rate of this reaction is different in different experiments (the half-decomposition period varies from 2 to 20 h) and is greater than the disproportionation rate for pure $XeO_3$ in alkaline solution; it has been suggested[104] that the reaction is catalysed by impurities. However, the results of experiments on the disproportionation of solutions with $XeO_3$ concentrations < 0.0003 M in 1–4 M KOH previously treated with ozone to destroy reducing impurities were also non-reproducible.

In the dissolution of $Na_4XeO_6$ in water a strongly alkaline solution is produced (0.0036 M solution has, for example, pH 11.61 at 24°C):

$$Na_4XeO_6+H_2O \rightarrow HXeO_6^{3-}+OH^-+4Na^+.$$

An aqueous solution of $Xe^{VIII}$ slowly liberates oxygen and is converted into $Xe^{VI}$ solution; the rate of this process increases as the pH is reduced and at pH 7 the decomposition is almost instantaneous. The strong and rapid oxidising action of $Xe^{VIII}$ solutions is accompanied by the reduction of $Xe^{VIII}$ to $Xe^{VI}$. $Xe^{VIII}$ solutions oxidise iodide to iodine very rapidly even in 1 M solution of a base; bromide is almost instantaneously oxidised to bromine at pH 9 and less, and chloride is converted into chlorine in dilute acid. The rapid oxidation of $Co^{II}$ into $Co^{III}$ and iodate into periodate takes place both in acid and in alkaline solution.

The results of studying the dependence of ultraviolet spectra of $Xe^{VIII}$ solutions on pH and also the results of pH titrations are explained essentially by the equilibria [104,106]:

$$HXeO_6^{3-}+H^+ \rightleftarrows H_2XeO_6^{2-},$$

$$H_2XeO_6^{2-}+H^+ \rightleftarrows H_3XeO_6^-,$$

$$H_3XeO_6^- \rightarrow HXeO_4^-+0.5O_2+H_2O,$$

$$HXeO_4^-+H^+ \rightarrow XeO_3+H_2O.$$

The equilibrium constant of the reaction:

$$HXeO_6^{3-}+H_2O \rightarrow H_2XeO_6^{2-}+OH^-,$$

is $(2.4 \pm 0.5) \times 10^{-4}$.

The results obtained in investigating solutions of $Xe^{VI}$ and $Xe^{VIII}$ permitted an evaluation of the redox potentials [104]; the results can be expressed by the following schemes:

Acids

$$Xe—1.8—XeO_3—3.0—H_4XeO_6,$$

Bases

$$Xe—0.9—HXeO_4^-—0.9—HXeO_6^-.$$

The oxidising properties of xenic acid $H_6XeO_6$ with respect to a series of vicinal diols and organic alcohols was investigated qualitatively by Jaselskis and Vas [137]. The difference in oxidising action of xenic and iodic acids, which exhibit similar redox potentials, is attributed by these authors to the absence from aqueous solutions of stable oxidation states of xenon below $Xe^{VI}$. This conclusion agrees with the results of an investigation of the polarographic reduction of xenic acid [138]. The reduction of $XeO_3.xH_2O$ at a dropping mercury electrode proceeds in a single stage to xenon; the half-wave potential changes from -0.10 to -0.360 V relative to the $Hg_2SO_4$–Hg electrode, in the pH interval from 4.60 to 8.00. Sodium perxenate in alkaline solution is also reduced in a single stage; the half-wave potential changes from -0.21 to -0.31 V relative to the same electrode, in the pH interval from 10.1 to 11.3. [139]

The nuclear magnetic resonance spectrum of $^{17}O$ in $H_6XeO_6$ solution obtained by hydrolysis of $XeF_6$ showed a single line of width 420 Hz with chemical shift 278 ± 2 parts per million relative to water. The chemical shift which is close to that found earlier for perchloric acid and also for bromate, chlorate, and perchlorate ions, indicates that the xenon–oxygen bond in $H_6XeO_6$ possesses some double-bond nature [140].

As already noted repeatedly, $Xe^{VIII}$ deposits precipitates of stable perxenates — salts of the acid $H_4XeO_6$ — which in many instances have been isolated and investigated.

Malm and coworkers [63] made the first experiments on the preparation of sodium perxenate. To a weighed portion of $XeF_6$, sublimed into a Pyrex glass vessel at a temperature close to that of liquid nitrogen, a large excess of 2 M NaOH was slowly added, the mixture was heated to room temperature, diluted with an equal quantity of water, and kept for about a day. The initial yellow colour of the solution gradually paled and a white precipitate came down; its analysis led to the formula intermediate between $Na_4XeO_6.2H_2O$ and $Na_6XeO_7.H_2O$. The yield of the product reached 80%. The substance obtained was completely stable, could be kept without change at room temperature and was decomposed with liberation of xenon and oxygen above 300°C, by which temperature the salt had not melted. The solubility of the dry salt in water at 25°C was 7 g litre$^{-1}$.

Further investigations [104] showed that this product contained sodium fluoride as an impurity. Purer preparations were obtained by ozonisation of a solution of $XeO_3$ in 1 M NaOH. The precipitation of sodium perxenate takes place in this almost quantitatively. The solubility of sodium perxenate in water is 0.025 M at room temperature, which permits the excess of base to be readily washed from the precipitate. The substance obtained is a white crystalline powder of composition $Na_4XeO_6$, containing from 0.6 to 6 molecules of crystallisation water per 1 g-atom Xe, depending on the conditions of drying, and a little sodium carbonate. Sodium perxenate is completely stable at room temperature, is dehydrated to the anhydrous salt at ~100°C and decomposes vigorously at 360°C. [141]

The reaction of 0.2 M $Ba(OH)_2$ with 0.007 M $XeO_3$ followed by drying in a stream of nitrogen, grinding and repeat drying in a vacuum over magnesium perchlorate gave a white stable product of empirical composition $Ba_2XeO_6.1.5H_2O.0.05BaCO_3$. As with the sodium salt, barium perxenate is stable at room temperature and is decomposed at ~300°C. [141] It is almost insoluble in water; at room temperature a saturated solution has a total concentration of only $2.3 \times 10^{-5}$ M. [104]

Potassium perxenate could not be obtained by hydrolysis of $XeF_6$ with KOH solution, by disproportionation of a solution of $Xe^{VI}$ in KOH and by ozonisation of a solution of $Xe^{VI}$ in KOH; a salt $K_4XeO_6.2XeO_3$ was isolated [104]. However, $K_4XeO_6.9H_2O$ was obtained by the action of a little solid potassium permanganate on concentrated KOH solution, holding the solution at 70°C for 3 d (until the colour disappeared) and adding xenic acid (obtained by dissolving $XeO_3$) at 0°C in a vacuum [142].

Yellow uranyl and lead perxenates and black silver perxenate were obtained by the action of solid sodium perxenate on aqueous solutions of uranyl, lead, and silver nitrates [143]. Furthermore, there are reports of the preparation of calcium, lithium, and caesium perxenates [144].

The attempts of Appelman and Malm [104] to obtain barium xenate were unsuccessful, but Kirshenbaum and Grosse [105] prepared it and also reported the results of preliminary experiments on the preparation of the sodium and potassium salts of xenic acids.

The initial preparations of $H_6XeO_6$ were obtained by slow hydrolysis of $XeF_4$ or xenon oxide fluorides with water at 0°C. Removal of HF was effected by shaking the solution with a small excess of $CaCO_3$ or $Ca(OH)_2$ at 0°C; $CaF_2$ was formed, which was readily removed from the reaction zone. Solutions of $H_6XeO_6$ can be kept at temperatures from -20° to -30°C without decomposition for a few weeks [105].

On adding a solution of 3 moles $Ba(OH)_2$ to 1 mole $H_6XeO_6$ at 0°C a white amorphous precipitate was obtained, whose analysis gave the formula $Ba_3XeO_6$.[105] The yield of $Ba_3XeO_6$ reached almost 100% when the solution of the base was added rapidly enough to prevent decomposition of the acid.

Barium xenate is very poorly soluble in water: 0.25 g × × litre$^{-1}$ at 20°C. At room temperature $Ba_3XeO_6$ is completely stable; slow decomposition starts at 125° and ends at 250°C. The decomposition of $Ba_3XeO_6$ follows the reaction:

$$Ba_3XeO_6 \rightarrow 3BaO+Xe+1.5O_2.$$

Sodium and potassium xenates have also been obtained[105], but have not been characterised completely. These salts are also stable at room temperature for at least a few months.

With the aim of determining the structure and configuration of the perxenate ion X-ray diffraction investigations have been made of $Na_4XeO_6.6H_2O$,[145] $Na_4XeO_6.8H_2O$,[146] and $K_4XeO_6.9H_2O$.[142] The results showed that these perxenates are orthorhombic and that the $XeO_6^{4-}$ ion has the configuration of a regular octahedron: the mean Xe–O distance is 1.84 Å in $Na_4XeO_6.6H_2O$, 1.875 Å in $Na_4XeO_6.8H_2O$, and 1.86 Å in $K_4XeO_6.9H_2O$.

The investigation of the infrared spectra of the sodium, uranyl, lead, and silver perxenates[143] showed that all these compounds have an intense absorption band in the region 650–680 cm$^{-1}$, the position of which is independent of the nature of the cation. This band is related to the principal vibration of the $XeO_6$ octahedral group, which agrees with the results of the structural investigation.

The structural and spectrographic information and equally the results of studies of the Mössbauer effect in sodium perxenate[51,52], have been used to judge the structure of the perxenate ion.

The first investigation of the physiological action of compounds of Group 0 elements was made using sodium perxenate as example, by Finkel and coworkers[147]. They studied the metabolic and toxicological effects of injections of an aqueous solution of sodium perxenate on mice. It was established that sodium perxenate is of average toxicity in intravenous injection; the lethal does lie between 15 and 30 mg kg$^{-1}$. The perxenate introduced is rapidly reduced to elemental xenon, the bulk of which is lost from the body a few minutes after injection.

## III. COMPOUNDS OF RADON AND KRYPTON

### A. Radon Fluorides

The production of a stable radon fluoride of unknown composition[6] was described in the previous review[1]. In addition, there are indications of a volatile radon hexafluoride[148], which has still not been confirmed.

### B. Krypton Compounds

1. Krypton tetrafluoride. After the preparation of compounds of xenon and radon, the natural interest concerned the problem of the possibility of preparing compounds of other Group 0 elements, above all those of krypton.

Experiments on the reaction of krypton with platinum and ruthenium hexafluoride on heating to 50°C were unsuccessful[121]. Attempts to prepare krypton fluorides by the reaction of gaseous krypton and fluorine at 400–500°C in a nickel vessel and also by irradiating mixtures of these gases with ultraviolet light at -60°C were also unfruitful[32].

Krypton tetrafluoride $KrF_4$ was obtained[54,149] by the action of an electric discharge on a mixture of krypton and fluorine. The experimental method was the same as was used in preparing xenon tetrafluoride (see p. 406). A 1 : 2 mixture (by volume) of krypton and fluorine was passed at 7–12 mmHg and at a rate of 125 cm$^3$ h$^{-1}$ (s.t.p.) into a reactor cooled to -188°C by a mixture of liquid oxygen and nitrogen; the current was 24–37 mA and the potential 700–2200 V. The krypton tetrafluoride, whose yield reached 100% in isolated experiments, was deposited on the glass walls of the reactor as a white solid. After removing the unreacted krypton and fluorine by evacuation at -78°C, (as well as silicon tetrafluoride and oxygen), the $KrF_4$ was sublimed at -30° to -40°C into a glass vessel in which was dry powdered KF (as a getter for HF).

Krypton tetrafluoride forms colourless transparent crystals (Fig. 22). Thermally, $KrF_4$ is less stable than $XeF_4$, but at -78°C it can be kept without decomposition for several weeks. At 20° in a poly(chlorotrifluoroethylene) vessel with copper taps, $KrF_4$ slowly decomposes; it decomposes rapidly by the reaction:

$$KrF_4 \rightarrow Kr+2F_2,$$

at 60°C; the method of analysing $KrF_4$ is based on this reaction.

The temperature dependence of the vapour pressure of $KrF_4$ is expressed by the equation:

$$\log P_{mm} = 8.531 - 1930/T.$$

Fig. 23 shows the corresponding curve together with the vapour pressure curve of $XeF_6$ (see p. 410) for comparison. The heat of sublimation of $KrF_4$ is found to be 8840 ± ± 300 cal mole$^{-1}$ by extrapolating to the sublimation temperature (at 760 mmHg), ~70°C.

The physical properties of $KrF_4$ have been insufficiently studied†. The ions $KrF^+$ and $Kr^+$ have been observed in

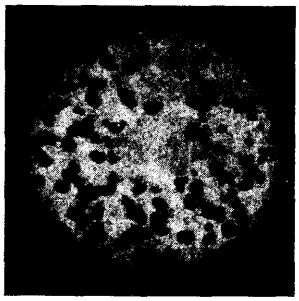


Fig. 22. Crystals of xenon tetrafluoride.

† The reader may like to consult F. Schreiner, J. G. Malm, and J. C. Hindman, J. Amer. Chem. Soc., 87, 25 (1965) who show that the preparation believed to yield $KrF_4$ actually gives $KrF_2$ (Ed. of Translation).

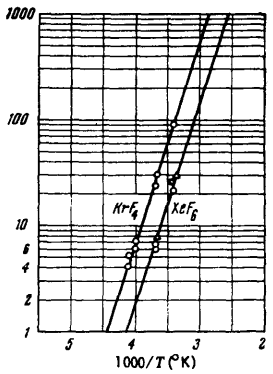



Fig. 23. Vapour pressure curves for $KrF_4$ [149] and $XeF_6$. [54]

the mass spectrum of $KrF_4$. [150] In the nuclear magnetic resonance spectrum of $^{19}F$ in krypton tetrafluoride dissolved in anhydrous HF a single $^{19}F$ resonance line was observed [151], with a chemical shift of 254 parts per million with respect to HF. On the basis of the nuclear resonance spectrum it was concluded [151] that the fluorine atoms in $KrF_4$ are equivalent and that exchange with the solvent does not take place to any significant extent. The absence of hyperfine structure obviously indicates a planar or pyramidal structure for the $KrF_4$ molecule.

2. Krypton difluoride. The first successful experiments on the preparation of krypton difluoride $KrF_2$ [152,153] employed the matrix-isolation technique [154]. A gaseous mixture with a molar ratio $F_2 : Kr : Ar = 1 : 70 : 220$ was slowly precipitated on a caesium fluoride window at 20°K. After recording the infrared spectrum of a specimen it was irradiated with the focussed light of a medium-pressure mercury lamp and the infrared spectrum again recorded. After it had been irradiated for 3 h a specimen gave an infrared spectrum with two absorption bands: at 580 $cm^{-1}$ (half-width ~3.5 $cm^{-1}$, optical density 0.19) and at 236 $cm^{-1}$ (optical density 0.04).

For the confirmation of the assignment of these bands to krypton difluoride, photolysis experiments were made under the same conditions with mixtures of fluorine and argon and of fluorine, xenon, and argon. In the first case there was no absorption, and in the second the spectrum showed the formation of $XeF_2$ and a trace of $XeF_4$.

The bands at 580 and 236 $cm^{-1}$ in the infrared spectrum of $KrF_2$ belong respectively to the asymmetric stretching vibration $\nu_3$ and the bending vibration $\nu_4$ of a linear symmetric molecule. The values calculated for the force constants ($k_\gamma - k_{\gamma\gamma} = 2.59$; $k_\gamma + k_{\gamma\gamma} = 2.91$; $k_\delta/l^2 = 0.21$ mdyn $Å^{-1}$) were close to those found for $XeF_2$ (see p. 405)‡.

The preparation of $KrF_2$ in amounts of ~100 mg was brought about by subjecting a mixture of krypton and fluorine to a beam of electrons with energy 150 MeV at -150°C in a nickel vessel [155]. When the reaction had finished, the unreacted krypton and fluorine were evacuated and the $KrF_2$ was frozen out in a quartz trap at solid carbon dioxide or liquid air temperatures. At these temperatures $KrF_2$ is a fine white powder. $KrF_2$ sublimes under gentle heating without noticeable decomposition; in one experiment a colourless crystal measuring ~1 mm was obtained. This crystal did not change appreciably in 5 min at room temperature, and then suddenly decomposed with a small explosion.

The composition of the specimens was determined by decomposing them with mercury and analysing the decomposition products. Difficulties were encountered in measuring the vapour pressure of $KrF_2$, owing to the instability of this compound, but it was established that at -40°C the vapour pressure is 1.5–2 mmHg. [155]

An X-ray investigation of $KrF_2$ showed [156] that krypton difluoride is tetragonal with parameters $a = 6.533$ and $c = 5.831$ Å; the density for four formula units in the unit cell is 3.24 g $cm^{-3}$. It was noted that $KrF_2$ is not isostructural with $XeF_2$. Because crystals of $KrF_2$ decompose appreciably on irradiation, the X-ray diagrams were insufficiently sharp.

3. The complex of krypton difluoride with antimony pentafluoride. During the interaction of $KrF_2$ with antimony pentafluoride at -20°C in glass or poly(chlorotrifluoroethylene) vessels a white crystalline substance, whose analysis led to the formula $KrF_2.2SbF_5$, was formed [157]. It dissolves in an excess of $SbF_5$ at room temperature with the formation of a transparent, pale yellow solution, from which, after evacuation of the solvent at 25°C, the original complex separated again.

The complex $KrF_2.2SbF_5$ is considerably more stable and much less volatile than the initial krypton difluoride. It melts at ~50°C, but in the liquid state it decomposes rapidly with the formation of $SbF_5$, krypton, and fluorine. As might have been expected, the complex is exceptionally reactive and ignites organic materials with explosion. Solutions of the complex in antimony pentafluoride decompose slowly at 25°C; they are also quite reactive and attack poly(chlorotrifluoroethylene). The hydrolysis of the complex in a base or weak acid leads to the formation of not only krypton and oxygen, but also considerable amounts of $OF_2$. In the infrared spectrum of $KrF_2.2SbF_5$ a strong characteristic band was observed at 813 $cm^{-1}$ and another strong, but badly resolved band in the region 600–700 $cm^{-1}$.

Preliminary experiments also showed that $KrF_2$ combines with $AsF_5$ at -78°C, but the addition product formed is very unstable and could not be isolated [157].

4. Kryptic acid and its barium salt. The hydrolysis of $KrF_4$ at room temperature proceeds almost quantitatively by the equation:

$$KrF_4 + 2H_2O \rightarrow Kr + O_2 + 4HF.$$

However, when hydrolysis takes place slowly at temperatures from -30° to -40°C the aqueous solution formed contains a very slight trace of a compound which exhibits oxidising properties and releases iodine from an acidified iodide solution. As careful experiments on the hydrolysis of $KrF_4$ with ice at -30°C showed [158], the solution after hydrolysis then contains 2–3 mole % kryptic acid, which oxidises potassium iodide solution by the reaction:

$$KrO_3 \cdot xH_2O + 6KI + 6HCl \rightarrow Kr + 3I_2 + 6KCl + (3+x)\,H_2O\,.$$

‡ The reader should refer to H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, J. Chem. Phys., 42, 1229 (1965) (Ed. of Translation).

The question of the valency of krypton in this acid, and consequently the formula of the acid, is still open.

To prepare the barium salt of kryptic acid[158], $KrF_4$ was hydrolysed at 0–5°C by $Ba(OH)_2$ solution. During the reaction gas was evolved and a white precipitate separated; it contained $BaF_2$ and barium kryptate. The precipitate was filtered off, washed with small portions of ice water, and dried at 0°C. The dry preparation is stable at room temperature, starts to decompose at ~50°C, and decomposes completely at 200°C. The results of chemical and mass spectrometric analyses of the gases evolved during the preparation, and also of the decomposition products of barium kryptate, agree with the formula $BaKrO_4$; the decomposition of the kryptate proceeds thus:

$$BaKrO_4 \rightarrow BaO + Kr + 1.5O_2,$$

and the reaction with acidified KI solution:

$$BaKrO_4 + 8HCl + 6KI \rightarrow BaCl_2 + 6KCl + 3I_2 + Kr + 4H_2O.$$

The yield of $BaKrO_4$ is ~7% , and the product contains $BaF_2$ ~ 95, $BaKrO_4$ ~ 5%. On the basis of studies of the salts of xenic and kryptic acids it is suggested that xenon and krypton may exist in nature not only in the atmosphere but also in hydrothermal minerals and in the oceans[105,158].

## IV. THE CHEMICAL BONDS IN COMPOUNDS OF THE ELEMENTS OF GROUP 0

The first attempts at a theoretical description of the chemical bonds in the compounds of the elements of Group 0, made even before the discovery of these compounds, were those of Pauling[159] and Pimentel[160], who used the methods of valency bonds[159] and molecular orbitals[160]. Today, when as a result of the preparation of several compounds of xenon and krypton and the investigation of their chemical and physical properties it is already possible to make some generalisation about the experimental material, a considerable number of theoretical studies have appeared which are devoted to explaining the structure and the nature of the chemical bonds in these compounds[11,12,38,47,136,161–184].

Allen's model[11], based on calculation of the correlation effects in pairs of electrons with antiparallel spins was developed to some extent in the later work of Allen himself[161] and also in Michels' work[162]. However, this model was subjected to serious criticism by Coulson[163], in his review of the theories of the chemical bond in compounds of the elements of Group 0. Nevertheless it must be stated that with the aid of the correlation model the linear configuration of the $XeF_2$ molecule and the square planar structure of the $XeF_4$ molecule were first explained successfully.

The valency bond method with allowance for the hybridisation with participation of the *d* electrons of xenon was used by Allen and Horrocks[12] to explain the linear and square structures of $XeF_4$ and $XeF_4$ and to predict the configuration of certain (then as yet unobtained) xenon oxide fluorides. In a somewhat altered form this approach, together with the use of molecular orbitals (MO) was employed by Bersohn[164]. Gillespie[136] has made the most detailed application of the valence bond method to the compounds of xenon and the other elements of Group 0; with a view to explaining and predicting the configuration of the known and still unknown molecules and also to evaluate the bond lengths in these molecules by comparison with the interhalogen compounds. According to Gillespie, eight of the electrons of the outer shell of the Xe atom and one electron of each F atom (or two electrons of an O atom) form pairs, which either form bonds between the atoms or exist as lone pairs. The form of the molecule is eventually determined by the degree and character of the electrostatic repulsion of unshared pairs, of ordinary Xe–F bonds and of Xe=O double bonds. For example, the distribution of ten electrons (two ordinary bonds and three unshared pairs) in $XeF_2$, 12 electrons (four ordinary bonds and two unshared pairs) in $XeF_4$, and 14 electrons (four ordinary bonds, one double bond, and one unshared pair) in $XeOF_4$ leads to the known structures of these molecules. This theory predicts a distorted octahedral structure for $XeF_6$. The interatomic distances Xe–F in $XeF_2$ and $XeF_4$, and Xe–O in $XeO_3$, which were estimated, agree well with the experimental values.

Smith[38,47] came to analogous conclusions, reducing to a minimum the part played by ionic bonds in xenon fluorides, on the basis of an analysis of the vibrational spectra. Smith showed that for $XeF_2$ and $XeF_4$ the ratio of the constant valency interaction to a constant principal valence vibration is considerably less than for the $ICl_2^-$ ion, the bonds in which are considered to be essentially ionic[185,186] and on this basis it was concluded that covalent bonds with participation of *d* orbitals play an extremely important part in xenon fluorides. According to this view, the structure of $XeF_6$ cannot be octahedral. Smith rejects the consideration of the bond in $XeF_2$ from the standpoint of the resonance of the $F–Xe^+F^-$ and $F^-Xe^+–F$ structures, but Coulson[163], in considering this possibility in greater detail, concluded that it leads to a charge distribution in agreement with the experimental results.

The MO method, in which delocalised MO are constructed from the atomic 5*p* orbital of xenon and the 2*p* orbital of fluorine (without any participation of the *d* orbital), was employed by Rundle[165], using his earlier proposal to treat the structure of the interhalogen compounds with the aid of three-centre four-electron bonds. For example, for the $XeF_2$ molecule three MO's are obtained: bonding, non-bonding, and antibonding, in which the first two are occupied by pairs of electrons. In $XeF_4$ there are two choices of such orbitals, and in $XeF_6$ three. In accordance with this the $XeF_6$ molecule is given an octahedral structure. By comparing $XeF_4$ with $IF_5$, Rundle evaluated some thermodynamic and structural characteristics of $XeF_4$ and these values agreed satisfactorily with the experimental data.

Rundle's ideas have been developed further in subsequent studies[166–174] in some of which[167–173] there is a more quantitative approach. The calculations of Lohr and Lipscomb[170,171] by the MO–LCAO method, in which the MO were constructed with allowance for the 2*s* and 2*p* orbitals of fluorine and the 4*d*, 5*s*, and 5*p* orbitals of xenon, showed that the 4*d* electrons of xenon played a very small part in the bonds. According to Lohr and Lipscomb[171] $KrF_4$ should be stable but $ArF_4$ unstable; in both cases the calculations were carried out assuming a square planar structure for the molecule.

Hinze and Pitzer[167] also concluded that there was hardly any participation of the *d* orbitals in the bond formation. Jortner and coworkers[168,169] using the same model in principle, as Rundle, employed the semiempirical MO–LCAO method and concluded that the bond in xenon fluorides is described with the aid of delocalised MO's, which are formed by a combination of the 5*p* σ orbitals of xenon and the 2*p* σ orbitals of fluorine. The results of the authors'

theoretical calculations[168,169] were compared with spectroscopic data for $XeF_2$ and $XeF_4$ in the far ultraviolet region[43,86] and also the results of determinations of the heats of sublimation of these fluorides[42]. The experimental results agree with the proposed model; comparison of theoretical and experimental data led the authors[168,169] to conclude that the essential contribution to the stability of crystalline $XeF_2$ and $XeF_4$ is provided by electrostatic interaction, due to the transfer of charge from the xenon atom to the fluorine atoms. The ionic character of the halides of the Group 0 elements also follows from Waters and Gray's calculations[172], made within the framework of the simple MO method.

Some authors have used the MO method with allowance for the *d* orbitals of xenon. Boudreaux[70] studied the 5*p*, 5*d*, 6*s*, and 6*p* orbitals of xenon and the 2*p* orbitals of fluorine and showed that the bond in $XeF_4$ has mainly a *p* character, but partially *d* and *s* character. The results of his calculations of the magnetic susceptibility of $XeF_4$ [69] agree with the experimental results and confirm his proposed model. The scheme of MO's proposed by Israéli[175,176] was also constructed with allowance for the *d* orbitals of xenon. In this case qualitative consideration led to agreement with the experimental results on the geometrical configuration of the xenon fluorides.

Nesbet[177] proposed that the bond in the xenon fluorides is similar to the mechanism of indirect exchange in the antiferromagnetic oxides of type MnO. Nesbet's ideas and conclusions were criticised by Allen[161].

The work of Bilham and Linnett[178] was devoted to the approximate calculation of $XeF_2$ by the valency bond method with allowance for four electrons and the island $F^+Xe^{2+}F^+$. The wave functions of the molecule are constructed from the $2p_z$ orbitals of two fluorine atoms and one $5p_z$ orbital of a xenon atom in the assumed linear structure of the molecule. Calculations for $XeF_6$, made by the MO–LCAO method, led to an octahedral structure for this molecule[179]. The electronic structure of the kryptates and xenates was considered by Urch[180]. The ion $XeO_6^{4-}$, in all probability, exhibits octahedral symmetry. In this problem there is no difference between the MO method and the valency bond method.

The above ideas were subject to some criticism both from theoretical positions and also by comparison with experimental results[110,163,181,183]. Coulson[163] discussed the merits and deficiencies of the various models and came to a conclusion that the correlation model[11] and the models using the hybridisation of the *d* electrons[12] (in this case the excitation energy of the electrons to the *d* level is too high) were inapplicable; Coulson considered that both the MO theory and the valence bond theory with allowance for resonance in the structure (see p. 419) are suitable for describing the chemical bonds in the compounds of the Group 0 elements. Both these theories give a charge distribution of $F^{-\frac{1}{2}}-Xe^{+1}-F^{-\frac{1}{2}}$ for $XeF_2$; in $XeF_4$ and $XeF_6$ the charge migration is somewhat less. Such a charge distribution agrees with the results derived from investigations of the nuclear magnetic resonance[49,50,91–94,187,188].

Hemmerlich[181] and Noyes[183] consider the most acceptable treatment from the position of the theory of three-centre four-electron MO.[165,169] This theory well explains the spatial configuration of the compounds of xenon and gives interatomic distances in these compounds which agree satisfactorily with the experimental values. The considerable degree of ionicity of the bonds in the xenon fluorides, resulting from this consideration, also agrees with the experimental results. Thus the essential role of ionic bonds in xenon fluorides is demonstrated by the chemical shifts measured by the nuclear magnetic resonance method (Fig. 24); for $XeF_4$ this is also apparent from the asymmetry of the resonance lines (see p. 409). The results of a study of the Mössbauer effect in the xenon fluorides[51,52], the heats of sublimation of $XeF_2$ and $XeF_4$,[42,168,169], and certain other physical and chemical properties of xenon compounds have also been interpreted from this viewpoint.

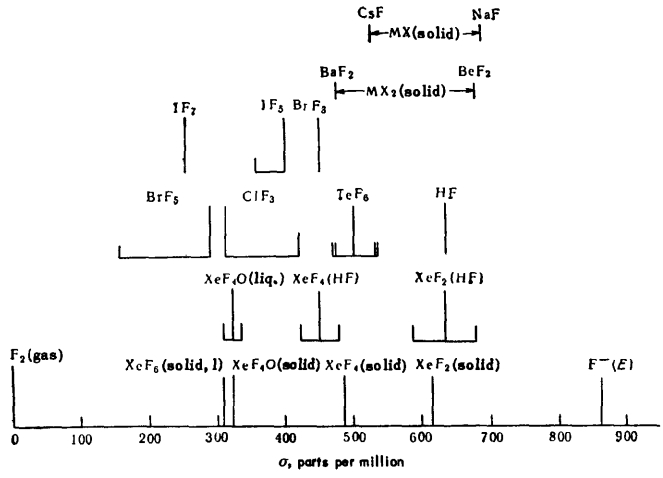



Fig. 24. Shielding constants σ for some fluorides[50].

Consideration by the valence bond method also gave a series of results agreeing with the experimental data[136]. In general, in most instances the MO theory and the valence bond theory lead to the same configuration and this agrees with experiment. The essential difference between the methods considered occurs, however, in the case of $XeF_6$. For this molecule the valence bond theory leads to a non-octahedral structure, whereas consideration by the MO method leads to regular octahedral structure. Unfortunately the experimental results have still not made possible the solution of this question.

Each of the theories has, naturally, its merits and its drawbacks; Coulson[163], for example, notes that the valence bond theory is simpler and more graphic, but states that the MO method is more suitable for considering different electron transitions. The most important conclusion, which can be drawn on the basis of the theoretical discussions, is the absence of a necessity to postulate any new type of bond for the compounds of the Group 0 elements and the possiblity of a semiquantitative explanation of the experimental facts with the assistance of existing theoretical concepts.

## V. SOME THERMODYNAMIC CONSIDERATIONS

One of the most astonishing experimental facts revealed in the process of investigating xenon compounds, was the thermodynamic stability of many of these compounds. The standard heat of formation of gaseous $XeF_2$ is $-37 \pm 10$ kcal × × $mole^{-1}$.[44] Evaluation of this value for solid $XeF_2$ from spectrographic data led to the value -20 kcal $mole^{-1}$,[116] but Hoppe[189], as the result of a comparison of the bond

energies of the xenon fluorides and the halogen fluorides, concluded that it should be greater. For $XeF_4$, $\Delta H^\circ$ = = -60 kcal mole$^{-1}$,[71] and $\Delta G^\circ$ = -29.4 kcal mole$^{-1}$. For $XeF_5$, $\Delta H^\circ$ = -79 kcal mole$^{-1}$.[72] The xenon oxides, however, are thermodynamically unstable.

Some investigators attempted, by more or less complex calculations, to evaluate the thermodynamic stability of Group 0 element compounds not yet obtained and so to decide the question of the possibility of obtaining these or other compounds. Waters and Gray[172] calculated by the simple MO method, the energy of formation from the elements and the energy of dissociation of the halides of the Group 0 elements. They found the following values (in kcal mole$^{-1}$) for the dissociation energy: $XeF_4$ 123.1, $KrF_4$ 23.5, $ArF_4$ -30.7, $NeF_4$ -507.1, $XeCl_4$ -50.9, $KrCl_4$ -137.4, $XeF_2$ 11.1, $KrF_2$ -5.3, $XeCl_2$ -42.9. Bartlett[18,190] started principally from a comparison of the mean bond energies of the compounds of the Group 0 elements with other halides and oxides. He evaluated the mean bond energy (in kcal): $KrF_2 \sim 30$, $KrF_4 \sim 19$, $KrF_6 \sim 18$, and $XeCl_4 \sim 10$, and concluded that the first three were exothermic and the fourth endothermic.

Although the results of all the calculations demonstrate sufficiently convincingly the thermodynamic instability of the compounds of even argon, Pimentel and Spratley[173,191] consider that the existence of a helium fluoride $HeF_2$ is possible; these authors calculated the infrared spectrum of the hypothetical molecule $HeF_2$ and considered possible methods for obtaining $HeF_2$ based on the $\beta$ discharge of tritium nuclei, the irradiation of lithium fluoride with slow neutrons and the bombardment of metal fluorides with $\alpha$ particles[191]. Noyes[183] briefly considered various possibilities for the formation of still unknown compounds of Group 0 elements and proposed for these elements the group name "aerogens".

## VI. POSSIBLE APPLICATIONS

The interest in the compounds of the elements of Group 0 is obviously not due solely to their theoretical importance. It must be supposed that such broad development in the investigations also had some practical aims. Unfortunately this question has only been touched upon and then in very few works.

The question of the potential applications of the compounds of Group 0 elements has received the most detailed consideration in the article by Pomeroy[192]. He noted the important part played by the xenon isotopes $^{133}Xe$ and especially $^{135}Xe$, which exhibits a very large cross-section for the capture of thermal neutrons ($> 10^6$ barns) in industrial nuclear energy and briefly considered the possiblity of using them as solid, and not gaseous compounds. On the other hand, there is the interesting possibility of recovering radioactive xenon and krypton, formed in the operation of a nuclear reactor, as fluorides or other compounds of low volatility.

The xenon fluorides can serve as "stores" of xenon and fluorine; it is possible that they will show promise as oxidants for rocket fuels[14,192]. The regeneration of xenon from its fluorides, particularly the complex ones, can prove to be a good method of obtaining pure xenon. The possibility of an analogous use of krypton fluorides is not excluded, although their instability can create obvious difficulties.

The xenon oxides very easily detonate and are highly explosive; it is possible that their ability to explode without leaving traces of solid substances can be utilised[14,192].

Compounds of xenon, especially the xenates and perxenates, may find many uses as oxidants in carrying out various processes[192].

Finally, it can be suggested that if the radon fluorides prove to be involatile they will find wider application in radiation therapy than gaseous radon, the use of which sometimes is hazardous[14].

Undoubtedly in the very near future a profitable use will be found for the compounds of the elements of Group 0. Even now for inorganic chemistry the immense value of the discovery and study of these substances is completely indisputable, and it is possible, finally, to visualise a further wide development of manifold investigations in this interesting and promising field.

## NOTE ADDED IN PROOF

Whilst this article was in the press several papers dealing with the compounds of the elements of Group 0 were published; they include both reviews[193-201] and original work[202-210].


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# THE CHEMISTRY OF DECABORANE AND ITS DERIVATIVES

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## 1. INTRODUCTION

Decaborane† is one of the most interesting representatives of the boron hydrides, information about which before the nineteen-fifties was restricted to Stock's unique monograph [1].

After World War II, in connection with the vigorous development of reaction propulsion for aviation there arose the need to devise a more effective aviation fuel than hydrocarbons. The high calorific value of boron hydrides served as an impetus to the intensive investigation of the chemistry of decaborane, the most stable boron hydride. In view of the complex constitution of decaborane the establishment of its structure was the first task.

This problem was solved by the combined forces of a large group of physicists and chemists.

This review surveys all the main literature on the chemistry of decaborane and also that on the structure and reactivity of its stable derivatives — anions of the $B_{10}H_{10}^{2-}$ type, barenes (carboranes), etc.

† Strictly, decaborane(14), according to the nomenclature recommended in the Preliminary Report of the Advisory Committee presented at the 125th Meeting of the American Chemical Society, 25th March, 1954. This nomenclature has been used where possible in this translation (Ed. of Translation).

## 2. STRUCTURE AND REACTIVITY OF DECABORANE

For long the structure of the boron hydrides was one of the principal unsolved problems of structural chemistry. Although decaborane is a solid crystalline compound and was studied by X-ray diffraction, the few attempts in this direction ended in failure, because of the complexity of the structure [2]. Finally Kasper and coworkers [3] succeeded in solving the problem in 1950, despite a series of difficulties, for example, the absence of heavy atoms from the decaborane molecule.

It was shown that the ordered structure of the unit cell of the crystal consists of eight units ($a$ = 14.45, $b$ = 20.88, $c$ = 5.68 Å). The $x$, $y$ coordinates of the boron atoms were determined from the initial map obtained for the electron density in the $\rho_z(x', y')$ plane. The $z$ coordinate was then found by trial and error. The use of the electron density method enabled the coordinates of the boron atoms to be defined accurately and the coordinates of the hydrogen atoms to be found. It transpired that ten of these were attached to the ten boron atoms by an ordinary bond and the other four act as bridges between six boron atoms.

Subsequently [4] a more accurate structure was deduced by the method of least squares. It appeared (see Fig. 1) that the skeleton of the molecule consists of two pentagonal pyramids linked by a common edge of the bases.

The molecule has a centre of symmetry and two perpendicular axes of the second order. It can be shown that the boron atoms in the skeleton occupy 10 of the 12 vertices of a slightly deformed icosahedron.

The structure obtained now required explanation from the standpoint of electronic theory, since it did not fit into the framework of the elementary bond theory. The first significant step towards the solution of this problem was the application of the three-centre bond theory to the structure [5]. The starting point for the calculations was two main assumptions: (1) each boron atom gives three electrons and four $2sp^3$ hybridised orbitals, and each hydrogen atom a 1$s$ orbital and one electron; (2) in addition, six boron atoms give one $2sp^3$ orbital and half an electron to each B–H–B bond. As a result it was found that the boron skeleton contains two σ bonds (between atoms 2 and 6, 4 and 9) and six three-centre bonds. Four of these are three-centre central bonds — between the atoms $B_{(10)}-B_{(1)}-B_{(5)}$; $B_{(1)}-B_{(2)}-B_{(3)}$, $B_{(1)}-B_{(4)}-B_{(8)}$, and $B_{(8)}-B_{(9)}-B_{(7)}$ — which are characterised by the direction of three atomic orbitals of boron to the centre of the triangle and the existence of one bonding and two non-bonding orbitals. The other two are open three-centre bonds — between the atoms $B_{(10)}-B_{(4)}-B_{(8)}$ and $B_{(5)}-B_{(2)}-B_{(7)}$ — which are characterised by a special direction of the constituent orbitals of boron and by the presence of bonding, non-bonding, and antibonding orbitals. Despite the undoubted importance of these theoretical concepts, they were insufficiently precise in reflecting the electronic structure of decaborane and led to an incorrect determination of the charges of the boron atoms.

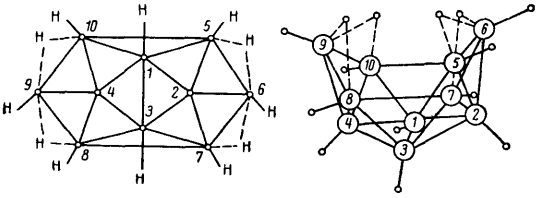



Fig. 1. Structure of the decaborane molecule.

The use of the standard calculation by the LCAO–MO single-electron method, assuming that 16 electrons and 22 atomic orbitals bond the boron skeleton was more fruitful [6]. The following distribution of the formal charge was obtained by calculation of eight wave functions for the given boron skeleton:

| $B_2$, $B_4$ | $B_5$, $B_7$ | $B_8$, $B_{10}$ | $B_1$, $B_3$ | $B_6$, $B_9$ |
|---|---|---|---|---|
| −0.254$e$ | −0.031$e$ | | +0.046$e$ | +0.268$e$ |

Starting from the distribution of the formal charge and the structure of the boron skeleton, the dipole moment was found, which agrees well with the value found experimentally [7].

The introduction of a correction with an allowance of 0.2$e$ negative charge on the bridging hydrogen atoms leads to the final distribution:

| $B_2$, $B_4$ | $B_1$, $B_3$ | $B_5$, $B_7$, $B_8$, $B_{10}$ | $B_6$, $B_9$ |
|---|---|---|---|
| −0.254$e$ | +0.046$e$ | +0.069$e$ | +0.268$e$ |

Although the calculation of the charges by the LCAO–MO method (even the latest improved values [8]) agrees with the chemical and physical properties of decaborane much better than the method of localised three-centre orbitals, the great difference in charges between the atoms 1, 3 and 2, 4:

| $B_2$, $B_4$ | $B_1$, $B_3$ | $B_5$, $B_7$, $B_8$, $B_{10}$ | $B_6$, $B_9$ |
|---|---|---|---|
| −0.329$e$ | −0.102$e$ | +0.011$e$ | +0.410$e$ |

does not agree with the chemical results and the electronic model [9], which requires further study.

One of the interesting features of decaborane is the presence of four three-centre B–H–B bonds. The nuclear magnetic resonance spectra and theoretical calculations showed [10] that bridge atoms of hydrogen in decaborane are more electropositive than the terminal ones. This is because after departure of the bridge proton the electron pair is employed in the formation of a new B–B bond, instead of the B–H–B bond, so that radical changes in the structure do not take place. As a result of this, decaborane is a strong acid [11] giving various salts with bases.

Furthermore, decaborane participates in interesting exchange reactions with nucleophilic reagents at the $B_{(6)}$ and $B_{(9)}$ atoms, which carry considerable positive charge. For these reactions (for example, with acetonitrile) the liberation of 1 mole hydrogen per 2 moles reacting base with an unshared pair of electrons is remarkable, the compound $B_{10}H_{12}L_2$ being formed with a changed electron balance. Reddy and Lipscomb [12,13], in establishing the structure of the diacetonitrile derivative of decaborane by X-ray diffraction, demonstrated a very small change in the B–B and C–C–N distances compared with the initial decaborane and acetonitrile.

Dickerson and Lipscomb [14] predicted the existence of then unknown stable boron hydrides, and subsequently the existence of stable anions based on boron hydrides was predicted [15]. One of the most interesting anions predicted was $B_{10}H_{14}^{2-}$, the existence of which was confirmed [13] by the preparation of $B_{10}H_{14}Na_2$, since of all the boron hydrides only decaborane is able to add on two electrons, giving a satisfactory valence structure [15].

The bis(acetonitrile) product $B_{10}H_{12}(CNCH_3)_2$ can be considered as a derivative of this anion having two B–H–B bonds between the atoms 7, 8 and 5, 10 and the two $BH_2$ groups at atoms 6 and 9. The suggested mechanism [13] presupposes the formation of two open three-centre bonds, $B_{(5)}-B_{(6)}-B_{(7)}$ and $B_{(10)}-B_{(9)}-B_{(8)}$ instead of four bridge bonds – with the formation of two new bridge bonds, $B_{(5)}-H-B_{(10)}$ and $B_{(7)}-H-B_{(8)}$ – as a result of which a molecule of hydrogen is detached and at the $B_{(6)}$ and $B_{(9)}$ atoms is released by the orbital occupying the unshared electron pair of the attacking base (Fig. 2).

Furthermore, it is suggested [16] that bis(acetonitrile)-decaborane exists in solution in two tautomeric forms in which the acetonitrile groups are either in the terminal positions, as described above, or occupy the place of two bridge hydrogen atoms. This suggestion was formulated on the basis of the different nuclear magnetic resonance spectra of solutions of $B_{10}H_{12}(CH_3CN)_2$ in acetonitrile and in dimethylformamide.

On the other hand, in view of the presence of negative charges on atoms 2 and 4, in principle decaborane should participate in electrophilic substitution reactions. Stock himself showed [1] that on reaction with halogens decaborane is halogenated. Comparatively recently [17] the structure of an halogeno-derivative was established for the first time, using X-ray diffraction – diiododecaborane. Having found the presence of a second-order axis in the molecule and by using the probable B–I distance (the sum of the covalent radii), the authors calculated the I–I distances for all possible pairs of positions at which the iodine atoms are situated symmetrically relative to the second-order axis (5 pairs) and compared these quantities with the value found experimentally (6.25 Å). Positions 2 and 4 satisfied these requirements, the I–I distance then being 6.21 Å. All this supports the hypothesis of the electrophilic mechanism of iodination of decaborane at the places with maximal electron density.

Due to the non-uniform charge distribution in the molecule, decaborane can also act as a donor of hydride ions. For example, it reduces acetals and ortho-esters to ethers on heating [18].

Although Kasper and coworkers provided sufficient evidence for the structure of decaborane, it has been investigated carefully by many physicochemical methods. The principal merit of these methods, one which they retain unaltered in decaborane chemistry, is the possibility of determining the characteristics of all the types of hydrogen bonds in the molecule. This permits the determination of the mobility of the B–H bonds in different types of reactions and rapid establishment of the structure of the products obtained.

Shoolery made the first interpretation of the proton and $^{11}B$ nuclear magnetic resonance spectra of decaborane, in 1955 [19]. In this and subsequent investigations [20,21] it was found that the $^{11}B$ nuclear resonance spectrum (Fig. 3*a*) consists of a high-field doublet and a low-field triplet (ratio of intensities 1 : 4), the latter being, in its turn, the result of the overlap of two doublets of the same intensity.

It was shown that the high-frequency doublet of the spectrum belongs to the vertex atoms $B_{(2)}$ and $B_{(4)}$, the central doublet of the triplet to the equivalent atoms $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$, and the low-field doublet to the atoms $B_{(1)}$, $B_{(3)}$, $B_{(6)}$, and $B_{(9)}$. The last is not completely understood, since these four boron atoms are not equivalent. Actually, the nuclear magnetic resonance spectrum of perdeuterodecaborane [21] (Fig. 3*d*) – in which, because of the weak B–D spin–spin coupling, the number of peaks should equal the number of types of boron atoms in the molecule – showed distinct splitting of the low-field peak into two. Hence the low-field triplet in the nuclear magnetic resonance spectrum of decaborane can be considered as the result of superposition of three doublets with an intensity ratio of 1 : 1 : 2.

The proton spectrum of decaborane (Fig. 3*b*) is a resolved multiplet, with the following interpretation [19]. It is suggested that it consists of two quartets displaced relative to one another, and on these is superimposed a multiplet in the high-field region, which belongs to the bridge protons. The small quartet (shifted to the right) belongs to the two protons bonded with the vertex boron atoms, and the large one to the eight remaining protons. Attempts to interpret this spectrum by saturation of the signal of the proton nuclear magnetic resonance and by excitation of $^{11}B$ at the frequency 9.6257 MHz (double resonance), that is, by cancelling the B–H spin interaction, led to the spectrum represented in Fig. 3*c*. [20] It was shown that the high-field singlet of the spectrum belongs to the bridge protons, the low-field doublet to all the terminal protons except the "vertex" ones, and the plateau between them to the "vertex" protons. The low-field doublet is the result of the overlap of two peaks of the same intensity [21], in which the high-field singlet of the doublet belongs to four equivalent protons at $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$, and the low-field component may in its turn be a split singlet – protons at $B_{(1)}$, $B_{(3)}$, $B_{(6)}$, and $B_{(9)}$.

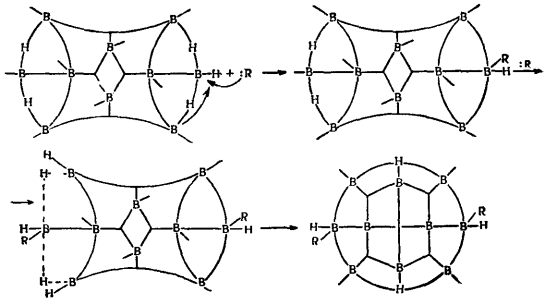


Fig. 2. Mechanism of reaction of decaborane with nucleophilic agents.

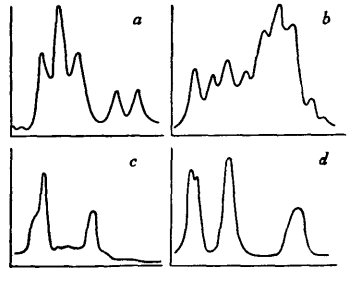



Fig. 3. Nuclear magnetic resonance spectra of decaborane and perdeuterodecaborane.

Hence in the study of the proton and $^{11}B$ nuclear magnetic resonance spectra of decaborane the hydrogen bridge atoms can easily be distinguished from the terminal ones and the "vertex" terminal hydrogens from the "non-vertex" ones. To distinguish the $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$ hydrogen atoms from $B_{(1)}$, $B_{(3)}$, $B_{(6)}$, and $B_{(9)}$ is more laborious, and the direct establishment of the position of the hydrogen in positions 6 and 9 is almost impossible, compared with 1 and 3.

The use of infrared spectroscopy to study decaborane does not give better results. It was shown [22,23] that the valency vibrations of all the B–H terminal bonds of the molecule (as in the other boron hydrides) produces an absorption band in the spectrum in the region 2350–2630 $cm^{-1}$, mainly in the form of badly resolved multiplets. The valency vibrations of the B–H–B bridge bonds produce an absorption band in the 1600–2220 $cm^{-1}$ region. However, it seems impossible to distinguish by this method the "non-vertex" from the "vertex" B–H terminal bonds, since the deformation vibrations of the latter produce a band in the 900 $cm^{-1}$ region. The deformation vibrations of the "non-vertex" B–H bonds are difficult to determine, but they are evidently in the 1075–1010 $cm^{-1}$ region.

The mass spectrum of decaborane contains several peaks from unity to one hundred and twenty-four [24]. The theoretically calculated monoisotopic spectrum showed that the maximal mass peak corresponds with the ion of decaborane with *six hydrogen atoms removed.* As this number agrees with the number of terminal hydrogen atoms at the boron atoms which participate in the formation of hydrogen bridges, the authors consider that these hydrogens are the most labile in the molecule (in the sense of ionisation by electrons).

From the near ultraviolet absorption spectrum of decaborane [25] (in the gas phase from 90° to 140°C, in solution at room temperature, and in crystals at 4–4.2°K), the mean value of the minimum energy required for the first electron transition was 3.90 ± 0.1 eV. It is difficult to determine the existence of another electronically excited state of somewhat higher energy, since it is masked by the first transition.

Thermochemical calculations [26] give the following values for the dissociation energies of the various types of bond in decaborane: B–H (σ bond) 93.1 kcal per bond; B–B (σ bond) 83.1 kcal per bond; B–H–B (three-centre bond) 107.2 kcal per bond; B–B–B (three-centre bond) 97.7 kcal per bond.

Decaborane in diamagnetic. Its specific magnetic susceptibility, determined experimentally, is $(-116 \pm 1.5) \times \times 10^{-6}$.

The difference between the measured value and that calculated on the basis of the magnetic susceptibilities of boron and hydrogen ($-108 \times 10^{-6}$) is obviously due to the presence in the molecule of the bridge atoms of hydrogen.

The dipole moment of decaborane, determined by the Debye and Guggenheim methods, is between 3.17 D (in carbon disulphide solution) and 3.62 D (in benzene solution) [7].

## 3. DEUTERIUM EXCHANGE IN DECABORANE

Information about the deuteration of decaborane is extremely contradictory. Thus in investigating the nucleophilic reaction of deuterium exchange of decaborane with $D_2O$ and DCl at room temperature in solvents — Lewis bases (dioxan and water) — Hawthorne and Miller [27,28] showed that the hydrogen bridge atoms are exchanged first. The analysis was made using infrared spectra; it was first demonstrated that in what was known synthetically to be perdeuterodecaborane the stretching vibrations of the B–D bonds lie in the 1925 $cm^{-1}$ region and those of the B–D–B bonds in the 1400 $cm^{-1}$ region (in decaborane itself, 2565 and 1800–2140 $cm^{-1}$ respectively). The second stage of the reaction was the slow exchange of deuterium bridges with terminal hydrogen atoms bound to the atoms $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$. In this process, the maximum exchange was eight protons with $D_2O$ and only about six with DCl.

Shapiro and coworkers [29], in studying the kinetics of this reaction, confirmed that the first act is the exchange of the bridge hydrogen atoms, with a subsequent slow migration of deuterium to the atoms $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$. However, there is concurrent deuteration in the $B_{(6)}$ and $B_{(9)}$ terminal positions. If specimens of $B_{10}H_{10}D_4$ are isolated from the reaction medium and dissolved in anhydrous dioxan, then there is only regrouping of D atoms in the $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$ positions.

According to the suggested mechanism, deuterium exchange in decaborane takes place with participation of the Lewis acids and bases. The authors think that the first act is the transfer of the electron pair of the Lewis base to the sixth and ninth boron atoms. In this, the bridge hydrogen atom becomes terminally bound with the neighbouring boron atom ("equatorial") and is rapidly exchanged with deuterium from $D_2O$. The deuterium subsequently entering into the molecule can be exchanged with the terminal hydrogen atoms at $B_{(5)}$, $B_{(7)}$, $B_{(8)}$, and $B_{(10)}$.

The terminal hydrogen atoms at $B_{(6)}$ and $B_{(9)}$ are exchanged intramolecularly in the complex of $D_2O$ with these boron atoms.

The proposed mechanism seems sufficiently satisfactory since it explains why in the case of DCl in dioxan less atoms of deuterium are exchanged than in the case of $D_2O$ [29] — here intramolecular exchange at the $B_{(6)}$ and $B_{(9)}$ terminal positions is impossible. However, Shapiro further maintains that the deuterium exchange with $D_2O$ in aqueous dioxan during prolonged interaction is quantitative, giving in a sense nucleophilic substitution, since the boron atoms 2, 4, 1, and 3 carry a significant negative charge. In methylene dichloride the deuteration of decaborane with $D_2O$ goes only in the bridge positions and the deuteration with DCl does not take place at all [27]. Sodium tridecahydrodecaborate($1^-$) exchanges only the bridge hydrogens with DCl. [28] In carrying out electrophilic deuteration of decaborane with DCl in carbon disulphide in the presence of aluminium chloride (at room temperature), Dupont and Hawthorne [30] showed that the reaction proceeds at the terminal hydrogen atoms bonded with the most negative atoms $B_{(2)}$, $B_{(4)}$, $B_{(1)}$, and $B_{(3)}$ and stops at this. The $B_{10}H_{10}D_4$ obtained does not exchange deuterium atoms for hydrogen on interaction with HCl, but reacts with DCl in dioxan almost to complete exchange, giving perdeuterodecaborane. This communication was published in refutation of a previous one [31], where it was maintained that in this reaction there is exchange of six hydrogen atoms in positions 2, 4, 5, 7, 8, and 10.

Apart from the methods described above, partly deuterated decaborane can be obtained by pyrolysis of partly deuterated diborane [32], there then being a statistical distribution of the deuterium in the molecule. A second

method is to heat decaborane with perdeuterodiborane at 100°. As the infrared spectra show, the exchange here is entirely in the terminal positions. Recently[33] an interesting paper reported isotopic exchange of boron atoms between [$^{10}$B]diborane and ordinary $B_{10}H_{13}Na$, in which all ten boron atoms of the decaborane skeleton participate (62.7% of the $^{10}$B is in the recovered diborane). It is suggested that the exchange takes place by formation and splitting of the intermediate anion $B_{11}H_{16}^-$, having the structure of an incomplete icosahedron.

## 4. PYROLYSIS OF DECABORANE

Stock himself noted[1] the stability of decaborane in the absence of oxygen at elevated temperature (up to 170°C), but a detailed investigation of the pyrolysis of decaborane has been made only recently.

Beachell and Haugh[34] showed that at 170–238° the main product is a polymeric hydride, containing, according to the infrared spectra, decaborane units. Volatile products other than hydrogen were not observed. These results were confirmed by Siegel and Mack[35] who isolated a polymeric product of composition $(BH)_x$ after pyrolysis at 200–250°C. They found that the pyrolysis rate rises sharply with temperature within the limits stated.

Finally, Owen[36] made a complete kinetic investigation of pyrolysis in the gas phase at 220°, 230°, and 250°C and various initial decaborane pressures (from 60 to 600 mmHg) and proposed a complete mechanism for the reaction:

$$B_{10}H_{14} + B_{10}H_{14} \rightleftarrows B_{10}H_{14}^* + B_{10}H_{14}, \quad (1)$$

$$B_{10}H_{14}^* \rightleftarrows B_{10}H_{12} + H_2, \quad (2)$$

$$B_{10}H_{14} + B_{10}H_{12} \rightleftarrows B_{20}H_{24} + H_2, \quad (3)$$

$$B_{20}H_{24}\ (\text{gas}) \rightleftarrows B_{20}H_{24}\ (\text{solid}), \quad (4)$$

$$2B_{20}H_{24} \rightleftarrows H_2 + \text{involatile solid hydrides}. \quad (5)$$

He showed that the pyrolysis is a first-order reaction with respect to decaborane and Eqn. (2) is the rate-determining stage for the reaction. This dependence is strictly obeyed for the first 60% of the conversion, but as the decaborane concentration falls the rate of reaction (3) approaches the rate of reaction (2) and the overall order becomes greater than first. An attempt was made to isolate the intermediate hydride $B_{20}H_{24}$ from the pyrolysis products at 230°C; a viscous liquid with a very low vapour pressure and an infrared spectrum similar to that of decaborane was obtained. It was shown by deuteration[34] that in the polymerisation of decaborane the terminal, not the bridge, hydrogen atoms are preferentially removed. Moreover, in carrying out the pyrolysis in the presence of ethyl bromide the main product was 2-ethyldecaborane[36]. The authors to suggested that the initial stage of the pyrolysis is the detachment of hydrogen atoms from the "vertex" positions.

The thermal interaction of diborane with decaborane was an interesting reaction. On passing diborane into molten decaborane (100°C), the liberation of hydrogen and the formation of a yellow crystalline product[37] were noted. Diborane itself under these conditions does not change. The following reaction mechanism was proposed on the basis of an analysis of the proton nuclear magnetic resonance spectrum, infrared spectra, and mass-spectra:

$$B_2H_6 + B_{10}H_{14} \rightarrow (BH)_{12} + 4H_2,$$

$$(BH)_{12} \rightarrow B_nH_{n-x} + \frac{x}{2}H_2.$$

The authors think that the $(BH)_{12}$ structure is a complete icosahedron in which the bridge hydrogen bonds are replaced by a $B_2H_2$ "cap". The polymer consists of chains of icosahedra. This is confirmed by the absence of intermediate boron hydrides between $B_{10}H_{14}$ and $B_2H_6$ and by the presence of tetraborane and hexaborane — the hydrolysis products of decaborane itself — in the hydrolysis of the polymer.

## 5. HYDROLYSIS, ALCOHOLYSIS, AND THIOLYSIS

As noted above, Stock[1] found that decaborane is slowly hydrolysed by water on heating. Later this reaction was studied in detail by Atteberry[38], who made a kinetic investigation of the hydrolysis of decaborane by water at 80° and 100°C. It was shown to be a first-order reaction:

$$B_{10}H_{14} + 30H_2O \rightarrow 10B(OH)_3 + 22H_2,$$

the rate constants being:

$$K_{100} = 4.27 \times 10^{-5}\ s^{-1} \quad \text{and} \quad K_{80} = 1.43 \times 10^{-5}\ s^{-1},$$

and the energy of activation $E_a$ = 14.5 kcal mole$^{-1}$.

On the basis that the activation energy agrees with the quantity found by Guter and Schaeffer[39] for the initial dissociation of decaborane in aqueous dioxan, the author concluded that the most probable mechanism was the ionic-dipolar hydroxylation of boron–hydrogen bonds.

A reaction of interest in this connection is the alcoholysis of decaborane by alcohols, of which there have been several kinetic studies:

$$B_{10}H_{14} + 30ROH \rightarrow 10B(OR)_3 + 22H_2.$$

Beachell and Meeker found[40] that the reaction of decaborane with primary alcohols is second order overall, first order in each of the components. The rate constants and activation energies were determined; there was an increase in the rate constant with the number of carbon atoms in the primary alcohols from 2 to 5. A more detailed study of this reaction with a larger number of alcohols[41] showed that is proceeds through the intermediate donor–aceptor complex $B_{10}H_{14}$.HOR. It appeared that the rate of alcoholysis by halogenated alcohols decreases as the halogen atom approaches along the carbon chain towards the OH group and increases as a $CH_3$ group approaches. The alcoholysis of decaborane by phenol is much slower than that by cyclopentanol. On the basis of these results and also in connection with the previously observed increase in alcoholysis rate with increase in the number of carbon atoms in the primary alcohol it was concluded that the decisive factor in alcoholysis is the inductive and not the steric effect. The stages determining the reaction rate are the breaking of the O–H bond in the $B_{10}H_{14}$.HOR complex, since there is a strong isotope effect on replacing alcohol by deuteroalcohol. A radical mechanism has been proposed for the breaking of the O–H bond, since in the case of an ionic mechanism:

$$B_{10}H_{14}HOR \rightleftarrows [B_{10}H_{14}OR]^- + H^+,$$

the addition of a base would rapidly shift the equilibrium to the right, that is, the reaction rate would be greatly increased. However, the addition of bases only slightly retards the process, which suggests that the second mechanism is impossible.

Thiols also destroy the decaborane molecule[42]. Thus on boiling in butanethiol for a few days, decaborane is converted quantitatively into tributyl thioborate. The reaction

with lower thiols necessitates heating in a autoclave, since at lower temperatures the reaction is very slow:

$$B_{10}H_{14} + 30RSH \rightarrow 10B(SR)_3 + 22H_2.$$

## 6. DECABORANE AS AN ACID

It was noted earlier that to a greater extent than the other boron hydrides decaborane is a dual reagent: in some reactions it behaves as a donor of hydride ions and in others as an acid, dissociating to $H^+$ ions. Guter and Schaeffer[39] found that the curve for the titration of a solution of decaborane in protolytic solvents (alcohol, aqueous alcohol, aqueous dioxan, 0.1 *N* NaOH) is characteristic for a strong monobasic acid. Two possible mechanisms for the formation of the acid are suggested:

$$B_{10}H_{14} + H_2O \rightarrow [B_{10}H_{14}OH]^- + H^+ \text{ (solution)},$$
$$B_{10}H_{14} \rightarrow [B_{10}H_{13}]^- + H^+ \text{ (solution)}.$$

In acetonitrile, decaborane behaves as a weak acid with $pK_a = 3.5$ and in dimethylformamide as a strong acid, the first potential jump being observed at pH 1.2 and the second at pH 6. It is thought that this difference is due to the different electron-donor properties of the solvents, which are stronger in the case of dimethylformamide[43]. However, according to Griffiths and Williams[44] the difference in the titration curves of decaborane in acetonitrile and dimethylformamide is due to the existence in the latter of dimethylamine impurity. In the pure solvents the curves are identical.

The acid properties of decaborane, that is, the presence in it of mobile protonised hydrogen atoms, forms a basis for its reaction with methylenetriphenylphosphorane and trimethylammoniomethylenide, as a result of which substituted phosphonium and ammonium salts with the anion $B_{10}H_{13}^-$ are obtained[45,46]:

$$(C_6H_5)_3P{=}CH_2 + B_{10}H_{14} \rightarrow [(C_6H_5)_3P^+CH_3]\,B_{10}H_{13}^-,$$
$$(CH_3)_3N^+{-}CH_2^- + B_{10}H_{14} \rightarrow [(CH_3)_4N^+]\,B_{10}H_{13}^-.$$

## 7. DECABORANE GRIGNARD REAGENTS AND SODIUM TRIDECAHYDRODECABORATE(1⁻)

The acidic properties of decaborane explain the ease of formation of its metal derivatives with sodium and magnesium, from which alkyldecaboranes were obtained in turn.

The magnesium derivative was first obtained by Siegel and coworkers[47] in 1958. They studied the reaction of decaborane with methylmagnesium iodide in ether and found that when an excess of decaborane was used a monomangesium derivative was produced:

$$B_{10}H_{14} + CH_3MgI \xrightarrow{\text{ether}} B_{10}H_{13}MgI + CH_4,$$

and when the methylmagnesium iodide was in excess, a dimagnesium derivative, $B_{10}H_{12}(MgI)_2$.

In hydrolysis with moist ether decaborane is regenerated. Benzyldecaborane is obtained by the reaction of decaborane Grignard reagent with benzyl chioride:

$$B_{10}H_{13}MgI + 2C_6H_5CH_2Cl \rightarrow B_{10}H_{13}CH_2C_6H_5 + C_6H_5CH_2I + MgCl_2.$$

The investigation of this compound by infrared spectroscopy and the $^{11}B$ nuclear magnetic resonance did not allow the authors to discover the precise position of the benzyl group in the decaborane molecule but positions 2 and 4 are excluded because the high-field doublet does not change in intensity compared with that for decaborane.

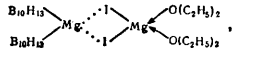
Dunstan and coworkers[48] made a special study of this reaction and found that in the reaction of decaborane with ethylmagnesium iodide a little ethyldecaborane is formed in addition to the magnesium iodide tridecahydrodecaborate(1⁻), and on subsequent addition of dimethyl sulphate to the decaborane Grignard reagent equal amounts of two isometic methyldecaboranes are formed.

In interpreting the $^{11}B$ nuclear magnetic resonance spectra the authors assigned to the products the structures of 5- and 6-methyldecaboranes. Benzyldecaborane, obtained by the method described above, was also given the structure of the 6-derivative.

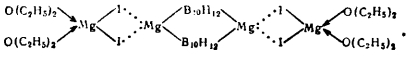
It was shown that of the ordinary alkyl halides only benzyl bromide and chloride[49] and allyl bromide[50] undergo condensation with the decaborane Grignard reagent. In the case of alkyl fluorides and trialkyloxonium salts, various alkyldecaboranes were obtained with good yields[49]:

$$B_{10}H_{13}MgX + RF \rightarrow B_{10}H_{13}R + MgFX,$$
$$B_{10}H_{13}MgX + R_3O^+X^- \quad B_{10}H_{13}R + R_2O + MgX_2.$$

Attempts were made to reveal the structure of the decaborane Grignard reagent by infrared and ultraviolet spectra. It was shown that the infrared spectrum of $B_{10}H_{13}MgI$ is very similar to the spectrum of methylmagnesium iodide; the ultraviolet spectra also showed great similarity. From these results the authors gave magnesium iodide tridecahydrodecaborate(1⁻) the following structure:



and



A convenient reagent for the preparation of alkyldecaboranes is sodium tridecahydrodecaborate(1⁻), which can be obtained by the action of such reagents as sodium, sodium hydride, sodium amide, sodium tetrahydroborate, and dry powdered sodium hydroxide in ether on decaborane[51]:

$$B_{10}H_{14} + NaH \xrightarrow{\text{ether}} B_{10}H_{13}Na + H_2.$$

By carying out this reaction with decaborane with deuterated bridges it was shown that one of the bridge hydrogen atoms is substituted:

$$B_{10}H_{10}D_4 + NaH \xrightarrow{\text{ether}} B_{10}H_{10}D_3Na + HD.$$

The action of benzyl bromide in ether on sodium tridecahydrodecaborate(1⁻) gives benzyldecaborane identical with that obtained from the decaborane Grignard reagent, as described above. The deuteration of benzyldecaborane with $D_2O$ in dioxan showed that four deuterium atoms were rapidly introduced into the molecule, and this is evidence of the rearrangement of the benzyl group from a bridge position to a terminal one. There are only two possibilities for such regrouping: in the 6- or the 5-position. The nuclear magnetic resonance spectrum showed unambigously that the benzyl group is in position 6.

Sodium tridecahydrodecaborate(1⁻) boiled in ether with dimethyl and diethyl sulphate gives the same products as magnesium iodide tridecahydrodecaborate(1⁻), that is, a mixture of the 5- and 6-methyl- or 5- and 6-ethyl-decaboranes[52]. Reaction with iodine in ether at -80°C gave a

mixture of products, consisting of decaborane, ethoxydecaborane, and ethoxyiododecaborane [51]:

$$B_{10}H_{13}Na \xrightarrow[-80^\circ]{\text{ether}} B_{10}H_{13}I + B_{10}H_{14} + B_{10}H_{13}OC_2H_5 + B_{10}H_{12}IOC_2H_5.$$

By using various ethers in this reaction, various alkoxydecaboranes can be obtained [53]. The precise position of the RO group could not be established, but the $^{11}B$ nuclear magnetic resonance spectrum excludes substitution at boron atoms 2 and 4.

Finally, sodium tridecahydrodecaborate(1$^-$) reacts with chloro(diphenyl)phosphine, forming a phosphorus(III) compound [54]:

$$B_{10}H_{13}Na + (C_6H_5)_2PCl \rightarrow B_{10}H_{13}P(C_6H_5)_2 + NaCl.$$

## 8. NUCLEOPHILIC SUBSTITUTION IN DECABORANE

It was noted earlier that hydrolysis and alcoholysis of decaborane take place through an intermediate complex, $B_{10}H_{14}.HOR$. This complex is formed because, despite the high degree of symmetry and stability, the decaborane molecule is an electron-deficient system striving to make up the deficiency from molecules having unshared pairs. This property of decaborane appears in many reactions with various nucleophilic reagents.

For example, a solution of decaborane in acetone at low temperatures gives a $^{11}B$ nuclear magnetic resonance spectrum in which the low-field doublet is degenerate, which indicates the formation of a complex at positions 6 and 9 in the decaborane molecule. On raising the temperature to room temperature or above, the spectrum becomes identical with that in benzene, that is, the complex is decomposed into the initial components [55].

Stock himself noted [1] that decaborane reacts with liquid ammonia, adding up to six molecules of the latter; on heating, the ammonia molecules are split off in stages, and later the decaborane structure is broken down and hydrogen released.

Fitch and Laubengayer [56] studied in detail the reaction of decaborane with dimethylamine at low temperature [56]:

$$B_{10}H_{14} + n(CH_3)_2NH \rightarrow [(CH_3)_2NH]_n.B_{10}H_{14}.$$

By studying the reaction kinetics, the existence of addition compounds with four and five molecules of dimethylamine per molecule of decaborane has been demonstrated. They are very unstable compounds and decompose with formation of dimethylamine and lower addition products even at low temperatures (-60° to 40°C)‡. The addition products with $n$ = 1, 2, or 3 are rather stable and were characterised by X-ray diffraction. Treatment of the addition products with water formed decaborane again. In an excess of dimethylamine at elevated temperatures decaborane undergoes aminolysis with liberation of hydrogen and destruction of the skeleton; in particular, a crystalline product with the ratio B : N = 9 : 1 has been identified.

Interestingly, for most amines at elevated temperature the reaction proceeds with liberation of hydrogen and formation of complexes of the type $B_{10}H_{12}.2L$. The addition products obtained and isolated at low temperatures decompose only by splitting off the amine but without releasing hydrogen. This was confirmed by Burkardt and Fetter [57] for the pyridine derivatives. Under these conditions the addition products $B_{10}H_{14}.2BrC_5H_4N$ and $B_{10}H_{14}.3C_5H_5N$ were obtained, stable on heating to 100°. Investigation of the reaction of decaborane with substituted anilines [32] showed that in every case of the reaction of an amine (*p*-anisidine, *p*-toluidine, *p*-chloroaniline, *N*-methylaniline, *NN*-dimethylaniline) with decaborane at room temperature 1 mole hydrogen is liberated per 1 mole decaborane:

$$B_{10}H_{14} + 2RC_6H_4NH_2 \rightarrow B_{10}H_{12}.(RC_6H_4NH_2)_2 + H_2.$$

Alkylpyridines and alkylquinolines at room temperature dissolve decaborane without releasing hydrogen, giving strongly coloured solutions from which a solid is slowly precipitated. The same reaction in pentane proceeds with evolution of hydrogen. Aliphatic amines give solid products without evolution of hydrogen even in pentane. The reaction with diethylthiourea proceeds with liberation of hydrogen and the formation of a stable crystalline substance, $B_{10}H_{12}[(C_2H_5NH)_2CS]_2$. [58]

A method for the direct colorimetric determination of decaborane has been developed, based on the formation of orange-red solutions with *NN*-diethylnicotinamide with an absorption maximum in the 430–500 mμm region [59]. The value of this method is that neither other boron compounds, nor proteins hinder the determination. The method is applicable to solutions in aqueous systems (for example, blood plasma), and this defines its practical value in view of the considerable toxicity of decaborane.

Nitriles, as substances with very weak basic properties, react with decaborane on heating, hydrogen being liberated [60,61]:

$$B_{10}H_{14} + 2RC{\equiv}N \rightarrow B_{10}H_{12}.(RCN)_2 + H_2,$$

and crystalline products precipitated. The bis(acetonitrile) complex, which is involatile and stable in air, melts with decomposition above 200°C, is diamagnetic, and soluble in acetonitrile. The structure of the substance was determined by X-ray analysis [13]. It was shown that the acetonitrile ligands are in positions 6 and 9. This agrees completely with the fact that these are the most electropositive atoms in the decaborane molecule.

Besides the above nitrogen compounds, amides and cyanamides can enter into reactions analogous to those with nitriles, and so can many Lewis bases not containing nitrogen, such as sulphides, phosphines, phosphites, thiophosphites, ethers, alkylphosphinic acids [alkylphosphonic acids or even alkyl hydrogen phosphonates may be meant (Ed. of Translation)], arsines, and sulphoxides [62–67]. They all have the formula $B_{10}H_{12}L_2$ (where L is the Lewis base) and a structure which is obviously analogous to that of bis(acetonitrile)decaborane.

All the complexes of this type are covalent compounds, as is shown by a study of their infrared and $^{11}B$ nuclear magnetic resonance spectra, compared with those of the ionic complex $[B_{10}H_{10}]^{2-}.2(C_2H_5)_3\overset{+}{N}H$. [63]

On the basis of complexes of decaborane with phosphines, polymers of the type [67]:

$$[-OP(C_6H_5)_2.B_{10}H_{12}P(C_6H_5)_2-]_x.$$

have been obtained [68].

Kinetic investigation of the reactions of decaborane with various nitriles and sulphides [69] in dioxan at 70–80°C showed that this reaction is first order with respect to each of the reagents and of second order overall. Electron-donor substituents in nitriles and sulphides increase the

‡ These figures appear to be in error; see Fitch and Laubengayer [56] (Ed. of Translation).

reaction rate, electron-acceptor constituents decrease it. The following reaction scheme is proposed:

$$B_{10}H_{14}+L \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} B_{10}H_{14}L \xrightarrow{\text{slow}} H_2+B_{10}H_{13}L \xrightarrow[\text{rapid}]{L} B_{10}H_{13}L_2.$$

Not only uncharged molecules, but also anions can act as complex-forming agents in this reaction[64-70]. For example, hydrogen is also liberated in the reaction of decaborane in ether with sodium cyanide:

$$NaCN+B_{10}H_{14}R_2 \xrightarrow{25^\circ} [NaB_{10}H_{14}CN] \rightarrow NaB_{10}H_{12}CN+H_2.$$

An ionic compound is formed in which the CN group is obviously situated at one of the boron atoms 6 or 9. The salts $B_{10}H_{11}X^-$, where X = NCO, SCN, $OCH_3$, and $C(CN)_3$, have also been obtained. $^{11}B$ nuclear magnetic resonance spectra have shown that all the decaborane complexes of type $B_{10}H_{12}.2L$ and $B_{10}H_{12}.L^-$ are isostructural and are derivatives of the ion $B_{10}H_{14}^{2-}$.

A convenient method has been developed[71] for obtaining the anion $B_{10}H_{14}^{2-}$ by the reaction of decaborane with an aqueous solution of potassium tetrahydroborate:

$$B_{10}H_{14}+H_2O \rightleftarrows B_{10}H_{13}^-+H_3O^+,$$
$$B_{10}H_{13}^-+BH_4^- \rightleftarrows B_{10}H_{14}^{2-}+[BH_3],$$
$$[BH_3]+3H_2O \xrightarrow{\text{rapid}} B(OH)_3+3H_2.$$

$Rb_2B_{10}H_{14}$ and $Cs_2B_{10}H_{14}$ were isolated. The reaction of decaborane with sodium tetrahydroborate in Diglyme [di-(2-methoxyethyl) ether (Ed. of Translation)] at the boiling point is a simple method for preparing[72] the dianion $B_{12}H_{12}^{2-}$. The reaction follows the scheme:

$$B_{10}H_{14}+BH_4^-+R_2O \rightarrow B_{10}H_{13}^-+R_2O\cdot BH_3+H_2;$$
$$B_{10}H_{13}^-+R_2O\cdot BH_3 \rightarrow B_{11}H_{14}^-+H_2+R_2O;$$
$$B_{11}H_{14}^-+BH_4^- \rightarrow B_{12}H_{12}^{2-}+3H_2.$$

The first stage takes place at room temperature, the second at 90°, and the last at the boiling point of Diglyme.

Donor–acceptor complexes including the $B_{10}H_{12}$ unit in their composition undergo characteristic ligand-exchange reactions[10,19,66]:

$$B_{10}H_{12}\cdot 2L'+2L \rightarrow B_{10}H_{12}\cdot 2L+2L',$$

in which the displacement sequence obviously depends on the strength of the base. Thus Hawthorne and Pitochelly[62] found the following displacement order for acetonitrile, diethylcyanamide, and triphenylphosphine:

$$B_{10}H_{12}(CH_3CN)_2 \xrightarrow{2\,(C_2H_5)_2NCN} B_{10}H_{12}[(C_2H_5)_2NCN]_2 \xrightarrow{2P\,(C_6H_5)_3} B_{10}H_{12}[P(C_6H_5)_3]_2.$$

The reverse reactions do not take place.

A series of pyridine complexes of decaborane were obtained by analogous reaction of the dimethyl sulphide complex with substituted pyridines[73]. Since some of these products are coloured the authors suggest the interaction of the pyridine $\pi$ electron with the three-centre bonds in $B_{10}H_{12}^{2-}$.

Subsequent investigations of the exchange reactions of bis(acetonitrile)decaborane showed that in its reaction with triethylamine in boiling benzene two products with the same overall formula $B_{10}H_{12}.[N(C_2H_5)_3]_2$ should be expected[74]. One of these is a covalent compound of the general type $B_{10}H_{10}.L_2$, and the other the saltlike compound $B_{10}H_{10}^{2-}.2[NH(C_2H_5)_3]^+$. Unlike the first compound, the latter is confirmed by deuterium exchange with $D_2O$, is insoluble in organic solvents, and soluble in water; in aqueous solutions the $NH(C_2H_5)_3^+$ is exchanged for other cations:

$$B_{10}H_{10}^{2-}\cdot 2NH(C_2H_5)_3^+ + N(CH_3)_4^+Cl^- \rightarrow B_{10}H_{10}^{2-}\cdot N(CH_3)_4^+ + NH^+(C_2H_5)_3Cl^-.$$

It was found[75] that substituted decaboranes also form (like decaborane) complexes with Lewis bases. Thus 2-bromodecaborane reacts with acetonitrile, diethyl sulphide, and triphenylphosphine to give corresponding complexes:

$$2\text{-}B_{10}H_{13}Br \xrightarrow{\begin{array}{l}(C_2H_5)_2S\\ CH_3CN\\ (C_6H_5)_3P\end{array}} \begin{array}{l}[(C_2H_5)_2S]_2B_{10}H_{11}Br\\ (CH_3CN)_2B_{10}H_{11}Br\\ [(C_6H_5)_3P]_2B_{10}H_{11}Br\end{array}.$$

Monoethyldecaborane, containing 60% 2-ethyl- and 40% 1-ethyl-decaborane, is also readily converted into analogous complexes.

However, it has been noted[75] that boiling 2-iododecaborane with triethylamine in benzene yields not only the salt mentioned, $B_{10}H_{10}[NH(C_2H_5)_3]_2$, but also $B_{12}H_{12}[NH(C_2H_5)_3]_2$, which can also exchange cations, giving, for example, $K_2B_{12}H_{12}$.

2-Bromodecaborane also forms a complex with triethylamine[75], $B_{12}H_{12}[NH(C_2H_5)_3]_2$. However, bis(triethylammonium) nonahydrobromodecaborate is readily obtained by the action of triethylamine in benzene at 20° on $[(C_2H_5)_2S]_2B_{10}H_{11}Br$:

$$[(C_2H_5)_2S]_2B_{10}H_{11}Br+2N(C_2H_5)_3 \rightarrow [(C_2H_5)_3NH]B_{10}H_9Br.$$

A similar product is formed on heating $B_{10}H_{13}Br$ with trimethylamine in boiling toluene. Monoethyldecaborane and triethylamine in toluene give

$$[(C_2H_5)_3NH]_2B_{10}H_9C_2H_5,$$

in high yield.

The symmetry of the stable anion $B_{10}H_{10}^{2-}$ has been demonstrated and an icosahedral structure has been proposed for it.

Hawthorne and coworkers[76] have observed that in the reaction of the disulphide complex of decaborane with ethanol $B_9H_{13}(SR_2)$, a derivative of nonaborane(15) $B_9H_{15}$ is formed. An analogous reaction with the acetonitrile complex takes place thus:

$$B_{10}H_{12}(CH_3CN)_2+2C_2H_5OH \rightarrow B_9H_{12}(CH_3-\underset{\underset{OC_2H_5}{|}}{C}=NH)+CH_3CN+H_2+B(OC_2H_5)_3.$$

Organic sulphide ligands in the last type of compound can be replaced by other ligands:

$$B_9H_{13}(SR_2)+X \rightarrow B_9H_{13}X+SR_2,$$

where X = $CH_3CN$; $R_3N$; $R_2NH$; $RNH_2$; $R_2NCN$, $P(C_6H_5)_3$. When a sulphide complex of nonaborane(15) is treated with methylenetriphenylphosphane, a salt of the $B_9H_{12}^-$ anion is formed:

$$B_9H_{13}(SR_2)+(C_6H_5)_3P{=}CH_2 \rightarrow [(C_6H_5)_3PCH_3]^+[B_9H_{12}]^-+SR_2.$$

The direct alkylation of decaborane by methyllithium and ethyllithium can also be classified as nucleophilic reactions. A mixture of the mono- and di-substituted derivatives is formed[77], which was separated by preparative gas–liquid chromatography and the structure of the

products was established by $^{11}B$ nuclear magnetic resonance spectra. They are the 5- and 6-alkyl and the 6,9- and 6,5(8)-dialkyl derivatives. These results agree completely with the electron density distribution at the boron atoms of decaborane: 2, 4 > 1, 3 > 5, 7, 8, 10 > 6, 9.

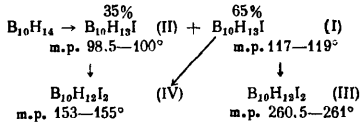
The most electropositive positions, 6 and 9, are the first to undergo nucleophilic attack by alkyllithiums, then 5, 7, 8, and 10; the 2, 4 and 1, 3 positions do not participate in the reaction at all.

## 9. ELECTROPHILIC SUBSTITUTIONS

As well as nucleophilic substitutions, decaborane is also characterised by electrophilic substitutions. From the electronic non-equivalence of the boron atoms in the decaborane molecule, it is to be expected that electrophilic agents would attack positions 2, 4 and 1, 3.

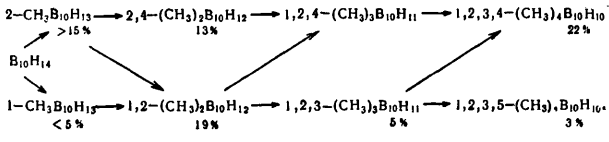
Stock was the first to observe, in 1914, that halogens do not destroy the structure of the decaborane molecule, but only replace from one to three hydrogen atoms by halogen. By heating decaborane with iodine at 100°, diiododecaborane $B_{10}H_{12}I_2$ was obtained and isolated in the pure state. Bromination and iodination under mild conditions gave monobromodecaborane and two monoiododecaboranes[78]. In the $^{11}B$ nuclear magnetic resonance spectra of the monobromo-derivative and the high-melting monoiodido-derivative a triplet in the low field is unchanged and a doublet in the high field is altered, the intensity of one of the peaks being decreased. This indicates that the halogen atom is in position 2 in both compounds. The spectrum of the low-melting monoiodido-complex shows a decrease in the high-field part of the triplet, belonging to atoms 5, 7, 8, and 10, whereas the low-field doublet is unchanged. Consequently, this substance must be 5-iododecaborane. The formation of this product can be explained by the parallel reaction of radical substitution[78].

Iodination was studied in greater detail by Hillman[79]. He iodinated separately decaborane itself and the monoiododecaboranes which were obtained:



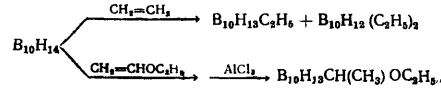

It was established, by deuterium exchange and the earlier X-ray structural analysis of 2,4-diiodo-derivative[17] (III), that compounds (I), (II), and (IV) are respectively 2-iodo-, 5-iodo-, and 2,5-diiodo-decaborane.

Williams and coworkers[80,81] studied the electrophilic alkylation of decaborane under the conditions of the Friedels–Craft reaction. On heating decaborane with methyl bromide in the presence of aluminium chloride in carbon disulphide in a sealed ampoule for 36 h, a mixture of polymethylated decaboranes was obtained:




Alkyldecaboranes, especially ethyldecaboranes, have been obtained by another method, the pyrolysis of ethyldiboranes[82]. 5-Ethyldecaborane (and other products) was isolated from the reaction mixture.

Decaborane adds on to ethyl vinyl ether and the lower alkenes in the presence of aluminium halides[83,84]:




The reaction takes place in a medium of an inert organic solvent. The products are liquids and have been proposed as additives to high-energy rocket fuels.

Finally, decaborane is alkylated by alkyl halides in the presence of metal halides to give a mixture of alkyldecaboranes[85].

## 10. THE STABLE ANION $B_{10}H_{10}^{2-}$

In 1959 Hawthorne and Pitochelly[74] reported that bis-(acetonitrile)decaborane reacts in two ways with tertiary amines, giving either the covalent compound $B_{10}H_{12}[N(C_2H_5)_3]_2$ or the ionic $B_{10}H_{10}^{2-}[HN^+(C_2H_5)_3]_2$, insoluble in organic solvents. This reacts with tetramethylammonium chloride, giving $B_{10}H_{10}^{2-}[\dot{N}(CH_3)_4]_2$.

The absence of $BH_2$ groups and hydrogen bridge atoms was shown by infrared spectra[86]. The $^{11}B$ nuclear magnetic resonance spectrum showed the presence of only two types of boron atom, in the ratio 8 : 2. These results indicate that the system is of high symmetry.

It was suggested[86] that the structure of the $B_{10}H_{10}^{2-}$ anion consists of two $B_5H_5$ "groups" — tetragonal pyramids, joined to one another by their bases. Hence the molecule contains two "vertex" and eight "equatorial" boron atoms. This structure was confirmed experimentally. Dobrott and Lipscomb[87] made an X-ray diffraction study of the salt $Cu_2B_{10}H_{10}$. The calculations showed that there are three types of B–B distance in the anion (Fig. 4): (1) the distance between the vertex boron atoms and the atoms lying in the base of the pyramid (1.73 ± 0.02 Å); (2) the distance between the atoms lying in the base of each pyramid (1.86 ± 0.03 Å); (3) the distance between atoms lying in the bases of pyramids ("equatorial belt", 1.815 ± ± 0.015 Å).

The calculated bond orders agree well with the data obtained by the LCAO–MO method[88] and are 0.56, 0.40, and 0.51 respectively. The Cu–B distance varies from 2.13, to 2.33 Å, which greatly hinders the calculations. From these results and from the B–Cu–B angle found (46°) the authors think a three-centre bond between the copper atom and the B–B edge the most probable (*sp* hybridisation of copper).

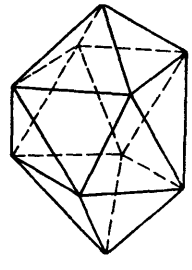


Fig. 4. Structure of the $B_{10}H_{10}^{2-}$ anion.

Calculation of the $B_{10}H_{10}^{2-}$ anion by the LCAO–MO method[88] showed that the vertex atoms are the most electropositive and are the first to be attacked by electrophilic agents.

A mechanism for the formation of the $B_{10}H_{10}^{2-}$ anion from bis(acetonitrile)decaborane has been proposed (Fig. 5).[89] The two bridge hydrogen atoms in bis(acetonitrile)decaborane leave as protons, giving a transition state containing two filled two-centre orbitals between the boron atoms 5 and 10, and 7 and 8. This transition state is stabilised by ejection of the ligands from positions 6 and 9. There is then a general rearrangement of the molecule in which the vertices of the polyhedron formed should be positions 10 and 7 or 5 and 8. This was confirmed by the nuclear magnetic resonance spectra of $B_{10}H_{10}^{2-}$ and $B_{10}H_6D_4^{2-}$, obtained from $B_{10}H_{10}D_4$ with deuterium in positions 1, 2, 3, and 4. The spectra showed the absence of deuterium from the vertex positions of the anion. The infrared spectra confirmed that the anion $B_{10}H_{10}^{2-}$ does not undergo deuterium exchange with $D_2O$ or $(C_2H_5)_3ND$.

Salts of the anion $B_{10}H_{10}^{2-}$ (and also $B_{12}H_{12}^{2-}$) exhibit an astonishing stability with respect to strong acids, bases, and oxidants. They do not react with hot sodium hydroxide, but acids convert them into the acid $B_{10}H_{10}(H_3O)_2 \cdot xH_2O$, which is stronger than sulphuric acid[90]. Many different salts of the anions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ have been obtained.

In aqueous and or alcoholic solutions, the anion $B_{10}H_{10}^{2-}$ reacts smoothly with chlorine, bromine, and iodine, giving derivatives in which from one to ten hydrogen atoms have been replaced by halogen[91]. It is suggested that such halogenation takes place by radicals. Thus, $B_{10}H_2Cl_8^{2-}$, $B_{10}H_3Br_7^{2-}$, $B_{10}H_7I_3^{2-}$, $B_{10}H_6I_4^{2-}$, $B_{10}H_4I_6^{2-}$, $B_{10}Cl_{10}^{2-}$, $B_{10}Br_{10}^{2-}$, and $B_{10}I_{10}^{2-}$ have been obtained. Halide derivatives of the anion containing other substituents have also been obtained, for example, $B_{10}Cl_9COC_6H_5^{2-}$ and $B_{10}H_2Cl_6[S(CH_3)_2]_2$. The anion $B_{12}H_{12}^{2-}$ undergoes analogous reactions. The halogenated compounds are strong acids, show great stability to acids and bases, and high thermal stability. $Cs_2B_{10}Cl_{10}$ loses only 4% of its weight when heated in a vacuum at 600°C; $B_{10}H_3Br_7^{2-}$ is unchanged after 1 h with $CH_3ONa$ in boiling methanol; $B_{10}H_7I_3^{2-}$ is inert to a solution of $KNH_2$ in liquid ammonia, but gives $B_{10}H_{10}^{2-}$ by the action of potassium in liquid ammonia. The crystalline acid $(H_3O)_2B_{10}Cl_{10} \cdot .5H_2O$ is reversibly dehydrated in a vacuum at 150°:

$$(H_3O)_2B_{10}Cl_{10} \cdot 5H_2O \rightleftarrows 3H_2O + (H_3O)_2B_{10}Cl_{10} \cdot 2H_2O.$$

Irreversible decomposition starts above 200° and a new compound is formed: octachlorononaborane(9), $B_9HCl_8$. Its properties have been studied[92], especially its conversion into the anion $B_9Cl_8H^{2-}$.

The caesium salt of the $B_{10}H_{10}^{2-}$ anion is unchanged after heating to 810°C. Some salts of $B_{10}H_{10}^{2-}$ are coloured; thus the pyridinium salt is yellow[93].

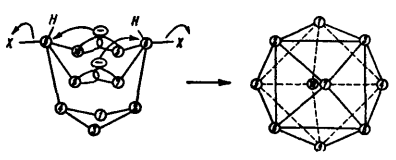
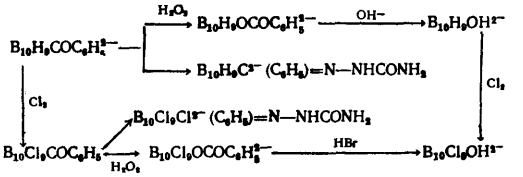


Fig. 5. Mechanism of formation of the $B_{10}H_{10}^{2-}$ anion from bis(acetonitrile)decaborane.

Benzoyl chloride reacts with $B_{10}H_{10}(H_3O)_2$, giving the anion $B_{10}H_9COC_6H_5^{2-}$, which takes part in various reactions[90]:



Amides react with the anion in acid medium, for example:

$$B_{10}H_{10}^{2-} \xrightarrow[[H^+]]{HCON(CH_3)_2} B_{10}H_9^{2-}OCHO + B_{10}H_9N^{2-}.$$

$B_{10}H_{10}^{2-}$ also reacts with donor compounds oxygen- and sulphur-containing compounds. The acid $B_{10}H_{10}(H_3O)_2$ hydroborates styrene. Furthermore the anion reacts with dimethyl sulphoxide:

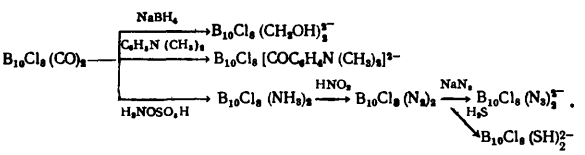
$$B_{10}H_{10}^{2-} + 2(CH_3)_2SO \rightarrow B_{10}H_8[S(CH_3)_2]_2 + H_2O.$$

The mechanism of this reaction is obviously electrophilic under the conditions of an electrophilic reaction; the $S(CH_3)_2$ group occupies the vertex positions (according to the nuclear magnetic resonance spectra). Under these conditions deuteration also takes place at the vertex atoms.

In the treatment of the $B_{10}H_{10}^{2-}$ anion with a large excess of aqueous nitrous acid with subsequent reduction of the precipitate formed, using sodium tetrahydroborate in methanol, a diazonium derivative is formed, $B_{10}H_8(N_2)_2$.[94] The action on this of amines, nitriles, ammonia, and carbon monoxide at 115–140°C releases nitrogen and gives the corresponding $B_{10}H_8L_2$. On carrying out the reaction with carbon monoxide in the presence of cyclohexane, $C_6H_{11}B_{10}H_7(CO)_2$ and $(C_6H_{11})_2B_{10}H_6(CO)_2$ are formed. This reaction proceeds by a free radical mechanism. The carbonyl derivative $B_{10}H_8(CO)_2$ exhibits very interesting chemical properties:

$$B_{10}H_8(CO)_2 + \begin{cases} 2CH_3OH \rightleftarrows (H^+)_2B_{10}H_8(COOCH_3)_2^{2-} \\ 4NH_3 \rightarrow (NH_4^+)_2B_{10}H_8(CONH_2)_2^{2-} \\ LiAlH_4 \rightarrow B_{10}H_8(CH_3)_2^{2-} \\ NaN_3 \rightarrow B_{10}H_8(NCO)_2^{2-} \\ H_2O + H_2NOSO_3H \rightarrow B_{10}H_8(NH_3)_2 + 2CO_2. \end{cases}$$

On heating above 300° the caesium salt $Cs_2B_{10}H_8(CONH_2)_2$ is dehydrated to $Cs_2B_{10}H_8(CN)_2$. On halogenating $B_{10}H_8(CO)_2$ in water, $B_{10}Cl_8(CO)_2$ and $B_{10}Br_8(CO)_2$ are obtained. The octachloro-derivatives undergo the following reactions:



In the oxidation of the $B_{10}H_{10}^{2-}$ anion, two new anions of the same composition, but different structure (A and B), ($B_{20}H_{18}^{2-}$) were obtained. The first anion (A) was obtained by oxidation of the triethylammonium salt of $B_{10}H_{10}^{2-}$ by the $Fe^{3+}$ ion in aqueous solution[95]. The second anion (B) was obtained by oxidation of the triethylammonium salt of $B_{10}H_{10}^{2-}$ with a cold aqueous solution of $Ce^{4+}$.[96] Study of the

nuclear magnetic resonance spectra of the freshly prepared anions showed that they consist of two unchanged polyhedra of the $B_{10}H_{10}^{2-}$ initial ion joined to one another by hydrogen bridge atoms.

Because ion B is quantitatively converted into ion A in an aqueous solution containing catalytic amounts of hydrochloric acid, it is thought that ion B is formed as the result of attack by the $Ce^{4+}$ ion on the more negative vertex atoms of the initial anion. The authors [96] think that the acid catalysis of the isomerisation of B into A takes place without rupture of the bridging bonds by the simple migration of the polyhedra relative to one another.

After passing an ethanol solution of the triethylammonium salt of A through an acid ion-exchange resin, evaporating off the ethanol, and adding water to an ethereal solution of the residue, rapid hydrolysis, accompanied by liberation of hydrogen, is observed [95]. As a result, a new hydride, stable in air was obtained, $B_{18}H_{22}$, acting as a strong acid and containing bridge and terminal hydrogen bonds (according to the infrared spectra).

There is a very interesting reaction between the triethylammonium salt of $B_{10}H_{10}^{2-}$ and nitrogen oxides [97]. By oxidation of the salt with nitrogen dioxide in aqueous acetonitrile or by nitrogen monoxide in the presence of $Fe^{3+}$ the compound $B_{14}H_{12}NO[NH(C_2H_5)_3]_2$ was obtained, and by passing $NO_2$ into 10% aqueous acetonitrile solution of the initial substance, two other such compounds, $B_{10}H_6(NO)_2N(CH_3)_4$ and $B_{10}H_4(NO)_3N(CH_3)_4$, were isolated. The NO group here is reduced to the $NH_2$ group by Raney nickel.

It is obvious that the study of the properties of the $B_{10}H_{10}^{2-}$ anion undertaken in recent years — like the study of the properties of decaborane, other higher hydrides, and other anions — is only the start of a larger investigation, judging from the quite interesting and unexpected discoveries in the field of polyhedral molecules having a main skeleton of boron atoms.

## 11. CARBORANES

In the middle of 1962, Onak and coworkers reported [98] that pentaborane(9) reacts with alkynes (propyne, butyne, and pentyne) in the presence of 2,6-dimethylpyridine, giving compounds with the general formula $B_4C_nH_{2n+4}$:

$$B_5H_9 + R{-}C{\equiv}C{-}R_1 + \text{2,6-dimethylpyridine} \rightarrow$$
$$\rightarrow B_4H_6C_2RR_1 + \text{2,6-dimethylpyridine}.BH_3$$

Side reactions include the cleavage of pentaborane with the formation of two moles of amine.$BH_3$ complex and $(BH)_x$ polymer.

The proton and $^{11}B$ spectra of the class of compounds obtained agree with the structure shown in Fig. 6.

The high-field doublet of the $^{11}B$ nuclear magnetic resonance spectrum is reminiscent of the same doublet, which corresponds to the vertex atom in hexaborane. The low-field doublet corresponds to the boron atoms in hexaborane lying in the base. However, in view of the fact that this doublet is split in the proportion 2 : 1, the non-equivalence of the boron atoms lying at the base of the structure of the compounds obtained is confirmed.

The proton spectrum consists of two overlapping quadruplets in the ratio 3 : 1 (a vertex proton and three lying in the base) and an unresolved multiplet, corresponding to the bridge hydrogens.

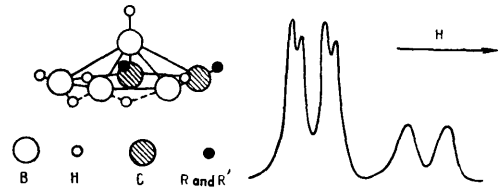



Fig. 6. Structure and $^{11}B$ nuclear magnetic resonance spectrum of dihydrocarborane(4),

Shapiro and coworkers [99] isolated $B_3C_2H_5$ from the mixture of products obtained by repeated circulation of an equimolecular mixture of pentaborane(9) and acetylene through a silent discharge apparatus (15 kV) at room temperature. The substance obtained (m.p. -126.4°, b.p.-3.7°C) is stable in air and unchanged on contact with acetone, trimethylamine, $CO_2$, and water at room temperature.

A study of the deuterium exchange of this compound with $B_2D_6$ showed that only three of the hydrogen atoms bound to boron atoms exchange with deuterium.

The infrared spectrum of $B_3C_2H_5$ shows a highly symmetrical molecule (the band in the 2800–3300 $cm^{-1}$ region, belonging to the C–H bonds, is absent). The spectrum includes bands corresponding to the stretching vibrations of the terminal B–H bonds (but not B–H–B bridges), stretching vibrations of B–B bonds (in the 780 $cm^{-1}$ region) and B–C bonds (in the 1000–1100 $cm^{-1}$ region). The proton nuclear magnetic resonance spectrum suggests the existence in the molecule of two types of proton: those attached to carbon atoms (singlet) and those attached to equivalent boron atoms (quadruplet). The $^{11}B$ nuclear magnetic resonance spectrum shows a single type of boron atom (single doublet).

The information obtained suggests [98] a trigonal bipyramid as the most probable structure of the $B_3C_2H_5$ molecule, in which all the boron atoms lie in a single plane and the carbon atoms are perpendicular to it.

The compounds of the general formula $B_nC_2H_{2n+2}$ were named carboranes. It was suggested [100] that the polyhedral molecules of the carboranes constitute a superaromatic system, since they satisfy the requirements of the existing theory of aromaticity.

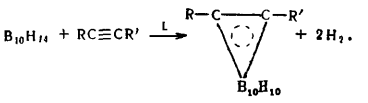
On the basis of the attractive LCAO–MO calculations, great stability was predicted for this class of compound and an ability to participate in electrophilic and nucleophilic substitutions. However, the position of the most electropositive and electronegative atoms could not be found from the calculations.

In view of the stability of the well-known icosahedral ion $B_{12}H_{12}^{2-}$, which is isostructural with the proposed carborane $B_{10}H_{12}C_2$, it was suggested that the latter should exist and might contain three normal $\sigma$ bonds and ten three-centre bonds in the skeleton, analogous to $B_{12}H_{12}^{2-}$. Possible models for intramolecular migrations of the boron atoms in $B_{10}H_{12}C_2$ through an intermediate cuboctahedral structure were considered [101].

Three groups of investigators recently published communications about the synthesis of $B_{10}H_{12}C_2$ and many of its derivatives (saturated and unsaturated hydrocarbons,

halogenoalkyl compounds, alcohols, acids and their derivatives, amines, ketones, ethers, etc.)[102-106]. The first member of the series $B_{10}H_{10}C_2H_2$, was named barene by Soviet chemists, carborane-10 by the Americans.

Barene and its derivatives were synthesised by the reaction of decaborane with acetylenic compounds in the presence of certain Lewis bases, which form with decaborane the $B_{10}H_{12}L_2$ complexes described above:

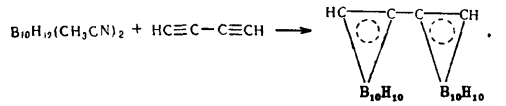


It has been shown[102] that the reaction takes place in two stages: first decaborane and the Lewis base give the complex $B_{10}H_{12}L_2$, which then reacts with the acetylene compound:

$$B_{10}H_{14} + 2L \rightarrow B_{10}H_{12}L_2 + H_2;$$

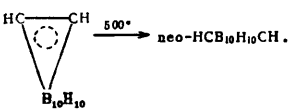
$$B_{10}H_{12}L_2 + RC{\equiv}CR' \rightarrow B_{10}H_{10}C_2RR' + H_2 + 2L.$$

Previously prepared complexes can be introduced into the reaction for the preparation of barenes. $CH_3CN$, $(C_2H_5)_2S$, $(C_2H_5)_3As$, $HCON(CH_3)_2$, $CH_3CON(CH_3)_2$, and $C_6H_5N(CH_3)_2$ are among the catalysts which have been used. A bisbarenyl compound has also been obtained[107]:



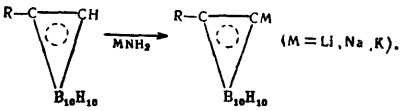
In the formation of a barene (carborane) from $B_{10}H_{12}L_2$ and acetylene a molecule of hydrogen is liberated[103] from the two bridge hydrogen atoms in $B_{10}H_{12}L_2$ – between $B_{(5)}$ and $B_{(10)}$, $B_{(7)}$ and $B_{(8)}$. The structure of the barenes has still not been finally established. A study of their structure using the example of di(bromomethyl)barene by X-ray diffraction showed that the decaborane structure is mainly retained[108]. From X-ray diffraction studies of *B*-octachlorobarene[109], $B_{10}H_2Cl_8C_2H_2$, obtained by chlorinating barene with ultraviolet irradiation, a structure close to icosahedral has been proposed (the isoelectronic structure of a right icosahedron of the dianion $B_{12}H_{12}^{2-}$). The C–C distance is 1.68 ± 0.02 Å and each carbon atom of the nucleus is bound by two three-electron bonds with four neighbouring boron atoms. Isomers of barene were also obtained.

Neocarborane was obtained[110] by heating barene at 465–500°C:

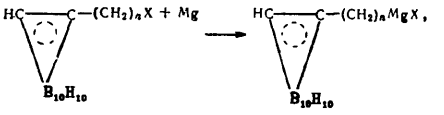


The structure of this isomer has also not been finally established. From studies of the $^{11}B$ nuclear magnetic resonance spectrum of neo-$B_{10}Cl_{10}C_2H_2$ it was suggested[111] that neocarborane has an icosahedral structure with carbon atoms in a "meta"-position (not bound with one another), as Lipscomb had already proposed[101]. On heating neocarborane at 615°C for 17 h, another isomer was isolated, termed "para"-carborane (it was suggested that the carbon atoms in it are in a "para"-position in the icosahedral structure)[112].

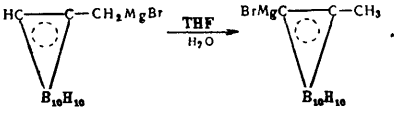
Barene has great thermal stability and is stable to the action of strong acids, several oxidants, and bases. The characteristic property of the barene nucleus is its electron-acceptor behaviour, which has a great effect on the chemical properties of barene compounds. It was shown that the barene nucleus deactivates a double bond towards addition reactions, inhibits nucleophilic substitutions at halogenomethyl derivatives, makes possible metallation at C–H, increases the strength of barenecarboxylic acids, etc.[103,113,114]. Many reactions of barene and its derivatives have been studied. It has been found that barene and its monosubstituted derivatives are metallated at a carbon of the nucleus by the action of alkyllithiums[115,116], sodium amide in boiling toluene[117], and alkali metal amides in liquid ammonia[118]:



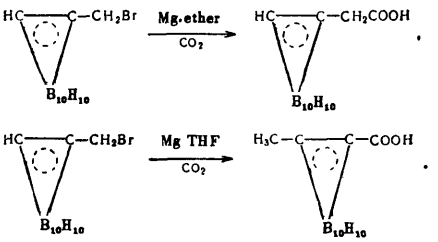
Barene forms both mono- and di-metal derivatives. With magnesium in ether or tetrahydrofuran, the halogenoalkyl derivatives form Grignard reagents[103,104,116]:



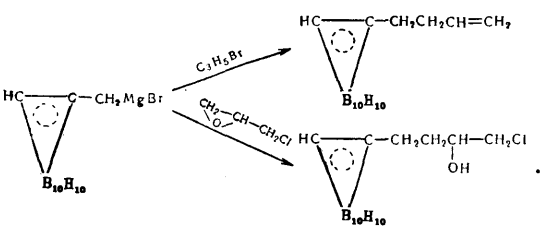
It has been shown that baren-1-ylmethylmagnesium bromide in tetrahydrofuran is isomerised into 1-methylbaren-2-ylmagnesium bromide[114,116]:

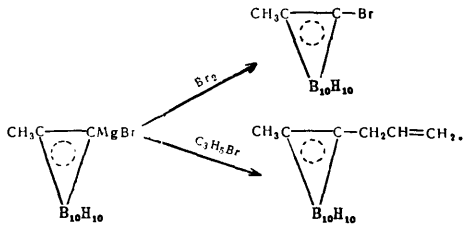


The carbonation of Grignard reagents from barenylmethyl bromide, prepared in either absolute ether or in tetrahydrofuran, has given the difficultly obtainable barenylacetic acid and methylbarenecarboxylic acid, respectively[119]:



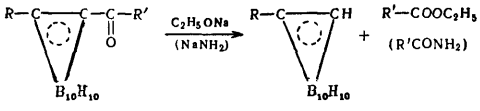
The barene Grignard reagents react with allyl bromide, epichlorhydrin, and bromine in the usual way:





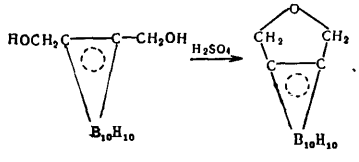
On hydrolysis, these Grignard reagents form alkyl derivatives of barene.

With esters of barenecarboxylic and barenedicarboxylic acids and barenyl phenyl ketones, it was shown that by the action of sodium ethoxide in absolute alcohol and sodium amide in liquid ammonia, rupture of the C–C bond takes place, because of the strong electron acceptor influence of the barene nucleus on the one hand and of the carbonyl group on the other [120,121]:

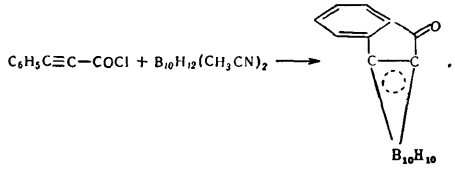


where R = H, $CH_3$, COOH; R′ = $OC_2H_5$, $C_6H_5$, $NH_2$.

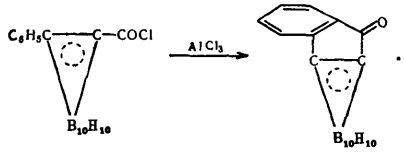
An interesting property of disubstituted barenes is their ease of cyclisation into three-membered exo-rings. When di(hydroxymethyl)barene is heated with sulphuric acid, a cyclic ether is readily formed [114,116]:



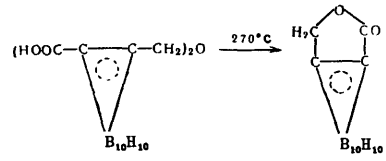
In the reaction of phenylpropynoyl chloride with bis(acetonitrile)decaborane, a cyclic ketone is smoothly formed [122]:



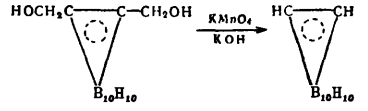
This same ketone is obtained from phenylbarenylcarbonyl chloride by the action of aluminium chloride:



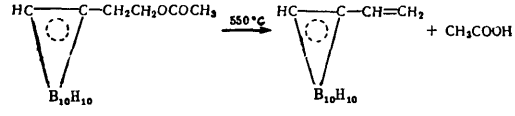
There is an interesting reaction when dicarboxylic acids are heated [123]:



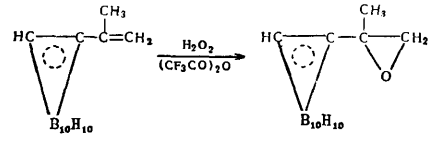
When alcohols of the barene series are oxidised in acid or alkaline media, acids of the barene series are obtained. Di(hydroxymethyl)barene and hydroxymethylbarene are exceptions, which form barene when oxidised by alkaline permanganate [103,114]:



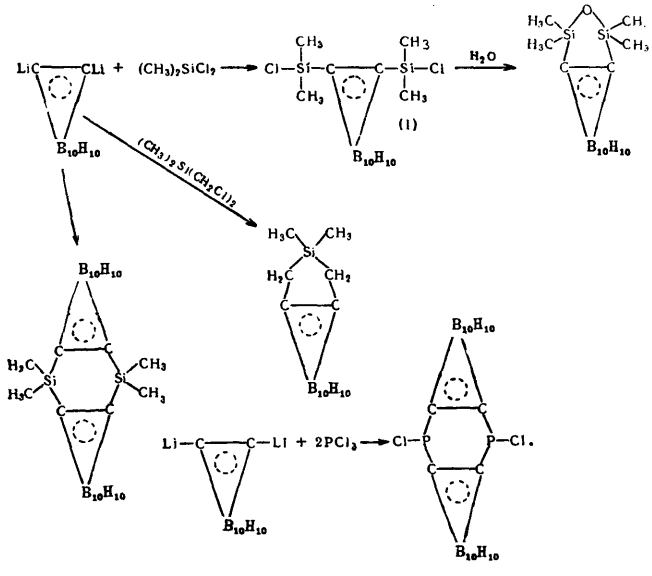
When the acetates of the barene alcohols are heated above 500°C, acetic acid is lost, and unsaturated compounds are obtained [116]:



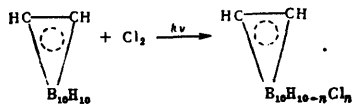
The action of peroxy-acids on the unsaturated compounds yields the corresponding oxides [104,116]:



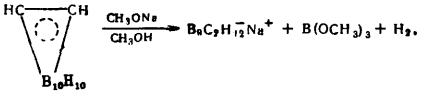
Several organoelemental compounds of the barene series have been prepared from the lithium derivatives: those of phosphorus, silicon, tin, and mercury [116,124,125]. The heterocyclic systems containing silicon and phosphorus are interesting [124,125]:



It has been shown that barene [126,127] and phenylbarene [126] are chlorinated under the action of ultraviolet light at the boron atoms, with formation of *B*-chloroderivatives:



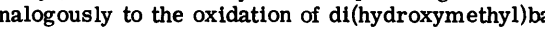
Polyhalogenobarenes from the di- to the decachloro-derivative have been obtained. It is reported [127] that undecachloro-derivative $B_{10}Cl_{10}C_2HCl$ has been made. *B*-Decachlorobarene and phenyl-*B*-decachlorobarene are rather strong acids and dissolve in aqueous alkali solutions [124]. Dodecachlorobarene was obtained by the action of chlorine on the alkali solution of *B*-decachlorobarene [126]. On reaction with alkyl halides in the presence of aluminium chloride, barene compounds are alkylated at boron atoms [128]. The action of strong bases on barenes liberates one mole of hydrogen and forms water-soluble salts of dicarboundecylcarboranes [114,129]:



The chemistry of neocarboranes has been studied little, but in their properties they are close to barenes. Metallation occurs by the action of butyllithium [110]:



The lithium derivatives undergo the usual reactions: carboxylation with $CO_2$, formation of alcohols with aldehydes, alkylation with alkyl halides. The oxidation of di(hydroxymethyl)neocarborane by alkaline permanganate takes place analogously to the oxidation of di(hydroxymethyl)barene:



neo-$B_{10}Cl_{10}C_2H_2$ was obtained by the chlorination of neocarborane under the action of ultraviolet light [111]. The investigation of barene and its derivatives has opened a new, interesting chapter in the chemistry of the organic compounds of boron.


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Institute of Organoelemental Compounds, Academy of Sciences of the USSR

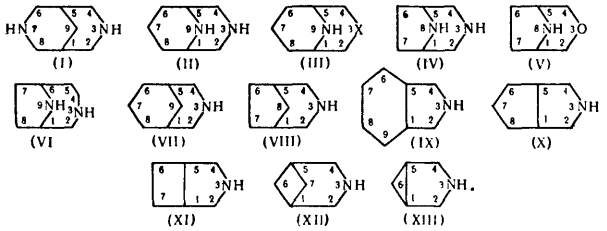
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# SYNTHETIC DIAZA- AND AZA-BICYCLIC SYSTEMS WITH NON-BRIDGEHEAD NITROGEN ATOMS

M. V. Rubtsov and E. S. Nikitskaya

## Introduction

Recently a large number of papers have been published on the chemical and biological studies of synthetic diaza- and aza-bicyclic systems with non-bridgehead nitrogen atoms. According to their chemical structure, these bicyclic systems may be divided into the following groups:

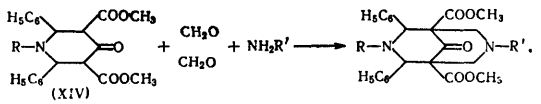


Aza- and diaza-bicyclic compounds are very interesting pharmacologically, since many of them exhibit biological activity and may be used for the investigation and preparation of new drugs. In this connection it appeared useful to give a systematic account of work dealing with the methods of synthesis of the above bicyclic systems, their chemical properties, and pharmacological activity. The present article does not include natural compounds of the tropane series and their synthetic derivatives, since a number of reviews dealing with them already exist[1-4].

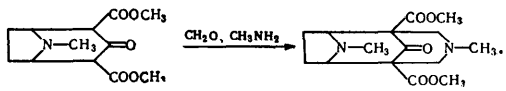
## 3,7-Diazabicyclo[3,3,1]nonane (I)

The derivatives of 3,7-diazabicyclo[3,3,1] nonane can be divided into two subgroups: 9-oxo-3,7-diazabicyclo[3,3,1]-nonanes or bispidones and the 3,7-diazabicyclo[3,3,1]nonanes themselves or bispidines. The methods available for the preparation of the two subgroups are different; bispidines cannot be obtained from bispidones.

Bispidones. Derivatives of 9-oxo-3,7-diazabicyclo-[3,3,1]nonane were first synthesised by Mannich and Mohs[5] by the condensation of substituted piperidonedicarboxylic ester (XIV) with formaldehyde and primary amines:

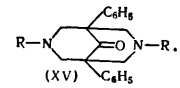


Compound (XIV) was obtained by the reaction of acetonedicarboxylic ester with the appropriate aldehyde and alkylamines[6-8]. The bicyclic system forms very readily at room temperature in aqueous alcoholic medium with a yield of 60–70%. By choosing appropriate derivatives of piperidine and alkylamines, it is possible to obtain easily various bispidones[9]†. Under these conditions the dimethyl ester of tropinonedicarboxylic acid yields a tricyclic system — the dimethyl ester of 6,8-ethylene-3,7-dimethyl-9--oxo-3,7-diazabicyclo[3,3,1]nonane-1,5-dicarboxylic acid:

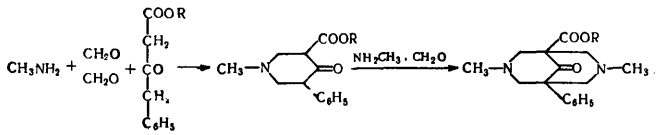


When an attempt was made to prepare a substituted γ-piperidone by the condensation of diphenylacetone, formaldehyde, and ammonia, the sole product isolated was 9-oxo-1,5-diphenyl-3,7-diazabicyclo[3,3,1]nonane[12].

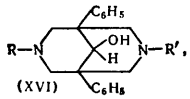
By using various alkylamines in the reaction with diphenylacetone, the authors of these investigations obtained a nunber of bispidone derivatives with the general formula (XV), where R = $CH_3CO$, $CH_3$, n-$C_2H_7$, $C_6H_5CH_2$, $HOCH_2CH_2$, and $ClCH_2CH_2$.



Similar results were obtained also by other workers[13], who allowed γ-phenylacetoacetic ester to react with methylamine and formaldehyde and instead of the expected product (3,5-dialkoxycarbonylphenyl-*N*-methylpiperidone), obtained bispidone derivatives, which are the products of the further interaction of the piperidone with formaldehyde and the amine:

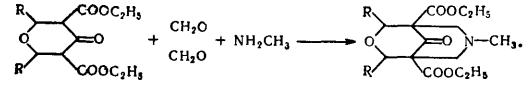


Numerous bispidone derivatives with the general formula (XVI) have been obtained by Chiavarelli and coworkers[14,15] by the condensation of diphenylacetone with formaldehyde and alkylamines followed by reduction of the ketones to alcohols with lithium aluminium hydride:

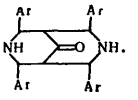


where R = R′ = $C_2H_5$, iso-$C_3H_7$, n-$C_4H_9$, $CH_3$, H, $ClCH_2CO$, $R_2NCH_2CO$, etc.

† A similar reaction[10] has been carried out with pyran derivatives[11]:

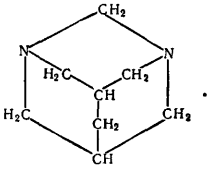


2,4,6,8-Tetraarylbispidones have been prepared by the reaction of acetone and ammonium acetate with benzaldehyde and *p*-methylbenzaldehyde[16]:

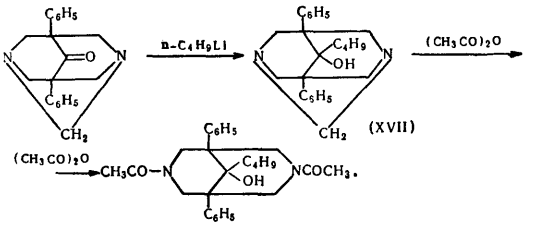


These were then reduced to the corresponding 9-bispidols.

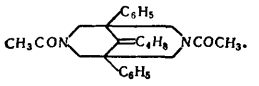
Certain diphenyl derivatives of diazaadamantane exhibit strychninelike activity[17-19]. This led to increased interest in bispidone, which is an intermediate in the synthesis of diazaadamantane:



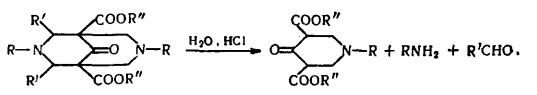
Substituted bispidones are readily obtained by the cleavage of diazaadamantane derivatives. Thus reaction of 9-oxodiazaadamantane with lithium alkyls yields tertiary alcohols, which on reaction with acetic hydride are cleaved with the formation of the *NN*-diazetyl derivative of 9-bispidol[18]:



When acetyl chloride acts upon compound (XVII), a molecule of water is split off and the ring is cleaved at the same time with the formation of an unsaturated compound[18]:



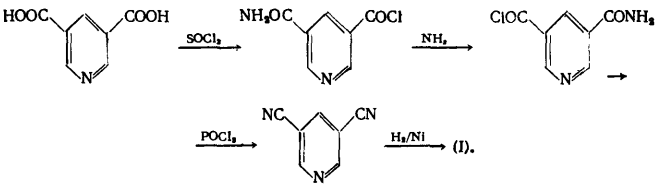
In a non-aqueous medium bispidones form dihydrochlorides, but one molecule of hydrogen chloride is easily lost (the hydrochloride "fumes"). The monohydrochloride is stable and almost insoluble in water. The carbonyl group does not undergo the characteristic reactions, and is not reduced in the presence of palladium or platinum black; on hydrogenation in methanol in the presence of palladium black, the molecule is cleaved with formation of an alkylamine and an aldehyde. Bispidones are readily hydrolysed to the corresponding piperidones, alkylamines, and aldehydes. Hydrolysis takes place even on boiling in water but the reaction is faster in the presence of acids, the substituted ring being cleaved as a rule[5,9]:



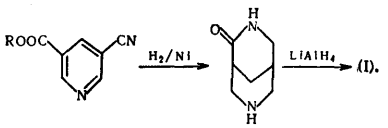
The pharmacological activity of bispidones has not been adequately investigated. Compounds with the general formula (XV) are weak anaesthetics and analgesics[12]. Among derivatives with the structure (XVI), compounds with antiarrhythmic activity have been found[14].

Bispidines. As stated above bispidone derivatives do not undergo reactions characteristic of the carbonyl group and are not reduced to bispidine derivatives. For this reason, the latter must be synthesised by different methods.

In an attempt to synthesise cytisine, the molecule of which incorporates bispidine, Bohlman and coworkers[20] obtained the latter from pyridine-3,5-dicarboxylic acid:

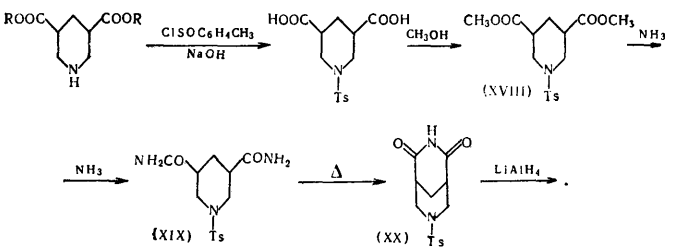


The yield of bispidine was 15%. When pyridine-3,5-dicarboxylic acid was replaced by 5-alkoxycarbonyl-3--cyano pyridine, compound (I) was again obtained[21]:



Galinovsky and Langer[22] obtained bispidine in 40% yield by heating 3,5-dibromomethylpiperidine with an alcoholic solution of ammonia in a sealed tube.

Bispidine may be synthesised from the diester of piperidine-3,5-dicarboxylic acid[23]:



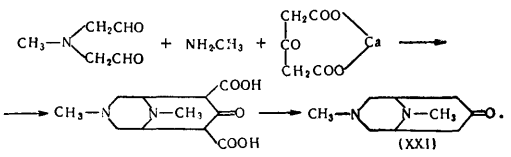
Reaction of the ester (XVIII) with boiling benzylamine gave a 95% yield of the extremely stable dibenzylamide which could not be cyclised into bispidine derivatives: for this reason the *trans*-configuration was attributed to this compound.

The ease of cyclisation of compound (XIX), which is obtained at low temperatures, and the impossibility of cyclising the dibenzylamide of *N*-tosylpiperidine-3,5-dicarboxylic acid, which is obtained at a high temperature, suggests that in the first case the formation of the diamide is preceded by the conversion of the *trans*-form of the ester (XVIII) into the *cis*-form and, conversely, in the preparation of the dibenzylamide at a high temperature the *cis*--form of the ester (XVIII) is converted into the *trans*-form. In subsequent papers the possibility of obtaining the cyclic imide (XX) directly from the ammonium salt of *N*-tosylpiperidine-3,5-dicarboxylic acid was indicated[24].

Bispidine consists of colourless crystals which avidly attract moisture and can be distilled in the form of a liquid hydrate. It is a strong diacidic base with an odour resembling that of piperidine. There are no data in the literature on the pharmacology of bispidine derivatives.

3,9-Diazabicyclo[3,3,1]nonane(II)

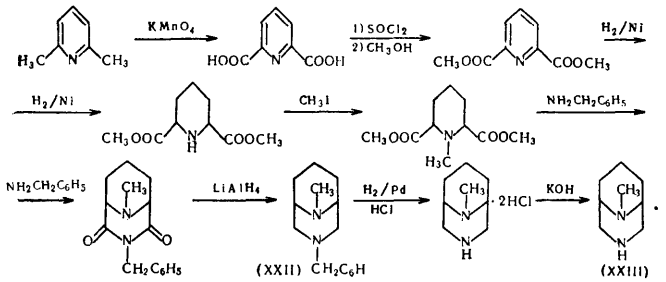
This bicyclic system was first obtained by Blount and Robinson[25] from methylaminodiacetaldehyde[26], methylamine, and the calcium salt of acetonedicarboxylic acid, the yield being 7.5%:



(XXI)

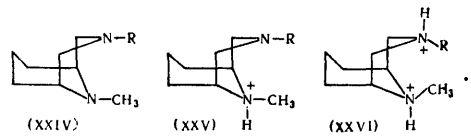
The reaction was continued to prepare the ketone (XXI).

Barnes and Fales synthesised 9-methyl-3,9-diazabicyclo[3,3,1]nonane from 2,6-lutidine[27]:



(XXII) (XXIII)

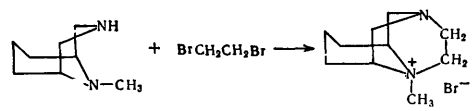
They established that the benzyl derivative (XXII) forms only the monomethiodide and the monopicrate, while 9-methyl-3,9-diazabicyclo[3,3,1]nonane (XXIII) yields both the dihydrochloride and the dipicrate. They explain this difference in behaviour by steric factors, and suggest that these compounds are most likely to have the configuration (XXIV):



(XXIV) (XXV) (XXVI)

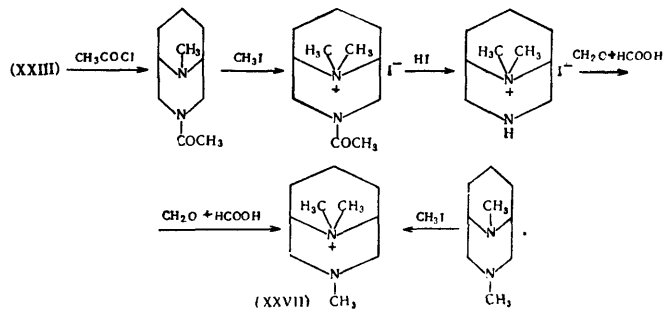
There is no steric hindrance in the formation of the mono-salt both when R = H and when R = $CH_2C_6H_5$ as in compound (XXV). However, the formation of the di-salt (XXVI) is impossible in the latter case because of steric hindrance, which occurs when methyl and benzyl groups approach one another. The steric hindrance is eliminated when the benzyl group in position 3 is replaced by hydrogen.

In order to prove the suggested configuration, Fales and Barnes synthesised 9-methyl-3,9-diazabicyclo[3,3,1,2$^{3-9}$]-undecane[28]:



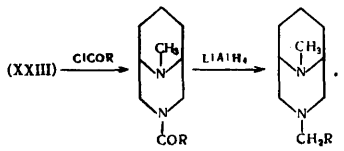
and demonstrated its structure by chemical reactions and by infrared spectroscopy.

The non-equivalence of the two nitrogen atoms in the bicyclic system (II) was noted also by other workers[29], and it has been shown that the formation of the mono-quaternary salt occurs at the nitrogen in position 9.[30] To form this salt, 9-methyl-3,9-diazabicyclo[3,3,1]nonane was acetylated, the acetyl derivative was converted into the quaternary salt, and the latter was then deacetylated and methylated with a mixture of formic acid and formaldehyde:

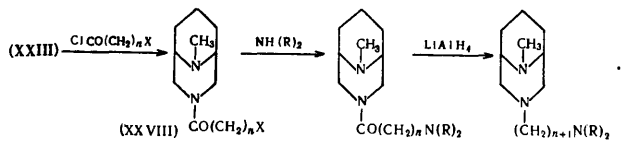


(XXVII)

The resulting quaternary salt (XXVII) proved to be identical with the methiodide of 3,9-dimethyl-3,9-diazabicyclo[3,3,1]-nonane prepared by the direct reaction of 3,9-dimethyl-3,9--diazabicyclo[3,3,1]nonane with methyl iodide. Derivatives of 9-methyl-3,9-diazabicyclo[3,3,1]nonane containing acyl, alkyl, hydroxyalkyl, carboxyalkyl, alkylaminoalkyl, and other groups at the nitrogen atom in position 3 have been synthesised recently for the purpose of pharmacological study[29]. The synthesis started with compound (XXIII) and the acid chlorides:



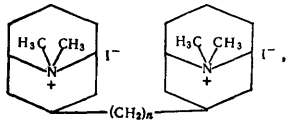
The amides thus obtained were then reduced with lithium aluminium hydride to the corresponding amines. The synthesis of 3-alkylaminoalkyl derivatives was achieved by the reaction of compound (XXIII) with the acid chlorides of halogeno-acids with subsequent substitution of the halogen in compound (XXVIII) by the dialkylamino-group and the reduction of the carbamoyl group with lithium aluminium hydride:



(XXVIII)

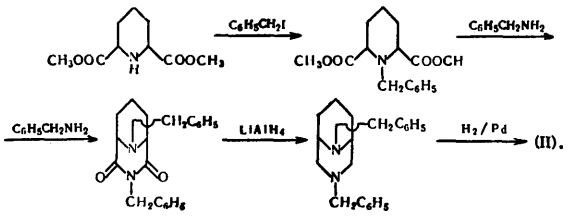
The dihydrochloride (XXIII) exhibits nicotine like activity, i.e. it stimulates ganglia[31]. Any substituent in position 3, starting with the methyl group, converts the compound into a ganglion-blocking agent. Apart from the ganglion-blocking effect, curarelike activity also appears. The greatest interest attaches to the dihydrochloride of 3,9-dimethyl-3,9-diazabicyclo[3,3,1]nonane which has approximately one twentieth of the ganglion-blocking activity of hexamethonium and is only 50% less active than the curarelike preparation diplacin which is used in the Soviet Union. When these compounds are converted into quaternary salts the ganglion-blocking and curarelike activities are intensified.

The series of symmetrical bis-quaternary salts with the general formula



is interesting. The tertiary bases were obtained by reducing the amides prepared by the reaction of compound (XXIII) with acid dichlorides[29] or the acid chlorides of halogeno--substituted acids[32]. The most active preparation, with the experimentally most pronounced curarelike activity, proved to be the symmetrical bis-quaternary salt with $n$ = 4.[31] It is somewhat more active than decamethonium and twenty times more active than diplacin.

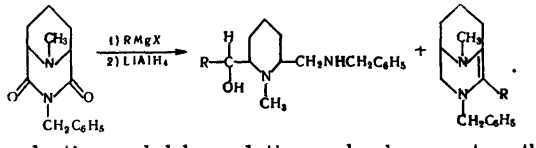
Unsubstituted 3,9-diazabicyclo[3,3,1]nonane (II) was obtained as follows[30]:



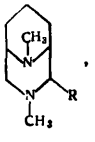
The reaction is carried out with benzyl iodide, benzyl chloride not reacting under similar conditions. The subsequent stages of the synthesis are similar to those in the synthesis of compound (XXIII).

Compound (II) is a homologue of piperazine and like the latter exhibits antihelminthic activity, which, however, is much weaker than in that of piperazine.

The synthesis of 3,9-diazabicyclo[3,3,1]nonane derivatives with substituents in position 2 does not take place smoothly[33]. The use for this purpose of the reaction between alkylmagnesium halides and cyclic imides[34] with subsequent reduction of the reaction products with lithium aluminium chloride yields mainly piperidine derivatives; unsaturated bicyclic compounds with a substituent in position 2 are obtained in only a very small yield:



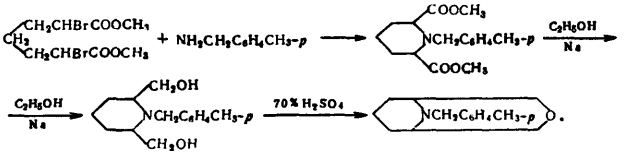
Their reduction and debenzylation and subsequent methylation at the nitrogen atom yields the compounds



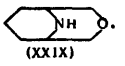
where R = $CH_3$ and $C_2H_5$.

3-Oxa(thia, selena)-9-azabicyclo[3,3,1]nonane (III)

The bicyclic system of 3-oxa-9-azabicyclo[3,3,1]nonane was obtained for the first time as 9-($p$-methylbenzyl)-3--oxa-9-azabicyclo[3,3,1]nonane[35]:

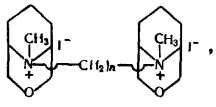


The study of 3-oxa-9-azabicyclo[3,3,1]nonane (XXIX) and its derivatives was begun in 1959 [36,37]:



The starting material for its synthesis was the diethyl ester of piperidine-2,6-dicarboxylic acid[38], whose reduction with lithium aluminium hydride yielded 2,6-dihydroxymethylpiperidine, which was cyclised to compound (XXIX) with 70% sulphuric acid. The cyclisation takes place with 50% yield and is accompanied by extensive charring.

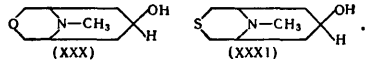
A number of derivatives of compound (XXIX) have been obtained with alkyl, acyl, alkylaminoacyl, and alkylaminoalkyl substituents at the nitrogen atom, including compounds whose acyl and alkyl substituents incorporated pharmacologically active systems such as phenothiazine, quinazolone, morpholine, and others. Ethers and esters of 9-($\gamma$-hydroxypropyl)- and 9-($\delta$-hydroxybutyl)-3-oxa-9--azabicyclo[3,3,1]nonane and the symmetrical bis-quaternary salts with the general formula



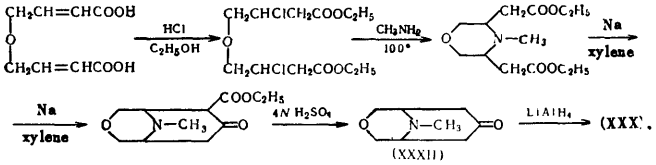
have also been prepared.

Some of these compounds exhibit nicotinelike activity and in large doses also traces of curarelike activity; none of these compounds are of practical interest.

The 7-hydroxy-derivatives of this bicyclic compound (XXX) and its thia-analogue (XXXI) proved to be more interesting[39].

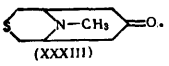


Starting from $\omega$-carboxyallyl ether, 9-methyl-3-oxa-9--azabicyclo[3,1,3]nonan-7-one (XXXII) was obtained as follows:

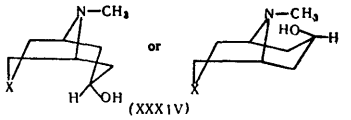


The overall yield of compound (XXXII) with respect to the $\omega$-carboxyallyl ether was 21%. The yield is low because the diethyl ester of 1-methylmorpholine-2,6-diacetic acid is formed as a mixture of the *cis*- and *trans*-isomers and only the *cis*-isomer cyclises into the bicyclic compound. Reduction of compound (XXXII) yielded compound (XXX).

Compound (XXXI) was synthesised by the method of Blount and Robinson[26] (see p. 441). Best results were obtained when the reaction was carried out in a weakly acid medium (pH 4). The ketone (XXXIII) was reduced to the alcohol with lithium aluminium hydride, only one isomer being isolated.



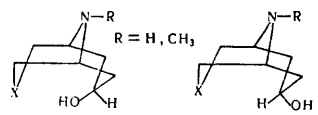
The *cis*-configuration (XXXIV) has been wrongly attributed to compounds (XXX) and (XXXI) obtained by the reduction of the ketones (XXXII) and (XXXIII):



(XXXIV)

(XXXIVa, X = O), (XXXIVb, X = S).

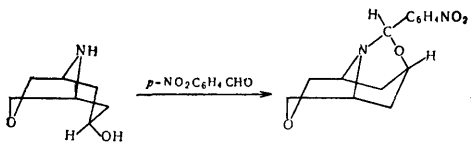
Zirkle and coworkers[40] studied the reduction of the ketones (XXXII) and (XXXIII) and the isolation in a pure form of the *cis*- and *trans*-isomers (XXX) and (XXXI). They reduced the ketones (XXXII) and (XXXIII) in different ways. When compound (XXXII) was reduced by means of a nickel catalyst in alcohol or ruthenium oxide in acetic acid, the main product was the axial (*trans*-)isomer (XXXVb, R = $CH_3$). The other isomer was obtained on reduction of compound (XXXII) with sodium in pentanol and on epimerisation of the axial isomer in the presence of aluminium isopropoxide. The isomer formed on epimerisation (XXXVIb, R = $CH_3$) is probably more stable and therefore its hydroxyl should be in the equatorial position.



(XXXV) (XXXVI)

(XXXVa, X = S), (XXXVIa, X = S),
(XXXVb, X = O), (XXXVIb, X = O).

The configuration of the epimers was demonstrated by the method of acyl migration which has been used in similar cases to study the steric structure of compounds of the tropane series[41-43]. Both epimeric alcohols (XXXVb, R = $CH_3$) and (XXXVIb, R = $CH_3$), were demethylated, and the nor-compounds were benzoylated and then heated in an acid medium. In this reaction the *N*-benzoyl derivative of the equatorial (*cis*)isomer (XXXVIb, R = H) isomerised to the *O*-benzoyl derivative while the axial (*trans*-)isomer (XXXVb, R = H) remained unchanged. In addition, the equatorial isomer formed a cyclic compound with *p*-nitrobenzaldehyde[44]:

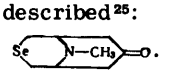


while the axial isomer charred under these conditions.

Because of the presence of sulphur, the thia-bicyclic ketone (XXXIII) does not undergo catalytic hydrogenation, but it is reduced with sodium in pentanol, the product being the equatorial (*cis*-)isomer (XXXVIa, R = $CH_3$). Reduction of the ketones (XXXII) and (XXXIII) with lithium aluminium hydride yields the axial (*trans*-)isomers (XXXVa, R = $CH_3$) and (XXXVb, R = $CH_3$).

A number of esters of compounds (XXX) and (XXXI) with diphenylacetic, benzilic, and other acids have been obtained[39,40]. Among these compounds the benzylic acid ester of compound (XXX), which exhibits considerable spasmolytic and high anaesthetic activity, is the most interesting[45]. In addition, it proved effective in the treatment of gastric ulcers and Parkinson's disease[40,45].

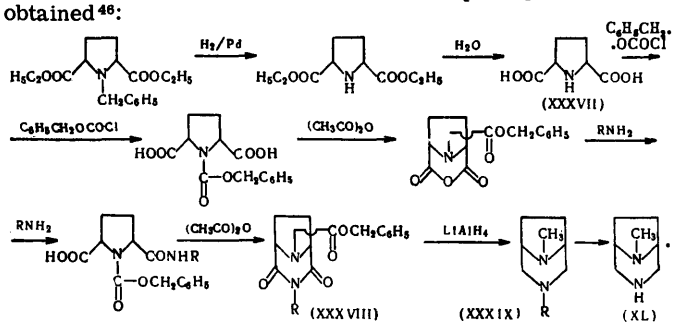
The synthesis of 9-methyl-3-selena-9-azabicyclo[3,3,1]-nonan-7-one has been described[25]:



No data concerning its biological properties have been given.

## 3,8-Diazabicyclo[3,2,1]octane (IV)

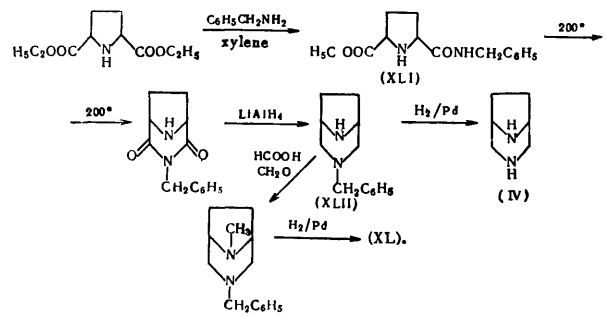
Bicyclic systems containing the pyrrolidine and piperidine rings are biologically very interesting, since they are similar to tropane and contain the piperazine ring, which is a component of many physiologically active substances. Numerous attempts to synthesise compounds of this series remained unsuccessful for a long time. It was not until 1961 that 8-methyl-3,8-diazabicyclo[3,2,1]octane was obtained[46]:



The acid (XXXVII) could be obtained from the ester only by using water as the hydrolytic agent In acid and alkaline media the pyrrolidine ring is cleaved. Since the acid (XXXVII) is very soluble in water and virtually insoluble in alcohol, it was isolated as the 1-benzyloxycarbonyl derivative, which was then converted into the anhydride using acetic anhydride. Reaction of the anhydride with alkylamines yielded monoamides, which on boiling with acetic anhydride were converted into the cyclic imides (XXXVIII). The imides were reduced with lithium aluminium hydride, the benzyloxycarbonyl group being converted into the methyl group.

Benzylamine was used to prepare 8-methyl-3,8-diazabicyclo[3,2,1]octane (XL). In this case reduction with lithium aluminium hydride gave 3-benzyl-8-methyl-3,8-diazabicyclo[3,2,1]octane (XXXIX, R = $CH_2C_6H_5$), which was debenzylated in the presence of palladium.

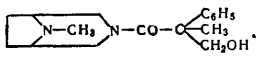
Later a simpler synthesis was developed for compound (XL), which permitted also the preparation of the unsubstituted bicyclic compound (IV) [47]:



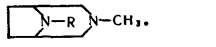
While in the first procedure, involving seven stages, the yield of compound (XL) was 16%, in the second procedure, consisting of five stages, the yield increased to 25%.[48] A more detailed study of the thermal cyclisation of the ester-amide (XLI) led to the isolation from the reaction mixture of two other substances[49]. One of these was the benzylimide of 1-ethylpyrrolidine-2,5-dicarboxylic acid and the other proved to be the *trans*-form of the ester-amide (XLI).

Derivatives of compound (XL) containing alkyl, aralkyl, and acyl groups in position 3 have been obtained. Like the derivatives of 3,9-diazabicyclo[3,3,1]nonane, the 3-alkyl derivatives of compound (XL) give only mono-quaternary salts, the quaternary nitrogen being in position 8.

Pharmacological study has established that 3-substituted derivatives of compound (XL) are antagonists of acetylcholine, 8-methyl-3-($\alpha$-methyltropoyl)-3,8-diazabicyclo[3,2,1]octane showing the greatest activity[50]:



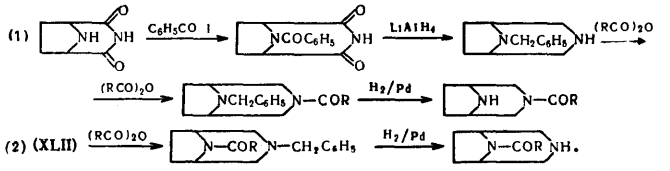
To compare the pharmacological activity of the 3-substituted derivatives of compound (XL) with their 8-isomers, a number of compounds having the following general formula were obtained[51]:



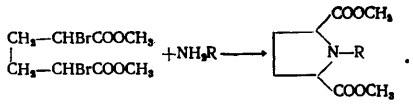
Here R is an acyl or an alkyl group. It was found that, in contrast to the 3-isomers, the 8-acyl derivatives exhibit analgesic activity, 3-methyl-8-propionyl-3,8-diazabicyclo[3,2,1]octane being the most effective.

Investigation of the properties of the 3- and 8-acyl derivatives of 3,8-diazabicyclo[3,2,1]octane showed that the acyl residue in position 8 migrates to position 3 under the influence of temperature or alkaline reagents[52]. The opposite migration has not been observed.

The 3- and 8-acyl derivatives required for this purpose can be obtained as follows:



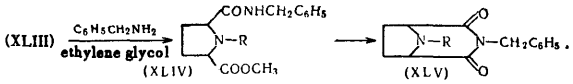
In the synthesis of the derivatives of 3,8-diazabicyclo[3,2,1]-octane a special study was made of the pyrrolidine ring closure reaction[53]:



(XLIII)

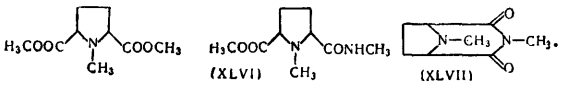
$\alpha\alpha'$-Dibromoadipic acid is shown to be a mixture of isomers[54-56]. In order to obtain from this acid 1-substituted *cis*-pyrrolidine-2,5-dicarboxylic ester (XLIII), the *meso*-form must be used in the reaction, the racemate being less suitable. In the reaction of the *meso*-form of $\alpha\alpha'$-dibromoadipic acid with aniline in a mixture of benzene and nitromethane 1-phenylpyrrolidine-2,5-dicarboxylic ester forms in 70% yield. The *cis*- and *trans*-isomers, in the proportions of three to one, can be separated by fractional crystallisation and by chromatography. Under the same condition the racemate of $\alpha\alpha'$-dibromoadipate gives compound (XLIII) in 10% yield, which can be separated into equal amounts of the *cis*- and *trans*-isomers.

Study of the synthesis of the imide (XLV) showed[53] that not only cyclisation but also the formation of the ester--amide (XLIV) proceeds with considerable difficulty:



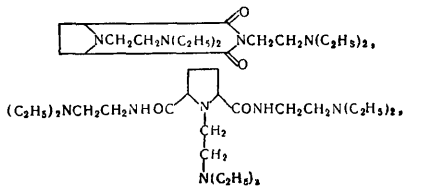
The product required can be obtained only when the reaction with benzylamine is carried out in boiling ethylene glycol in the presence of metallic sodium, followed by distillation of the reaction mixture without prior removal of the catalyst. During the distillation the cyclisation with the formation of compound (XLV) goes to completion, the yield of (XLV) being 40% from *cis*- (XLIII) and 12% from *trans*-(XLIII).

Schipper and Boehme[57] published interesting observations in 1961. They showed that in the reaction of dimethyl $\alpha\alpha'$-dibromoadipate with methylamine in the ratio 1 : 3 three products are formed:

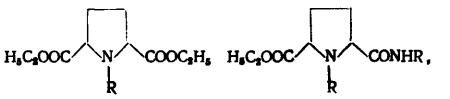


Compound (XLVII) can also be obtained in 50% yield on heating the ester-amide (XLVI) to 180°. Reduction of compound (XLVII) with lithium aluminium hydride yields, 3,8--dimethyl-3,8-diazabicyclo[3,2,1]octane.

The reaction of $\alpha\alpha'$-dibromoadipate proceeds in different ways with different alkylamines. For example, when $\beta$-diethylaminoethylamine is used, a mixture of the bicyclic compound and the diamide is formed:



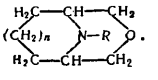
whereas with benzylamine or n-butylamine the reaction products are the ester and the ester-amide:



where R = n-$C_4H_9$ or $C_6H_5CH_2$.

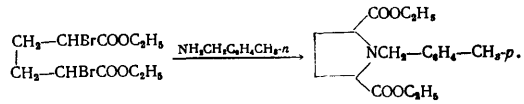
## 3-Oxa-8-azabicyclo[3,2,1]octane (V)

3-Oxa-8-azabicyclo[3,2,1]octane was obtained by Braun and Leistner[35], who synthesised a number of bicyclic derivatives of morpholine having the general formula

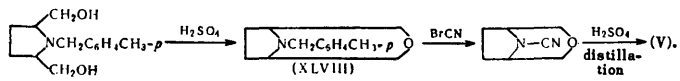


The simplest representative of this series, morpholinopyrrolidine or 3-oxa-8-azabicyclo[3,2,1]octane, was synthesised from diethyl *meso*-$\alpha\alpha'$-dibromoadipate and

*p*-methylbenzylamine via the 1-(*p*-methylbenzyl)pyrrolidine-2,5-dicarboxylic ester:



The latter was reduced with sodium in alcohol to the corresponding diol which was cyclised with 70% sulphuric acid at 175° into 8-(*p*-methylbenzyl)-3-oxa-8-azabicyclo[3,2,1]-octane (XLVIII):

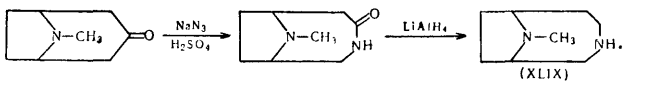


To prepare the nor-compound, the *p*-methylbenzyl derivative (XLVIII) was allowed to react with cyanogen bromide, the cyano-derivative being subsequently saponified with 25% sulphuric acid.

Like morpholinopiperidine (XXIX), morpholinopyrrolidine (V) shows little pharmacological activity[35].

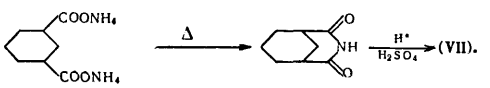
## 3,9-Diazabicyclo[4,2,1]nonane (VI)

In 1960 a short note was published concerning the synthesis of 9-methyl-3,9-diazabicyclo[4,2,1]nonane (XLIX) as the starting material for the preparation of pharmacologically active substances[58]. The synthesis was achieved by treating tropinone with sodium azide in sulphuric acid with subsequent reduction of the cyclic amide formed with lithium aluminium hydride. The yield of compound (XLIX) was 51% with respect to tropinone.



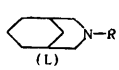
## 3-Azabicyclo[3,3,1]nonane (VII)

Compound (VII) was first prepared by the dry distillation of ammonium hexahydroisophthalate, the imide formed being subsequently reduced at a lead cathode in 65% sulphuric acid[59]:

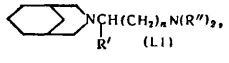


The yield of compound (VII) was only 17%, probably as a result of the hydrolysis of the imide during the reduction process.

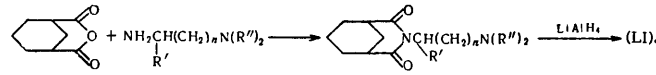
In recent years a number of papers have been published on the synthesis of derivatives of compound (VII). Compounds having the general formula (L) have been obtained[60]:



where R = $CH_3$, $C_2H_5$, $CH(CH_3)_2$, $CH_2CH{=}CH_2$, NO, etc., and also the mono- and bis-quaternary salts (LI)[61]:

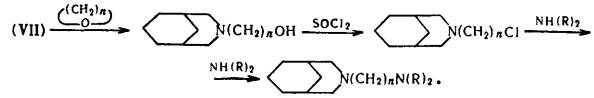


where $n$ = 1, 2, and 3, R′ = H and $CH_3$, and $N(R'')_2$ = $N(CH_3)_2$, $N(C_2H_5)_2$, pyrrolidyl, morpholinyl, etc. These compounds were synthesised by the reaction of compound (VII) with alkyl halides[60] or by the reaction of hexahydroisophthalic acid or its anhydride with the corresponding amines and subsequent reduction of the resulting imides with lithium aluminium hydride[61,62]:



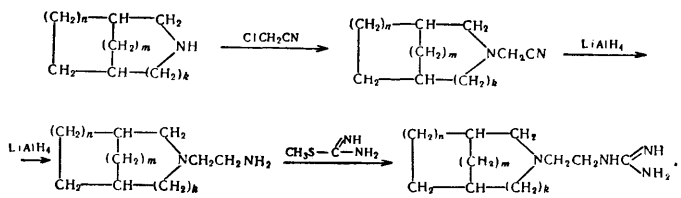
Later it was shown that substituted derivatives of (VII) can form from the di(*p*-toluenesulphonate) ester of 1,3-dihydroxymethylcyclohexane and the corresponding amine[63].

Compounds (LI) in which $n$ = 1 and R′ = $CH_3$ do not form bis-quaternary salts because of steric hindrance. The other compounds form mono-quaternary salts at 20°and bis-quaternary salts at 80–90°. Compounds (LI) in which $n$ = 1or 2 and R′ = H can be obtained by the reaction of compound (VII) with epoxyethylene and epoxypropene followed by treatment of the resulting alcohols with thionyl chloride and secondary amines[61]:



The compounds obtained[61] exhibit considerable ganglion-blocking activity, the most interesting being 3-(γ-dimethylaminopropyl)-3-azabicyclo[3,3,1]nonane methiodide[61] and 3-(ω-dimethylaminopentyl)-3-azabicyclo[3,3,1]nonane[64]. It is noteworthy that similar compounds containing an even number of methylene groups have been found by Rice and Grogan to have little activity[65].

Later studies showed[66-68] that certain derivatives of compound (VII) and also of its structural isomer 3-azabicyclo[3,2,2]nonane exhibit hypotensive properties. Among these 3-(β-guanidinoethyl) derivatives proved to be especially active, preliminary data showing that in the intensity and duration of the activity they are not inferior to guanethidine[66]‡. The synthesis of 3-(β-guanidinoethyl)-3-azabicyclo[3,3,1]nonane and its analogues were achieved as follows:

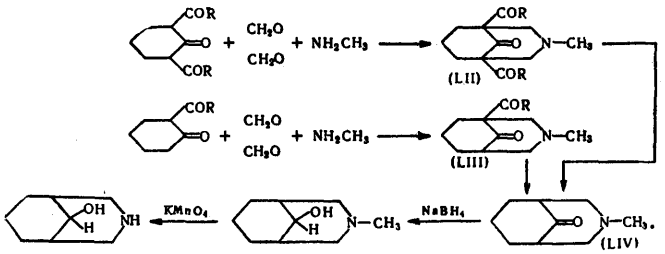


The azabicycloalkanes were converted into *N*-cyanomethyl derivatives and the latter were reduced with lithium aluminium hydride and then allowed to react with *S*-methylisothiourea.

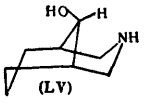
Derivatives of compound (VII) may be synthesised also by the Mannich reaction[71-75]. 9-Hydroxy-3-azabicyclo-

‡ Among the derivatives of 3-azabicyclo[3,2,2]nonane, a structural isomer of compound (VII), compounds have been obtained recently capable of giving rise to hypotonia, salivation, and convulsions[69,70].

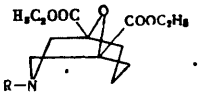
[3,3,1]nonane was obtained by this method from cyclohexanone derivatives[71]:



Condensation of diethyl cyclohexanone-2,6-dicarboxylate and ethyl cyclohexanone-2-carboxylate with formaldehyde and methylamine yields the diethyl ester (LII) and the ethyl ester (LIII). The amides of the acids can be used in the reaction instead of the esters. Hydrolysis and decarboxylation of compounds (LII) and (LIII) give compound (LIV); this can be reduced with sodium borohydride to the corresponding alcohol, which can be demethylated with an alkaline solution of potassium permanganate to 9-hydroxy-3-azabicyclo[3,3,1]nonane or isopseudogranatoline, the latter compound probably having the *trans*-configuration (LV), since it does not form a cyclic product with *p*-nitrobenzaldehyde[44]:

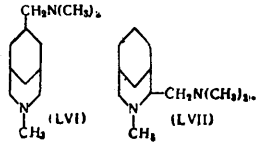


Study of the formation of compound (LII) by the Mannich reaction[72,73] showed that, depending on the temperature (25° or 100°), one of two compounds, differing in their boiling points but identical in all other properties and having the composition of compound (LII), is obtained. They are probably the *cis*- and *trans*-isomers with respect to the ethoxycarbonyl groups§. Compounds of this type must have the chair–chair structure:

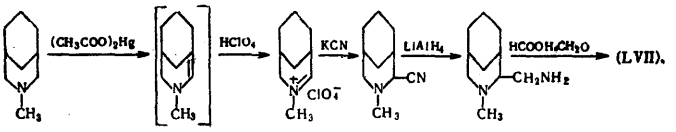


Their carbonyl groups do not give the characteristic reactions, which is evidently due to steric hindrance[73]. Hydrolysis and decarboxylation of both isomers yield the same ketone (LIV), which forms an oxime and can be reduced by the Wolff–Kishner method to compound (L, R = $CH_3$).

Other derivatives of 3-azabicyclo[3,3,1]nonane which have been synthesised are the 7- and 2-dimethylaminoethyl compounds[76]:

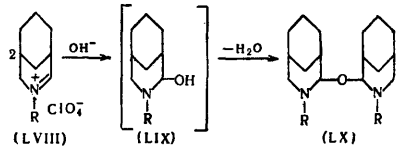


Compound (LVI) was obtained from cyclohexane-1,3,5-tricarboxylic acid, which was converted by dry ammonia at 200–220° into its monoamide, monoimide. The latter was reduced with lithium aluminium hydride and methylated with a mixture of formic acid and formaldehyde to give compound (LVI). Compound (LVII) was synthesised as follows:

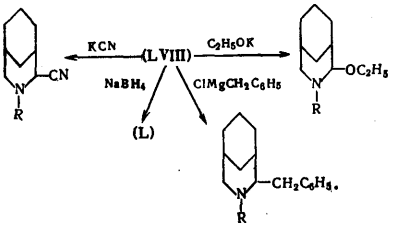


3-Methyl-3-azabicyclo[3,3,1]nonane was dehydrogenated at 80° with a solution of mercury acetate in 5% acetic acid; the unsaturated compound, isolated as the perchlorate, was converted by the action of an aqueous solution of potassium cyanide into 2-cyano-3-methyl-3-azabicyclo[3,3,1]nonane. The latter was reduced with lithium aluminium hydride and methylated with a mixture of formic acid and formaldehyde to give compound (LVII). No data on the pharmacological activity of thesecompounds have been published.

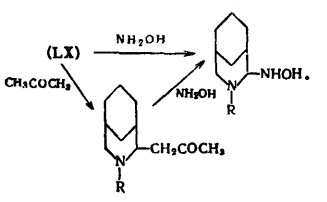
Schneider and Götz[77] found that, on being acted upon by sodium hydroxide, perchlorates of the type of (LVIII) do not form the hydroxy-derivative (LIX) but the dimeric compound (LX):



Reaction of compound (LVIII) with various nucleophilic agents gives 2-substituted derivatives of 3-alkyl-3-azabicyclo[3,3,1]nonane: 2-ethoxy-derivative with potassium ethoxide, 2-cyano-derivative with potassium cyanide, and 2-benzyl derivative with benzylmagnesium chloride. Reduction of compound (LVIII) with sodium borohydride gives compound (L).



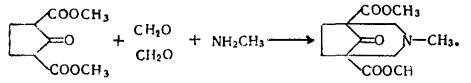
The dimer (LX) also reacts with nucleophilic agents, forming monomeric 2-substituted derivatives: reaction with hydroxylamine in absolute alcohol gives 3-alkyl-2--hydroxyamino-3-azabicyclo[3,3,1]nonane and the reaction with acetone gives a ketone which on being acted upon by hydroxylamine does not give an oxime but the hydroxylamino-derivative:



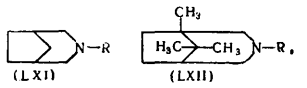
§ This does not appear to be possible (Ed. of Translation).

3-Azabicyclo[3,2,1]octane (VIII)

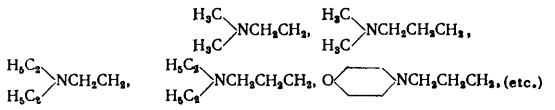
Derivatives of compound (VIII) can be obtained by the Mannich reaction from the cyclopentanone-1,5-dicarboxylic ester[75,78]:



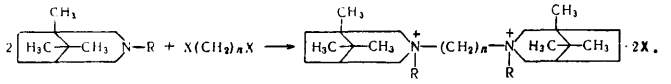
Another synthetic pathway for compound (VIII) is based on the use of the anhydride of *cis*-1,3-cyclopentanedicarboxylic acid[79] or the camphoric anhydride, which is converted into bicyclic amines via the corresponding imides[80-82]. Depending on the initial anhydride and amine, compounds having the structures (LXI) and (LXII) are formed:



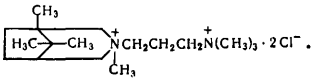
where R = alkyl,



Reaction of 3-alkyl-1,8,8-trimethyl-3-azabicyclo[3,3,1]-nonane with $\alpha\omega$-dihalogenoalkanes gave symmetrical bis--quaternary salts[80]:



Pharmacological investigation of the compounds synthesised showed that the tertiary bases are inactive, while the quaternary salts show hypotensive activity[83,84]. No differences were observed between the (+)- and (±)-forms. 3-($\gamma$-Diethylaminopropyl)-1,8,8-trimethyl-3-azabicyclo-[3,2,1]octane was found to have the greatest activity[84]:

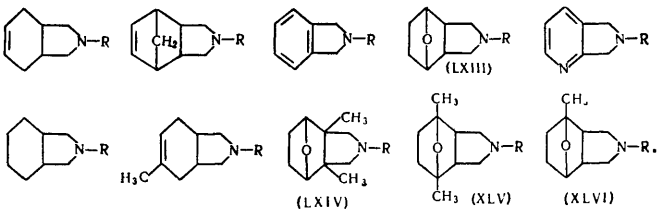


This substance exhibits pronounced hypotensive activity and also depressive activity on the central nervous system.

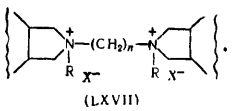
3-Azabicyclo[4,3,0]nonane (IX)

3-Azabicyclo[4,3,0]nonanes or isoindolines have been synthesised in different ways. Thus Tiffeneau and coworkers[85] obtained *N*-isopentylisoindoline by the reaction of *o*-bromomethylbenzyl bromide with diisopentylamine. In a similar way Braun and coworkers[86,87] obtained isoindoline and a number of its derivatives.

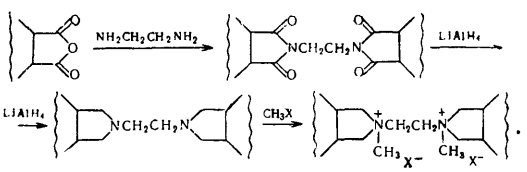
Substituted isoindolines are most simply obtained by the reduction of the imides of 1,2-dicarboxylic acids[88-91] which in turn are synthesised from the anhydrides of the corresponding dicarboxylic acids and alkylamines[92]. The following derivatives of isoindoline have been synthesised:



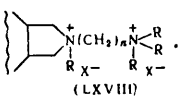
The amines used were dimethylamino-, diethylamino-, morpholino-, and piperidino-ethylamines, and others. The resulting bicyclic amines were converted into asymmetric and symmetric bis-quaternary salts (LXVII) [93] by standard methods[80]:



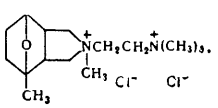
The quaternary salts are readily obtained when $n$ = 3 and more; when $n$ = 2 only one end of the dihalogenoalkane reacts with the amine. In this case, in order to obtain symmetric bis-quaternary salts, the corresponding anhydride of the dicarboxylic acid is allowed to react with ethylenediamine, the condensation product being reduced with lithium aluminium hydride and converted into the quaternary salt by means of methyl iodide:



Substituted acid imides and their methiodides are pharmacologically inactive. The isoindoline bases are only weakly active, but their conversion into bis-quaternary salts yields compounds with pronounced hypotensive activity and low toxicity. Compounds (LXVII) and (LXVIII), with $n$ = 2 or 3 and R = $CH_3$ or $C_2H_5$, and compounds with an oxygen bridge (LXIII–LXVI) exhibit very powerful hypotensive properties.

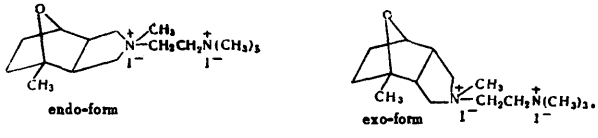


Among all the compounds of this series which have been investigated, preparation H-2 proved to be the most effective[94,95]:

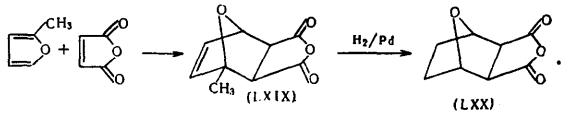


It is much more active and less toxic than hexamethonium. From their study of the structure of preparation H-2 (as

the dimethiodide), Rice and Grogan concluded that this compound can exist in one of two forms[96]:

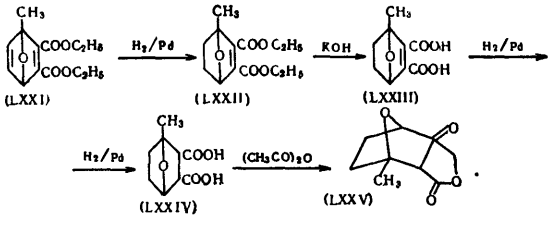



They synthesised both isomers and investigated their pharmacological properties. The synthesis was based on phthalic anhydride derivatives of different configurations. Condensation of maleic anhydride and 2-methylfuran gave the addition product (LXIX)[97] with the *exo*-configuration[98]:




Its reduction yields *exo*-perhydrophthalic anhydride (LXX).

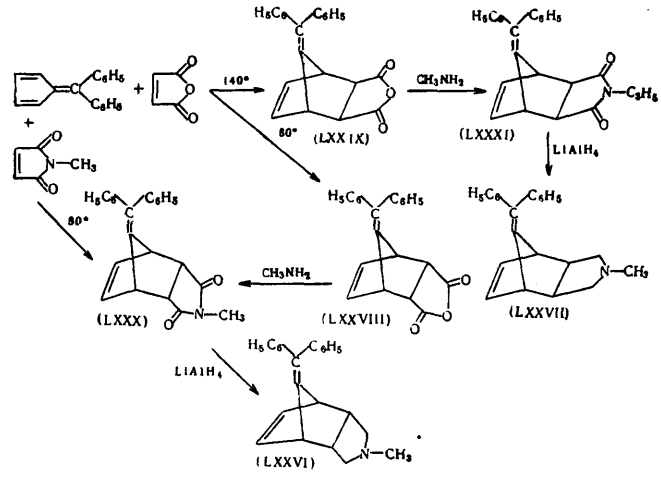
The condensation of diethyl acetylene-1,2-dicarboxylate acid with 2-methylfuran gives the addition product (LXXI)[99,100]:




On catalytic hydrogenation of compounds (LXXI), one mole of hydrogen adds on to give compound (LXXII), which can be hydrolysed to the acid (LXXIII). Reduction of compound (LXXIII) yields *endo-cis*-perhydrophthalic acid (LXXIV), which can be converted into the anhydride (LXXV) by treatment with acetic anhydride and acetyl chloride. The acid obtained from the anhydride (LXX) is not identical with the acid (LXXIV), just as the anhydride (LXX) is not identical with the anhydride (LXXV). Taking into account the work of Woodward and Baer[98], it may be assumed that the anhydride (LXXV) has the *endo*-form.

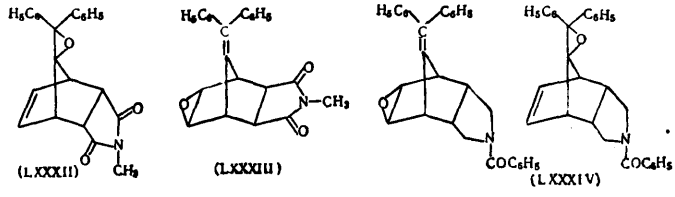
The anhydrides (LXX) and (LXXV) were allowed to react with dimethylaminoethylamine, the resulting imides being reduced with lithium aluminium hydride and converted into bis-quaternary salts. The pharmacological activity of the two compounds proved to be equally high[94].

In 1962 Poos and coworkers[101] synthesised the *endo*- and *exo*-isomers of 8-diphenylmethylene-2-methyltetrahydro-4,7-methanoisoindoline (LXXVI) and (LXXVII) and a number of its derivatives, starting from the corresponding fulvenes, by a method similar to that described above. Condensation of diphenylfulvene and maleic anhydride at 80° gives predominantly the *endo*-form of the addition product (LXXVIII), and at 140° the *exo*-form (LXXIX).[102] Condensation of diphenylfulvene with *N*-methylmaleimide at 80° gave only one addition product (LXXX), which proved to be identical with the compound formed on reaction of compound (LXXVIII) with methylamine, i.e. it has the *endo*-configuration. Subsequent reduction of compound (LXXX) with lithium aluminium hydride gave *endo*-8-diphenylmethylene-2-methyltetrahydro-4,7-methanoisoindoline (LXXVI):




The *exo*-derivative (LXXVII) was synthesised in a similar way via the *exo*-form of the addition product (LXXIX), by the reaction of the latter with methylamine followed by the reduction of *exo*-8-diphenylmethylene-2-methyltetrahydro-4,7-methanoisoindoline-1,3-dione (LXXXI), with lithium aluminium hydride to give compound (LXXVII).

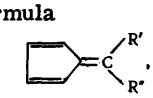
The unusual features of the reactions of compounds (LXXX) and (LXXXI) with perbenzoic acid are also noteworthy[103]. Compound (LXXX) forms an oxygen bridge at the double bond outside the ring to give compound (LXXXII), while compound (LXXXI) forms only the ring epoxide (LXXXIII):




However, the reaction of *endo*-8-diphenylmethylene-2-benzoyltetrahydro-4,7-methanoisoindoline with perbenzoic acid yields a mixture of epoxides (LXXXIV). Selective epoxide formation is probably due to the configuration of the molecule and the presence of the amide group.

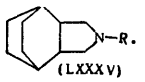
Compound (LXXVI) exhibits pronounced peripheral and central anticholinergic activity. Compound (LXXVII) is somewhat less active.

The authors also prepared a number of compounds, predominantly of the *endo*-series, using different fulvenes having the general formula



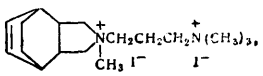
where R′ = R″ = $CH_3$(1), R′ = $C_6H_5$ and R″ = $CH_3$(2), R′ = = $C_6H_5$ and R″ = *p*-$C_6H_4Cl$(3), R′ = $C_6H_5$ and R″ = *m*-$CF_3C_6H_4$(4), R′ = $C_6H_5$ and R″ = *o*-$CH_3C_6H_4$(5), and R′ = $C_6H_5$ and R″ = 2-$C_5H_4N$(6). The compounds obtained included some with anticholinergic activity, but much weaker than that of compound (LXXVI).

Introduction of an ethylene group across positions 4 and 7 of the isoindoline system somewhat alters the mode of action of the substances. For example, among compounds with the general formula (LXXXV), which were obtained by Japanese investigators [104-106],

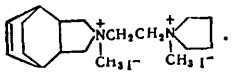


(LXXXV)

Some were found to have ganglion-blocking activity, for example the dimethiodide of 2-($\gamma$-dimethylaminopropyl)--4,7-ethanotetrahydroisoindoline:



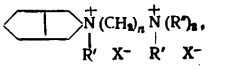
and the dimethiodide of 2-($\beta$-pyrrolidin-1-ylethyl)-4,7--ethanotetrahydroisoindoline:



3-Azabicyclo[3,3,0]octane (X)

Hypotensive activity, ranging from moderate to high, is shown by the following systems: 3-azabicyclo[3,2,1]-octane, 1,8,8-trimethyl-3-azabicyclo[3,2,1]octane, 3-azabicyclo[3,2,0]heptane, and also various modifications of the cyclic systems of isoindoline — 3-azabicyclo[4,3,0]-nonane [80,81,92,93,96,107]. However, the derivatives of 3-azabicyclo[3,3,1]nonane proved to have little or no activity [65]. The sharp difference in activity between compounds (IX) and (VII) led investigators to synthesise derivatives of compound (X) [108] to compare their pharmacological activity with that of 3-azabicyclo[3,2,1]octane.

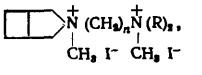
The starting material was the anhydride of *cis*-cyclopentane-1,2-dicarboxylic acid [109], which was converted into the corresponding derivative of compound (X) in the usual way — by reaction with amines followed by reduction with lithium aluminium hydride. The bis-quaternary amines obtained in this way were readily converted into bis-quaternary salts:



with marked hypotensive activity. Thus there is no difference in the mode of action and activity of 3-azabicyclo-[3,2,1]octanes and 3-azabicyclo[3,3,0]octanes.

3-Azabicyclo[3,2,0]heptane (XI)

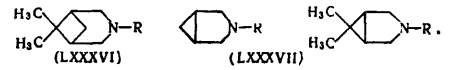
Derivatives of this bicyclic compound were first obtained in 1957 [107] from the anhydride of cyclobutane-1,2--dicarboxylic acid [110], which was converted in the usual way, by reaction with appropriate amines, into a substituted imide and then the corresponding amine. The bis--quaternary salts of this series of compounds exhibit hypotensive activity, the most active among them being, as in the case of isoindolines, substances with the general formula



where $n$ = 2 or 3 and R = $CH_3$ or $C_2H_5$.

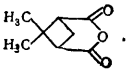
3-Azabicyclo[3,1,1]heptane (XII) and 3-Azabicyclo[3,1,0]-hexane (XIII)

The pharmacologically active bicyclic monoaza-systems which have been described above, can be classified as polymethylenepiperidines and polymethylenepyrrolidines with bridges consisting of 2, 3, and 4 methylene groups. Rice and coworkers synthesised the piperidine (LXXXVI) and pyrrolidine (LXXXVII) derivatives with a bridge containing one methylene group only [111]:



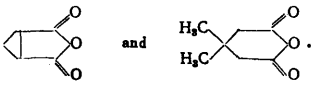
(LXXXVI) (LXXXVII)

The derivative (LXXXVI) was obtained in the usual way from the norpinic anhydride (LXXXVIII). [112]

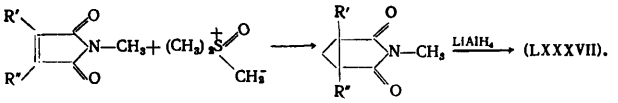


(LXXXVIII)

The synthesis of compound (LXXXVII) was based on the anhydrides [113,114]



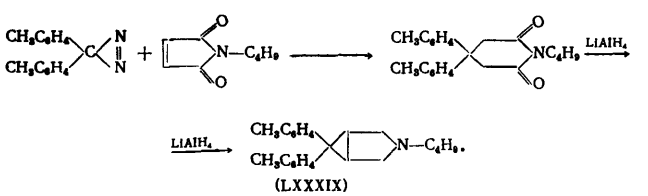
A recent paper describes a new synthesis of cyclopropane-1,2-dicarboximides [115], which consisted in the reaction of substituted *N*-methylmaleimides with trimethylsulphoxonium ylid [116]:



The 3-substituted derivatives of compound (LXXXVII) readily yield bis-quaternary salts, in contrast to the 3-substituted derivatives of compound (LXXXVI) which form bis-quaternary salts only at high temperatures and pressures. A similar difference in behaviour as regards quaternisation was noted earlier for other bicyclic systems containing pyrrolidine and piperidine rings [61,65,81,93].

Among the derivatives of the bicyclic compounds considered here, only the quaternary ammonium salts proved to be active. The dimethiodide of 3-($\gamma$-dimethylaminopropyl)-3-azabicyclo[3,1,0]hexane shows no activity, that of its 6,6-dimethyl homologue is higher, but the highest activity is shown by derivatives of compound (LXXXVI).

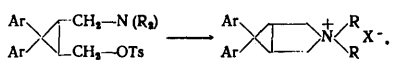
The synthesis of 3-butyl-6,6-ditolyl-3-azabicyclo[3,1,0]-hexane (LXXXIX), involving the reaction of diaryldiazomethane, with *N*-substituted maleimide followed by reduction with lithium aluminium hydride to compound (LXXXIX), was described in 1962. [117]



(LXXXIX)

Similar compounds can be obtained as quaternary salts by the cyclisation of 3-aminoalkyl-1,1-diaryl-2-hydroxy-

methylcyclopropane in the presence of *p*-toluenesulphonyl chloride:



If the tertiary amino-group consists of a piperidine or morpholine residue, spiro-quaternary salts are formed.

Pharmacological study of these compounds showed that the bicyclic imides are inactive; their reduction to the amines results in the appearance of some local anaesthetic and analgesic activity. The quaternary salts are somewhat more active than the tertiary bases, but they are not of practical interest either.


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# POLYMERISATION CONCEPTS IN THE CHEMISTRY OF CEMENTS

Yu. S. Cherkinskii

## 1. INTRODUCTION

The chief chemical elements present in cements are silicon, aluminium, oxygen, and calcium. In the inorganic world, silicon exhibits a remarkable ability to form polymeric chains[1]. These include the homochain polymer formed by elementary silicon, and a large number of heterochain polymers, of which the silicic acids and their salts — the silicates — are most widely encountered in nature and also in practical applications[2-8].

Aluminium is a metallic element but the great majority of its oxygen compounds, e.g. compounds such as corundum and hydrargillite, are heterochain polymers[2,9-13].

Oxygen in the polymeric chains formed by various elements acts as a bridge, and only in the peroxides is it capable of forming a homochain, consisting of two atoms[1].

Calcium on the other hand behaves as a cation.

Since the chief elements present in cements are capable of forming inorganic polymer chains, there is every justification for assuming that polymerisation and depolymerisation processes will also take place in the preparation and hardening of cement.

The ideas of Le Châtelier, subsequently developed by many workers, made it possible to understand the basis of the mechanism of the hardening of inorganic binding agents. In most work devoted to this question, the substance taken as standard model was gypsum — a compound which is not polymeric in character. In some cases, macromolecular compounds were also used as models. While drawing the analogy between the mechanisms of the hardening of cement and joiners' glue or silica gel, however, the supporters of the colloid theory (Michaelis and Kühl) saw in these substances only the high degree of dispersion, the high specific surface, and the ability to take part in sorption processes[14,15].

Modern theoretical views on the mechanism of the hydration hardening of cement are based on the concepts of physicochemical mechanics, whose basis principles were developed by Rebinder[16,17].

Work by Bernal[18], Belov and coworkers[19,20], and others established that the products of the hydration hardening of Portland cement contain isolated units of calcium hydrosilicates and compounds containing chains of condensed silicon–oxygen tetrahedra, i.e. polysiloxane chains. The periodicity of the manifestation of binding properties, related to Mendeleev's Table, was established by Zhuravlev[21] and confirmed by Moshchanskii[22].

In an examination of cement and concrete from the viewpoint of the chemistry of macromolecular compounds, Korshak and Mozgova[2] put forward the idea that "cement and concrete contain inorganic silicate polymers". The suggestion that silicate cements be regarded as three-dimensional polymers had been put forward earlier, in

less explicit form[11]. More recently the question of polymerisation has been raised with increasing frequency in papers devoted to inorganic binding agents[23-29].

The basic questions of the chemistry of Portland cement and alumina cement are considered below from the viewpoint of polymerisation reactions.

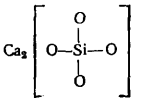
## 2. PORTLAND CEMENT

The raw material used for the preparation of Portland cement contains, firstly, elements capable of forming macromolecular compounds with oxygen (chiefly silicon and aluminium) and, secondly, an element (calcium) which acts as a cation.

Silicon and aluminium are introduced into the charge in the form of natural (clays, loams, or clay shales) or synthetic (e.g. the waste materials from the production of aluminium from nephelite) macromolecular compounds whose structure has a definite influence on the preparation of the clinker[30-33]. Calcium is introduced into the charge in the form of lime or limestone.

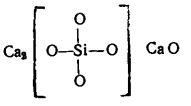
Preparation of cement. It is possible to distinguish the following main stages in the firing of the charge: (1) drying and preheating; (2) depolymerisation; (3) ionic solution; (4) cooling. From the viewpoint of polymerisation theories, the second and third stages are the most important and the most complex.

The second stage, which gives a monomeric silicon–oxygen compound by the thermal depolymerisation of the original polysiloxane (polyaluminosiloxane) in the presence of oxygen and calcium ions, is a *necessary* stage in the preparation of the binding agent, but this stage is still *insufficient* for the preparation of a binding agent which hardens rapidly. The process taking place in the solid phase[34] at this stage leads to the formation of belite, the chief component of which is calcium orthosilicate — a monomeric silicon–oxygen compound[35-38]



or $2CaO \cdot SiO_2$.

The preparation of the highly active binding agent alite, whose chief component is again the monomeric silicon–oxygen compound $3CaO.SiO_2$ or[38-42]




takes place in the third stage as a result of a liquid-phase process. This stage can be defined more precisely as the ionic solution stage[43-47]. This subdivision of the process of clinker preparation is not contradicted by a large amount of experimental data[48-54].

In the preparation of Portland cement, the macromolecular component of the charge — clay — is heated to a high temperature. Clay also forms ceramic tile. In the preparation of Portland cement, however, the clay is converted not into water-resistant ceramic but into a substance which exhibits new binding properties.

What is changed during the high-temperature transformation of the clay and at what stage does the change take place?

The first stage in the transformation of the original polyaluminosiloxane (the clay minerals) is evidently of the same general type in both cases and involves thermal depolymerisation.

The two processes differ in the subsequent stage, in which in the first case the products of the degradation of the polyaluminosiloxane are converted into inorganic macromolecular compounds of a new type as a result of thermal polymerisation (polyrecombination) on cooling. These include a vitreous phase, mullite, and certain other substances which form the basis of ceramics and porcelain. Depolymerisation in the case of kaolinite, for example, begins in the range of the endothermic effect (520–600°), whereas polyrecombination takes place at 900–1000° and is responsible for a sharp exothermic effect[55-59].

In the preparation of cement, the changes in the polymers taking place in a medium of calcium ions (and oxygen) stops at the depolymerisation stage, and the resulting monomeric silicon–oxygen groups (and polyaluminooxane chains) are fixed by the calcium ions, which prevent polymerisation in the melt during cooling.

Thus the changes in the silicon–oxygen component of a Portland cement charge are described by the left-hand side of the scheme illustrated in Fig. 1.

Clinker. The hydraulic activity of Portland cement clinker is determined chiefly by the presence of monomeric silicon–oxygen compounds taken in the form of the calcium salts (or strontium or barium salts[21]). Increase in the defect nature of the structure leads to an increase in the activity of the binding agent[41,60].

Reaction with water. The reaction of cement with water (with chemistry of the hardening process) is described by the right-hand side of the scheme (Fig. 1).

In the reaction of clinker (here and subsequently we shall refer to the silicate component, namely dicalcium silicate, but it should be noted that the aluminate and ferrite components also play some part in Portland cement) with water leads, as a result of the hydrolysis of calcium orthosilicate, to the formation of orthosilicic acid[61-63]:

$$Ca_2SiO_4 + 4H_2O \rightarrow 2Ca^{2+} + 4OH^- + H_4SiO_4, \quad (1)$$

which is an extremely unstable compound.

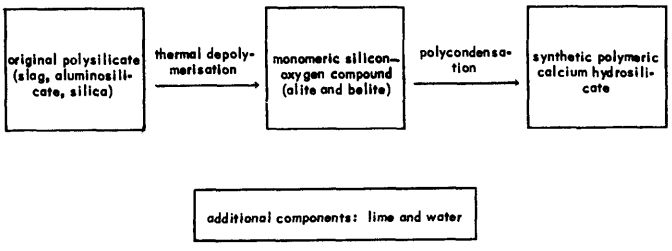



Fig. 1. Polymeric changes undergone by the silicate component of Portland cement.

Under the conditions of setting, the orthosilicic acid formed takes part in reactions of salt formation and polycondensation.

a. Salt formation:

$$\equiv Si-O^-H^+ + Ca^{2+} + 2OH^- \rightleftarrows \equiv Si-O^-Ca^{2+} + OH^- + H_2O. \quad (2)$$

This reaction involves the calcium ions which were liberated as a result of the hydrolysis of calcium orthosilicate, and also the "excess of lime" in $C_3S$. [64-66]. Under ordinary conditions, however, the hydrolysis is irreversible and reaction (2), when orthosilicate is taken as the original silicic acid, leads to the formation of acid salts of the afwillite type [67]. Orthosilicate is formed only under conditions of extremely high temperatures and pressures [67-68].

b. The polycondensation reaction is represented in general form by the equation

$$HO-\underset{\underset{OH}{|}}{\overset{OH}{|}}{Si}-OH + HO-\underset{\underset{OH}{|}}{\overset{OH}{|}}{Si}-OH \rightleftarrows HO-\underset{\underset{OH}{|}}{\overset{OH}{|}}{Si}-O-\underset{\underset{OH}{|}}{\overset{OH}{|}}{Si}-OH + H_2O, \quad (3)$$

or, in the limit,

$$n Si(OH)_4 \rightleftarrows (SiO_2)_n (OH)_m + p H_2O, \quad (4)$$

where $m \to 0$ and $p = \frac{4n - m}{2}$.

Opinions differ regarding the details of the mechanism of the polycondensation reaction [69-73] and the probability of condensation of $H_3SiO_4^-$ ions in alkaline medium has also been noted [74,75].

Reactions (2) and (3) take place simultaneously and the direction of the chemical reactions is decided by competition between these two types (ionic and molecular) of chemical change.

A vast amount of practical experience and experimental and theoretical data [76] indicate that the tendency of orthosilicic acid to undergo polycondensation is so great that this molecular reaction is one of the chief reactions determining the chemistry of the aqueous hardening of Portland cement and, in particular, the behaviour of cement block kept in water.

The equilibrium for the polycondensation reaction always tends to be displaced towards the formation of polymeric silicates; this takes place at the first opportunity, and in the limit leads to the formation of silica $(SiO_2)_n$. In the presence of calcium ions, however, monomeric calcium hydrosilicates (acid salts of orthosilicic acid), e.g. afwillite and the alpha-hydrate of $C_2S$, and polymeric hydrosilicates (salts of di- and poly-silicic acids) are formed. According to the phase diagram for the $CaO-SiO_2-H_2O$ system at normal temperature [18], hydrosilicates with a molar $CaO : SiO_2$ ratio less than 5 : 3 are polymeric, although polymeric calcium silicates (hillebrandite) with higher $CaO : SiO_2$ ratios are also known.

Calcium hydrosilicates. The composition and structure of individual calcium hydrosilicates in a number of cases have been established with certainty and in other cases they have been assumed [20,77,78]. On the basis of polymerisation principles, calcium hydrosilicates can be divided into two main groups: low-molecular and macromolecular (or simply polymeric).

Low-molecular calcium hydrosilicates include compounds with a monomeric or dimeric silicon–oxygen anion.

a. Compounds containing a monomeric silicon–oxygen anion include, for example, afwillite $Ca_3[SiO_3(OH)].2H_2O$ [79] and the alpha-hydrate of $C_2S$. [38] Afwillite and other calcium hydrosilicates containing an individual silicon–oxygen group and consisting of a definite combination of Si tetrahedra and hydroxide and calcium ions are the first members of a polymer homologous series of calcium polyhydrosiloxanates, whose existence is possible under conditions where the active degrading action of the calcium ions is a maximum.

b. Compounds with a dimeric silicon–oxygen anion include those of the cuspidine type $Ca_4[(Si_2O_7)(OH, F)_2]$. [80,81]

These hydrosilicates can be regarded as the second members of the above polymer homologous series. Calcium hydrosilicate containing a diorthosilicate anion obeys the crystal-chemical laws covered by the second chapter of "The Crystal Chemistry of Silicates Containing Large Cations". [19] It can therefore be regarded as the first member in a series of crystallographically and chemically similar calcium hydrosilicates in which the individual or linked diorthosilicate units are situated in the electric field of the calcium ions.

It is possible to assume the existence of the various [67] subsequent members of the polymer homologous series of calcium polyhydrosiloxanates, but it is more important to turn attention to the macromolecular compounds whose molecular or, more accurately, ionic weight amounts to several thousand units.

Macromolecular calcium hydrosilicates have ordered or disordered structures. Compounds with ordered structure include xonotlite $Ca_6(Si_6O_{17})(OH)_2$, [82,83] nekoite $Ca_3(Si_6O_{15}).2H_2O$, [84] and tobermorite $Ca_{10}(Si_{12}O_{31}).(OH)_6.nH_2O$. [66,85,86]

The first type of hydrosilicate has a polymeric silicon–oxygen anion in the form of linked six-unit rings [82]; the silicon–oxygen chain of hydrosilicates of the nekoite type consists of alternating eight-membered and double five-membered rings [84]. The chain in tobermorite is made up of doubled xonotlite chains which fit over one another in the condensation process to form corrugated layers [80].

Examination of polymeric calcium hydrosilicates shows that the structure of the silicon–oxygen chain may be comparatively simple or extremely complex.

The even greater complexity of the structure of the silicon–oxygen polymeric anion produced in the polycondensation process or on rearrangement of the ordered structure makes it impossible to determine the structure by existing crystallographic and chemical methods. These calcium hydrosilicates are combined in a subgroup of polymers with disordered structure. They include the gel-like phase and the X, Y, and Z phases [77,78].

Polymeric hydrosilicates and some properties of concrete. Belov attributes the cementing properties to polymeric hydrosilicates of the xonotlite type [42,80]. On the other hand, it has been noted [20] that the strength of cements decreases with the formation and increase in the quantity of the low-molecular readily-crystallising afwillite and the alpha-hydrate of $C_2S$.

The concentration of polymeric calcium hydrosilicates can be increased artificially; this increases the bending strength of the concrete but decreases the rate of hardening[87,88]. In practice, this is usually achieved by introducing, with the clinker, substances capable of forming polymeric hydrosilicates under the conditions of setting. These substances include silica gel, pozzolana, and diatomite, i.e. familiar mineral additives.

The chemical changes undergone by these additives are also defined by the scheme given in Fig. 1 with the fundamental difference that in this case the depolymerisation of the polysiloxane takes place as a result of the hydrolysis (hydrolytic depolymerisation) of the –Si–O–Si– siloxane bond under the influence of aqueous calcium hydroxide solution[89-93]. The depolymerisation leads to the formation of orthosilicic acid, which condenses according to the mechanism described above; the excess of the silicon–oxygen component makes it possible to increase the quantity of polymeric phase. Similar processes also take place in the preparation of autoclave silicate concretes[77]; the activation of the silicon–oxygen component as a result of the increase in temperature makes it possible to utilise effectively both calcium orthosilicate and metasilicate as well as silica[94].

The most important property of Portland cement — its hydraulic resistance — is determined by the ability of the original clinker materials and their hydrolysis products to form polymeric compounds — polymeric calcium hydrosilicates — since of the ionic and covalent bonds present in the products obtained by hydration hardening, only the covalent bond is sufficiently resistant to the action of the polar solvent water. Although in actual fact the quantity of polymeric silicates (crystalline silicates and the "amorphous" gel-like phase) in cement block is small, the thick network of siloxane chains formed when the cement block comes into contact with water is capable of blocking to a considerable extent the ionogenic components — lime and calcium ions; these are chemisorbed by the polymeric silicate, which prevents them from coming into contact with water and dissolving.

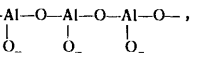
Methods of increasing the quantity of polymeric phase. One possible method of increasing the concentration of polymeric calcium hydrosilicates in concrete involves the use of active mineral additives. Autoclave silicate concretes and limestone–pozzolana concretes also contain a high concentration of polymeric calcium hydrosilicates.

The polymerisation reaction scheme (Fig. 1) may facilitate the search for other methods of preparing inorganic polymeric materials of the silicate–concrete type.

## 3. ALUMINA CEMENT

Raw material. The raw materials used for the preparation of alumina cement[38,95,96] include, firstly, polymeric coordination compounds of aluminium, such as hydrargillite, boehmite, and diaspore[9,11,12,97-104], and, partly, of iron (haematite), together with a small quantity of a silicate component which we shall not consider in this Section. The second component is lime (limestone).

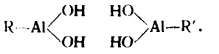
Preparation of cement. After the first preliminary stage involving drying, the second stage of the preparation of cement at temperatures up to approximately 500–600° involves the removal of water from hydrated forms of aluminium, i.e. deolation of hydrargillite (polyaluminodiolane) takes place. With further heating in the presence of $Ca^{2+}$ ions and oxygen, thermal depolymerisation takes place (see scheme in Fig. 2), accompanied by a change in the coordination number (c.n.) of the aluminium atoms from 6 to 4 and leading to the formation of calcium polyaluminooxanate (c.n. Al = 4) containing the chain



or, which is the same thing: $CaO.Al_2O_3$, CA, or $Ca(AlO_2)_2$. The formation of $Ca(AlO_2)_2$ takes place in the liquid phase and it is suggested[105] that the melt contains complex ions. Cooling of the melt is accompanied by thermal polymerisation of calcium aluminooxanates.

Clinker. The instability of oxygen compounds of aluminium with c.n. Al = 4 and their tendency to undergo conversion into stable oxygen compounds with c.n. Al = 6 are the chief factors determining the activity of alumina cement clinker, in which the chief component is calcium polyaluminooxanate (c.n. Al = 4).

Reaction with water. The first stage in the reaction of calcium aluminate (calcium polyaluminooxanate) with water involves rupture of the $^4Al–O–^4Al$ aluminooxane bond as a result of hydration, or more accurately as a result of the olation reaction specific for coordination compounds of aluminium (c.n. Al = 4).[98] During olation, the aluminooxane bond is first converted into the diol bond $R–Al<^{OH}_{OH}>Al–R'$, after which chain rupture takes place with the formation of two hydroxyl groups at the ends of the chain



During olation, the coordination number of the aluminium atom increases from 4 to 6 and the calcium ions go into solution.

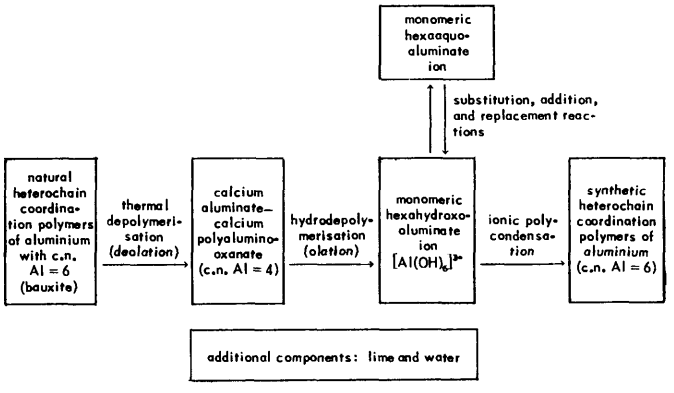


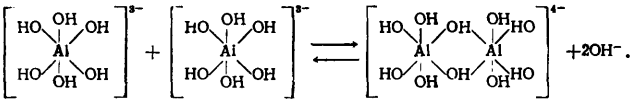

Fig. 2. Polymeric changes undergone by the aluminate component of alumina cement.

At the end of the first stage, further development of the olation process takes place, leading in the limit to the complete degradation of the polyaluminooxane (c.n. Al = 4) with the formation of a monomeric hydrated compound of aluminium with c.n. Al = 6, namely the $[Al(OH)_6]^{3-}$ anion.

Main reactions and compounds obtained. In order to picture the possible reactions in which the hexahydroxoaluminate ion may take part, we may recall that according to the modern theory of hydro-complexes [98,106,107], the amphoteric nature of aluminium hydroxide (hydrargillite) is expressed by the equation

$$[Al(OH)_6]^{3-} \overset{H_3O^+}{\rightleftharpoons} [Al(OH)_3(H_2O)_3] \overset{H_3O^+}{\rightleftharpoons} [Al(H_2O)_6]^{3+}.$$
$$\Big\| \; n\,[Al(OH)_3]_n$$
hydrargillite

The hexahydroxoaluminate ions undergo ionic condensation, probably according to the equation [108]



The dimeric ion undergoes further condensation with a monomeric ion with the formation of a trimer, hexamer, etc.; the hexamer undergoes ring closure and in the limit forms aluminium hydroxide — hydrargillite — a planar polymer with a reticulate structure made up of linked six-membered rings.

Both the monomeric and the more complex anions react with cations, particularly the $Ca^{2+}$ ion, to form salts, some of which are listed in Table 1, which gives complex compounds of aluminium in which the aluminium atom is present in a complex anion and in which only the limiting member of the series — hydrargillite — is neutral.

Hydrargillite exhibits one other characteristic feature. It is the most stable hydrated compound of aluminium in the biosphere [109].

It may therefore be stated that in the limit the reaction of calcium aluminate with water when $Ca^{2+}$ ions are deficient, leads to the formation of hydrargillite.

In an examination of the behaviour of the monomeric $[Al(OH)_6]^{3-}$ ion, it should be noted that the $OH^-$ groups in the inner coordination sphere of the aluminium atom may be replaced by univalent ($Cl^-$, $F^-$) or multivalent anions.

An important case in the chemistry of cement is that where the ligand is orthosilicic acid. In this case, inner-sphere substitution taking place under hydrothermal conditions [110] leads to the formation of a separate series of hydrogarnets and, in the limit, of the garnet grossular [the fraction indicates the proportion of the $(SiO_4)^{4-}$ ligand corresponding to one Al atom in the complex] (see p. 456).

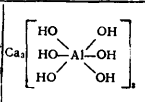
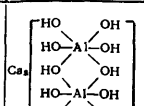
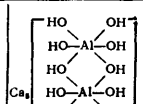
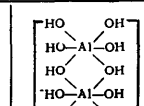
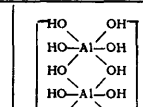
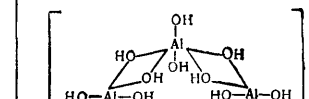
$$[Al(OH_6)]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot 6H_2O \rightarrow$$
$$\rightarrow [(OH)_6Al(SiO_4)_{1/4}]_2Ca_3 \equiv 3CaO\ Al_2O_3 \cdot {}^1/_3SiO_2 \cdot 5H_2O \rightarrow$$
$$\rightarrow [(OH)_4Al(SiO_4)_{2/4}]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O \rightarrow$$
$$\rightarrow [(OH)_2Al(SiO_4)_{3/4}]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot 1^1/_2SiO_2 \cdot 3H_2O \rightarrow$$
$$\rightarrow [(OH)_2Al(SiO_4)_{1/4}]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow$$
$$\rightarrow [(OH)\,Al(SiO_4)_{3/4}]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot 2^1/_2SiO_2 \cdot H_2O \rightarrow$$
$$\rightarrow [Al(SiO_4)_{6/4}]_2Ca_3 \equiv 3CaO \cdot Al_2O_3 \cdot 3SiO_2.$$

That this process is correct is confirmed by the preparation of the first, third (plazolite), fourth, fifth, and seventh compounds [111-113]; compounds with compositions close to those of the second [114,115] and sixth [111] compounds have also been prepared. The second and subsequent garnets are polymeric: the inner coordination spheres of the Al atom are joined by $(SiO_4)^{4-}$ groups.

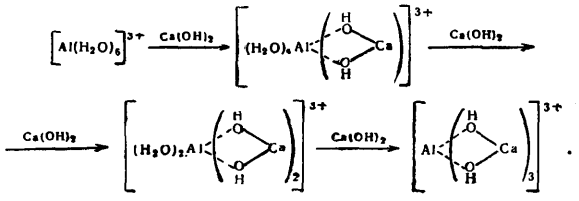
In addition, because of the amphoteric nature of aluminium, formation of the $[Al(H_2O)_6]^{3+}$ ion is also possible (see scheme in Fig. 2).

The behaviour of the $[Al(H_2O)_6]^{3+}$ cation, which is capable of forming salts with anions, differs fundamentally from that of $[Al(OH)_6]^{3-}$. First of all it should be noted that in calcium hydroxide and calcium sulphate solutions coordination compounds are formed, as a result of inner-sphere substitution, in which two aquo-groups in the inner-sphere

TABLE 1. Series of aluminodiolanes.

| Type | Anion | | | | | | |
|---|---|---|---|---|---|---|---|
| | monomeric | dimeric | trimeric | tetrameric | pentameric | hexameric | polymeric |
| Ratio OH/Al | 6 | 5 | 4.67 | 4.5 | 4.4 | 4 | 3 |
| *Oxide formula* | $3CaO \cdot Al_2O_3 \cdot 6H_2O$ | $2CaO \cdot Al_2O_3 \cdot 5H_2O$ | $5CaO \cdot 3Al_2O_3 \cdot 14H_2O$ | $3CaO \cdot 2Al_2O_3 \cdot 9H_2O$ | $7CaO \cdot 5Al_2O_3 \cdot 22H_2O$ | $CaO \cdot Al_2O_3 \cdot 6H_2O$ | $Al_2O_3 \cdot 3H_2O$ |
| Chemical structural formula |  |  |  |  |  |  | hydrargillite (hydrated aluminium oxide) $[Al(OH)_3]_n$ |

of the central atom are replaced by one molecule of calcium hydroxide, which occupies two coordination positions:



The calcium hydroxide molecules present in the inner coordination sphere of the Al atom in the calcium hydroaluminates formed during the hydration of alumina cement can be characterised as "combined lime".

When the complex cation is considered from the viewpoint of the octahedral model, a number of possibilities arise. The two calcium hydroxide molecules may be present in the complex in either the *trans*- or *cis*-positions; in the latter case, optically active forms are produced.

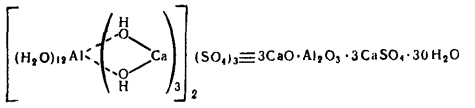
The complex containing three calcium hydroxide molecules should also exist in the form of mirror isomers or a racemate.

The $[Al(H_2O)_6]^{3+}$ cation or its derivatives containing calcium hydroxide molecules react with anions to give compounds with $[Al(OH)_6]^{3-}$, $OH^-$, $Cl^-$, $SO_4^{2-}$, etc. in the outer coordination sphere.

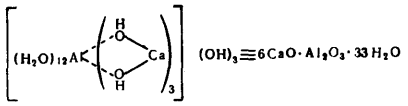
Table 2 gives complex cations which contain a central aluminium atom and can be regarded as derivatives of the $[Al(H_2O)_6]^{3+}$ ion. Thus the water present in the "oxide" formulae should be regarded as water of constitution, removal of which (particular attention must be paid to the possibility of hydrate isomerism) leads to breakdown of the coordination compound.

Calcium hydroaluminates containing much larger quantities of water are also known.

Deval's salt [116]



and hexacalcium hydroaluminate

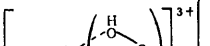
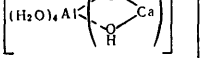
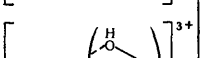
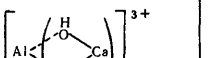


are super-complex compounds [117] in which the coordination sphere of the Al atom contains 12 "additional" water molecules.

Thus in the products of the hydration hardening of monocalcium aluminate it is necessary to distinguish the following [118].

1. Products of the incomplete hydration (olation) of monocalcium aluminate — calcium polyaluminooxanate with c.n. Al = 4.

TABLE 2. Most important hydroaluminates containing the Al atom in a complex cation.

| Cation | Anion | | | |
|---|---|---|---|---|
| | $[Al(OH)_6]^{3-}$ | $(OH)^-$ | $Cl^-$ | $(SO_4)^{2-}$ |
|  | $Al(OH)_3$ (hydrargillite) | $Al(OH)_3$ (hydrargillite) | $AlCl_3 \cdot 12H_2O$ | $Al_2(SO_4)_3 \cdot 12H_2O$ |
|  | $CaO \cdot Al_2O_3 \cdot 8H_2O$ | $2CaO \cdot Al_2O_3 \cdot 13H_2O$ | — | $2CaO \cdot Al_2O_3 \cdot 3H_2SO_4 \cdot 7H_2O$ |
|  *trans*- and *di-cis*-forms | $2CaO \cdot Al_2O_3 \cdot 7H_2O$ | $4CaO \cdot Al_2O_3 \cdot 11H_2O$ ($\alpha$-, $\beta$-, and $\gamma$-forms, hydrocalumite) | — | $CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 8H_2O$ |
|  *di-cis*-forms | $3CaO \cdot Al_2O_3 \cdot 6H_2O$ | $6CaO \cdot Al_2O_3 \cdot 9H_2O$ | $3CaO \cdot Al_2O_3 \cdot 3CaCl_2 \cdot 6H_2O$ | $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 6H_2O$ |

2. Coordination compounds of aluminium in which the aluminium atom (c.n. Al = 6) is present in a complex *anion*: (a) aluminolanes — monomeric (cubic $3CaO.Al_2O_3.6H_2O$), dimeric, and in the limit polymeric (hydrargillite) coordination compounds of aluminium; (b) inner-sphere substitution products in which the inner coordination sphere of the aluminium atom contains the ligands $Cl^-$, $(SiO_4)^{4-}$ — in the latter case the products are garnets and hydrogarnets (it is necessary to distinguish polymeric forms).

3. Coordination compounds of aluminium in which the aluminium is present in a complex *cation*, surrounded by $H_2O$ and $Ca(OH)_2$ ligands. This group includes hydrocalumite, calcium hydrochloroaluminate and hydrosulphoaluminate, etc.

4. Products obtained as a result of the deolation of hydrargillite, e.g. boehmite.

Additives to the cement. Since the polymeric components of concrete based on alumina cement are polyaluminodiolanes, hydrated forms of aluminium are used as characteristically active hydraulic additives to alumina cement.

Tervalent iron, like aluminium, is capable of forming polymeric coordination compounds [118], so that hydrated and oxide forms of iron, and also calcium ferrites, have no harmful action in alumina cement.

## SUMMARY

The ability of oxygen compounds of silicon and aluminium to undergo polymerisation and depolymerisation has a marked influence on the preparation of cement clinker, the reaction of the latter with water, and the properties of concretes. Polymeric compounds are present in the products of hydration hardening and also in the original raw material and the hydraulic additives. It is these polymeric compounds which determine to a considerable extent the technological methods for the processing of the raw material and the properties of cements and concretes. All this indicates that macromolecular compounds and inorganic binding agents (cements) are similar in character. The

main characteristic feature common to these two groups of substances is the presence of chains formed by covalently bound atoms.

In view of the important part played by polymeric substances in cements and concretes, the chemistry of Portland cement and alumina cement is an important field of the chemistry of silicon and aluminium polymers. The chemistry of cements leads to new synthetic procedures in the chemistry of macromolecular compounds.

Cements have their own characteristic features, shown only by this type of substance, so that the group of inorganic binding agents includes both cements and gypsum, magnesia, and lime binding agents.

During the hydration hardening of all inorganic binding agents, a fundamentally new disperse phase — new formations — not previously present in the system are formed from aqueous solution (the water not only acts as a dispersion medium but also takes direct part in the chemical reaction). The part played by the processes leading to the formation of the crystalline aggregate, in particular cement block, in the technological processes for the production of concretes is so great that up to the present the main attention has been directed to these processes. The similarity of these processes for a variety of substances has led to their classification as inorganic binding agents.

At the same time it is convenient to distinguish inorganic binding agents according to the possibility of formation and actual formation of polymeric chains; the latter are characteristic of Portland cement and alumina cement but not of gypsum.

Thus in an examination of inorganic binding agents (cements) it is necessary to take account of the dual nature of the chemical bonding (ionic and covalent) as a result of which the atoms joined to one another are capable of forming polymeric chains in these substances, and also of the chemical and physicochemical processes taking place during the preparation and hydration hardening of the binding agent. This becomes possible if cements are approached from the viewpoint of polymerisation and crystallisation theories[28]. A one-sided approach to cements will not reveal the great variety in their properties.


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# GRAFT COPOLYMERS OF CELLULOSE AND ITS DERIVATIVES

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## I. INTRODUCTION

The controlled modification of the properties of cellulose and its derivatives by the synthesis of graft copolymers based on them undoubtedly provides one of the most promising and effective methods for improving the quality and extending the range of application of cellulosic materials.

Several cellulosic materials possessing valuable new properties have already been obtained by the synthesis of graft copolymers. For example, cellulosic materials which are completely resistant to the action of microorganisms can be prepared by grafting on various carbon-chain polymers, and improved stability to light and heat is achieved by the synthesis of graft copolymers with polyacrylonitrile. Non-flammable cellulosic materials can be obtained by the grafting on of polymers containing phosphorus or chlorine; the grafting of water-repellent carbon-chain or silicon-containing polymers confers water-repellent properties and improved resistance to acids. The synthesis of graft copolymers of cellulose with a definite class of synthetic polymers makes it possible to

have cellulosic materials possessing specific new properties, in particular ion-exchange and bactericidal properties. The possibility of a controlled variation in the properties of cellulosic materials by the synthesis of graft copolymers is responsible for the interest taken by research workers in this method of modifying the properties of cellulose and its derivatives [1-16].

It is possible to envisage two main ways in which graft copolymers of cellulose and its esters can be synthesised — (1) by the synthesis of graft copolymers which are then processed into materials (fibres, films, etc.), and (2) by direct grafting to ready-made articles.

Each of these methods has its advantages and disadvantages. The advantages of the first method are — (*a*) the production in most cases of materials (fibres, films) having improved physical and mechanical properties, since in this case not only the macromolecules of the original cellulose derivative but also graft chains of synthetic polymers are involved in forming the supermolecular structures, and (*b*) the possibility of using a mixture of the graft copolymer and the homopolymer joined to it. A serious defect of the method is the impossibility of using it to obtain fibres and films of graft copolymers of cellulose, since such products are not usually soluble and do not show viscous flow.

The second method is considerably more promising and versatile. If certain requirements, indicated below, are satisfied, this method may find wide practical application in the immediate future. A method of synthesising graft copolymers which is acceptable in practice for the modification of ready-made goods must evidently satisfy the following requirements: (1) graft copolymerisation should occur without formation of the homopolymer; in isolated cases the homopolymer may be formed directly on the cellulosic material (not in the reaction medium), and then the homopolymer should not be removable when the goods are in service; (2) the synthesis of graft copolymers must be achieved without the use of organic solvents; and (3) the grafting process should not be accompanied by appreciable degradation of cellulose or its derivatives. It is also desirable that the method should permit ready control of the length and number of the graft chains, so that the properties of the graft copolymers can be varied without changing their composition.

In principle the synthesis of graft copolymers, like that of polymers in general, can be effected by the known reactions of polycondensation, polymerisation of rings, and chain polymerisation. A specific method for the synthesis of graft copolymers is the possibility of their production by the interaction of two polymers.

Below are considered the principal methods which have been proposed for the synthesis of graft copolymers of cellulose. These methods can be employed also to obtain graft copolymers based on other macromolecular compounds. The present review is confined to results obtained in the synthesis of graft copolymers of cellulose and its derivatives.

## II. SYNTHESIS OF GRAFT COPOLYMERS BY POLYCONDENSATION

Rogovin and his coworkers have synthesised graft copolymers of cellulose and its esters with polyamides by polycondensation of the monomer as a result of interaction with the functional group of the cellulose derivatives.

Polycondensation of methyl 7-aminoheptanoate, in the presence of methyl ethers of carboxy-containing polysaccharides (carboxymethylcellulose, dicarboxycellulose, alginic acid) or their amides with methyl 7-aminoheptanoate, yields graft copolymers of the cellulose derivatives with polyamides, together with a large quantity of the homopolyamide [17,18]. The reaction takes place according to the scheme

$$\text{poly-saccharide}\text{—}COOCH_3 + nH_2N(CH_2)_6COOCH_3 \xrightarrow[Ar]{100-110^\circ} \text{polysaccharide}\text{—}CONH(CH_2)_6COOCH_3 \rightarrow$$
$$\rightarrow \text{polysaccharide}\text{—}CO[NH(CH_2)_6CO]_xOCH_3 + H[NH(CH_2)_6CO]_yOCH_3 + (n-2)\,CH_3OH \quad (1)$$
(where $x+y=n$).

Graft copolymers of cellulose and polyamides have been synthesised [18] by treating cellulose with the hydrochloride of 7-aminoheptanoyl chloride in an organic base

$$\text{Cell}\text{—}OH + nClOC(CH_2)_6NH_2\cdot HCl \rightarrow$$
$$\rightarrow \text{Cell}\text{—}OCO(CH_2)_6NH[CO(CH_2)_6NH]_xH + H[NH(CH_2)_6CO]_yOH + nHCl \quad (2)$$
(where $x+y=n$).

When sodium cellulose xanthate is employed as starting material, the process can be carried out at the interface [18].

The complicated preparation of the initial cellulosic derivatives, the necessity of employing organic solvents, and the formation of a considerable quantity of homopolymer together with the graft copolymer at the present time prevent the practical application of these methods of synthesising graft copolymers.

## III. SYNTHESIS OF GRAFT COPOLYMERS BY THE INTERACTION OF TWO POLYMERS

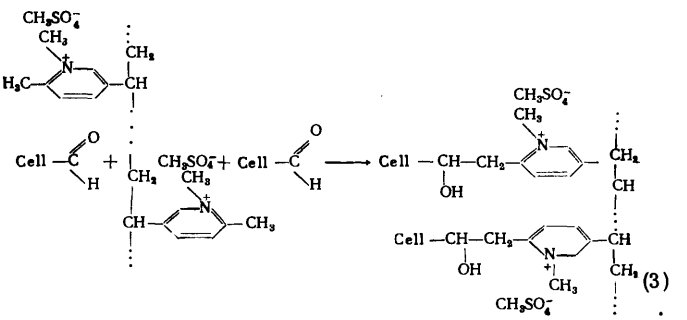
The chief advantage of this method is the possibility of synthesising graft copolymers having main and graft chains of specified length. The method is used to obtain graft copolymers based on synthetic polymers, but finds limited application for the modification of cellulosic derivatives.

Graft copolymers having a main chain of cellulose and protein side-chains have been obtained by condensation. These products are of great interest for polymer chemistry. In order to synthesise cellulose–protein graft copolymers, cellulose azide is condensed with proteins containing free amino-groups:

$$\text{Cell}\text{—}CON_3 + H_2N\text{—}\text{Prot} \rightarrow \text{Cell}\text{—}CONH\text{—}\text{Prot}.$$

Graft copolymers differing in composition can be obtained according to the concentrations of the two components in the reaction mixture. If the concentration of protein is considerably increased, insoluble products are formed [19].

Copolymers of three-dimensional structure have been synthesised by the interaction of cellulose acetate toluene-*p*-sulphonate and dialdehydocellulose with poly-2-methyl-5-vinylpyridine or a quaternary salt thereof [20]. When dialdehydocellulose is used, the reaction proceeds according to the scheme


(3)

Reaction between cellulose acetate toluene-*p*-sulphonate and poly-2-methyl-5-vinylpyridine is brought about by a method similar to that used to synthesise graft copolymers of poly(vinyl chloride) and methylvinylpyridine rubber[21]. Practical application of this method for the modification of cellulose is made difficult by the complexity of the synthesis of the initial cellulose derivatives and the insolubility of the final product.

## IV. SYNTHESIS OF GRAFT COPOLYMERS BY THE POLYMERISATION OF RINGS

When strained rings (ethylene oxide, ethyleneimine, β-propiolactone) are polymerised in the presence of alkali-cellulose, homopolymerisation and formation of cellulose ethers are probably accompanied by the formation of graft copolymers[22-25]:

$$\text{Cell}-\text{OH}+n\text{CH}_2\!-\!\text{CH}_2 \begin{cases} \rightarrow \text{Cell}-\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{H} \\ \rightarrow \text{Cell}-\text{OCH}_2\text{CH}_2\text{OH} \end{cases} \quad (4)$$

Formation of a graft copolymer by the interaction of aziridine (ethyleneimine) and alkali-cellulose has been demonstrated experimentally by isolating the grafted polyethyleneimine by hydrolysis of the cellulose followed by esterification of the glucopyranose end-group with benzoyl chloride[26]. The degree of polymerisation of the isolated polymer did not exceed 6.

It is of interest to undertake similar investigations on the products formed by cellulose with oxiran (ethylene oxide). The simplicity of their preparation and their several valuable properties (in particular solubility in water) of such products have provided reasons for their practical utilisation[27].

Graft copolymers of cellulose and polyethyleneimine are also of definite practical interest for obtaining cellulosic materials possessing specific properties (bactericidal power, non-flammability, etc.).[26,28-30] A final conclusion concerning the advisability of the practical application of products formed by the interaction of cellulose with ethyleneimine may be reached after determining the relative quantities of monomer which have reacted with the cellulose and have been used up in homopolymerisation.

American research workers, having studied the conditions for the synthesis of derivatives of cellulose and poly-β-propiolactone, and also the properties of these products, concluded that their practical application would serve no useful purpose[31-34].

The principal defect in the above methods for synthesising graft copolymers is the considerable loss of monomer by homopolymerisation.

Rogovin and Wu Jung-jui proposed a method for obtaining graft copolymers of carboxymethylcellulose and polycaprolactam which excludes formation of the homopolyamide[35]. Synthesis of the graft copolymer is effected by polymerising caprolactam in the presence of chloroformylmethylcellulose and sodium caprolactam. In the first stage of the reaction an imide of caprolactam and carboxymethylcellulose is formed, with polymerisation of the caprolactam, in the presence of which graft copolymers are formed:

$$\text{Cell}-\text{OCH}_2\text{COCl} \xrightarrow{\text{NaN}(\text{CH}_2)_5\text{CO}} \text{Cell}-\text{OCH}_2\text{CON}(\text{CH}_2)_5\text{CO} \xrightarrow[70-80^\circ,\ \text{Ar}]{n\text{HN}(\text{CH}_2)_5\text{CO}} \xrightarrow[70-80^\circ,\ \text{Ar}]{n\text{HN}(\text{CH}_2)_5\text{CO}} \text{Cell}-\text{OCH}_2\text{CO}[\text{HN}(\text{CH}_2)_5\text{CO}]_{n-1}\text{N}(\text{CH}_2)_5\text{CO}. \quad (5)$$

The employment of chloroformylmethylcellulose and sodium caprolactam for the synthesis of graft copolymers by this method precludes its practical application, although the synthesis of graft copolymers of cellulose and polyamides is of considerable interest.

## V. SYNTHESIS OF GRAFT COPOLYMERS BY IONIC POLYMERISATION

Only one attempt has been reported[36] to use ionic polymerisation to modify cellulose with carbon-chain polymers. The cellulosic material is wetted out at low temperatures in a solution of boron trifluoride in an organic solvent (boron trifluoride forms a complex with cellulose), and then the material is placed in the monomer. However, the paper gives no evidence to indicate the formation of a graft copolymer.

Ionic polymerisation can probably be used to obtain graft copolymers of cellulose by a scheme suggested for the synthesis of block copolymers of poly(ethylene oxide)[37] (with hydroxyethylcellulose as starting material). The complexity of the process for obtaining the starting materials and the necessity of carrying out the reaction in an organic solvent or in the 100% monomer make the method unpromising for practical application.

## VI. SYNTHESIS OF GRAFT COPOLYMERS BY RADICAL POLYMERISATION

The modification of cellulosic materials by the synthesis of graft copolymers by radical polymerisation has been investigated most. The following methods may be used — (1) chain transfer, (2) copolymerisation of unsaturated esters of cellulose with vinyl monomers, (3) a mechanico-chemical method, (4) exposure to high-energy and low-energy particles, (5) preliminary introduction of groups which break down to form macroradicals, and (6) by redox systems in which the polymer acts as reductant.

### 1. Synthesis of Graft Copolymers by Chain Transfer

The synthesis of graft copolymers by chain transfer presupposes that, as a result of detachment of a labile atom by interaction with a radical, the polymer molecule is converted into a macroradical capable of initiating the graft copolymerisation of a vinyl monomer in contact with it.

In principle chain transfer to a polymer can be effected by the interaction of (*a*) a growing macroradical or (*b*) an initiator radical with the polymer macromolecule. The composition of the product of graft copolymerisation will depend on which of these two mechanisms of chain transfer is operating. It is therefore useful to examine the two possibilities separately, but it must be borne in mind that such separation is arbitrary, and cases may occur in which chain transfer is accomplished by both mechanisms.

(*a*) Synthesis of graft copolymers by chain transfer from a growing macroradical. We include here those methods of graft copolymerisation in which an initiator is added to a solution of the monomer containing the polymer. Under these conditions interaction of the initiator radicals is thermodynamically more favourable with the monomer than with the polymer.

Graft copolymers have been synthesised by the initiated polymerisation of acrylonitrile in the presence of starch[38], methylcellulose, gelatin, cellulose acetates[39], and hydroxyethylcellulose[40].

A systematic investigation of the effect of process conditions on the quantity of homopolymer formed during the graft copolymerisation of 2-methyl-5-vinylpyridine and cellulose has been made by Kryazhev and Rogovin[41]. The efficiency of chain transfer to the polymer is increased if the reaction is carried out with the cellulose in a considerably swollen state. Even in this case, however, the quantity of monomer involved in graft copolymerisation does not exceed 25% of that which has reacted.

To improve the efficiency of chain transfer, groups containing labile atoms are introduced into the cellulose macromolecule, which markedly increases the possibility of this process. Mixed esters of cellulose with acetic and 11-bromoundecanoic acids[1] or cellulose preparations containing thiol groups[42,43] are used for this purpose.

The preliminary introduction of thiol groups for the synthesis of graft copolymers was first suggested by Gluckman[44,45]. J. J. Hermans and his coworkers obtained products containing thiol groups by treating modified cellulose and secondary cellulose acetate with ethylene sulphide. Graft copolymers can be obtained by the polymerisation of vinyl monomers in the presence of such esters[42,43]. The efficiency of chain transfer with preparations containing thiol groups is five times that with materials which have not been treated with ethylene sulphide.

In all cases of the synthesis of graft copolymers by chain transfer from a growing macroradical a considerable quantity of homopolymer is formed, which, together with the need to introduce groups to ensure a high efficiency of chain transfer, prevents the practical application of these methods.

(*b*) Synthesis of graft copolymers by chain transfer from initiator radicals. Chain transfer from initiator radicals is considerably more useful than the above. It probably occurs in the polymerisation of vinyl monomers in the presence of cellulose on the $Fe^{2+}$–$H_2O_2$ redox system[46–53]. In this case formation of a cellulose macroradical probably occurs by the following mechanism

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+OH^-+\dot{O}H,$$

$$\text{Cell}-OH+\dot{O}H \rightarrow \text{Cell}-O^{\bullet}+H_2O. \qquad (6)$$

Graft copolymerisation takes place when a cellulosic material is wetted out in a solution containing $Fe^{2+}$ ions and then immersed in a solution of a monomer containing 0.03% of hydrogen peroxide. Under the conditions chosen, however, the quantity of monomer involved in graft copolymerisation does not exceed 12.5% of the amount which has reacted[47]. The formation of considerable quantities of homopolymer is probably due to diffusion of $Fe^{2+}$ ions into the aqueous solution, where homopolymerisation of the monomer is initiated. The efficiency of chain transfer is considerably increased if the initiator or a component of the redox system is bound to the cellulosic material by a salt link, and its diffusion into the monomer solution is impeded. In this case initiator radicals are formed directly on the cellulosic material, and the probability of their interacting with the cellulose macromolecules is increased. This principle forms the basis of the method for synthesising graft copolymers proposed by Bridgeford, in which a cellulose preparation containing a small quantity of carboxy-groups is wetted with a solution of an iron(II) salt (when $Fe^{2+}$ is sorbed by the carboxy-groups of the cellulose) and, after excess $Fe^{2+}$ cations have been eluted, is immersed in an aqueous solution or an emulsion of the monomer containing hydrogen peroxide insufficient to initiate polymerisation in the absence of $Fe^{2+}$ ions. In this case formation of homopolymer in the reaction medium is not observed[53]. The efficiency of graft copolymerisation is determined by the nature of the cellulosic material. The amount of homopolymer formed within the cellulosic material is considerably lower with hydrocellulose fibres than with cotton fibres, constituting only 4–5% of the monomer which has reacted.

Chain transfer from initiator radicals also occurs when potassium peroxodisulphate is employed as initiator under conditions which make diffusion of the initiator into the monomer solution difficult[6,54,55]. The possibility of formation of a cellulose macroradical by interaction of the cellulose with radicals produced by decomposition of the persulphate is confirmed by investigations with alcohols of low molecular weight. When aqueous solutions containing peroxodisulphate ions are heated, these ions break down according to the equation[56]

$$S_2O_8^{2-} \rightarrow 2SO_4^{-}. \qquad (7)$$

When $K_2S_2O_8$ decomposes in the presence of an alcohol, $SO_4^{-}\cdot$ ion-radicals react with the alcohol molecule according to the equation[56–58]

$$CH_3OH+SO_4^{-}\cdot \rightarrow \dot{C}H_2OH+HSO_4^{-}. \qquad (8)$$

The probability of reaction (8) diminishes in the presence of a free-radical acceptor (monomer). Thus the synthesis of graft copolymers of cellulose is possible on reaction under conditions which impede interaction of $SO_4^{-}\cdot$ with the monomer. In fact, if a cellulosic material is wetted with a solution of potassium peroxodisulphate and then brought into contact with a monomer (by being kept in the monomer vapour or immersed in the pure monomer) under conditions which make diffusion of $S_2O_8^{2-}$ or $SO_4^{-}\cdot$ into the monomer phase difficult, graft copolymers of various compositions can be synthesised[54,55].

When graft copolymers are synthesised by chain transfer from initiator radicals, homopolymer is formed only directly on the cellulosic material. Therefore such methods can be expected to be applied in practice for the modification of ready-made goods in cases in which the presence of homopolymer on the cellulosic material does not impair the properties of the resulting materials in service. Among the defects of these methods must be reckoned the difficulty of controlling the degree of polymerisation and the number of graft chains.

## 2. Synthesis of Graft Copolymers by the Copolymerisation of Unsaturated Esters of Cellulose with Vinyl Monomers

The synthesis of graft copolymers by this method is based on the fact that, in the presence of initiators of radical polymerisation, the double bond of the polymer is opened to form a macroradical, which initiates polymerisation of the monomer or combines with the growing macroradical of the monomer. Both processes result in the formation of a graft copolymer. The presence of an initiator in the system makes simultaneous homopolymerisation of the monomer possible. Thus a considerable quantity of homopolymer is formed in all cases of graft copolymerisation by this method.

The possibility of synthesising graft copolymers by the copolymerisation of unsaturated esters of cellulose with various vinyl monomers was first pointed out by Ushakov[59]. Berlin and Makarova developed a method for preparing cellulose acetate methacrylates by the acetylation of cellulose monomethacrylate with acetic anhydride or by the esterification of secondary cellulose acetate with methacrylic anhydride. The resulting mixed esters of cellulose are copolymerised in the presence of benzoyl peroxide with methyl methacrylate and ethylene dimethacrylate to form graft copolymers of three-dimensional structure[60]. Graft copolymers containing 6–8% of polystyrene have been synthesised[61] by the copolymerisation with styrene of mixed esters of cellulose containing unsaturated bonds. Grafting is accompanied by the formation of a large quantity of homopolymer. Unsaturated groups are readily introduced into the macromolecule of cellulose nitrates by treating their solutions with

$$\left[\begin{array}{l}-ONO_2\\-ONO_2\\-OH\end{array}\right. + OCNRNHCOOCH{=}CH_2 \rightarrow \left[\begin{array}{l}-ONO_2\\-ONO_2\\-OCONHRNHCOOCH{=}CH_2\end{array}\right. \quad (9)$$

Graft copolymers are formed by the polymerisation of acrylonitrile in solutions of modified cellulose nitrates[62].

The formation of a considerable quantity of homopolymer, the low yields of graft copolymer, and the need for preliminary treatment of the cellulose to introduce unsaturated groups evidently make the synthesis of graft copolymers by this method unpromising.

## 3. Mechanicochemical Method of Synthesising Block and Graft Copolymers

The degradation of cellulose and its derivatives by mechanical energy is accompanied by the formation, at the ends of the newly produced chains, of free macroradicals[63] capable of initiating the block copolymerisation of monomers in contact with them. Formation of a macroradical by rupture of a bond with a substituent results in the formation of graft copolymers. The mechanicochemical method is the only method for the synthesis of block copolymers of polysaccharides which has yet been put into practice under laboratory conditions.

Ceresa obtained methylcellulose–polyacrylonitrile, ethylcellulose–poly(methyl methacrylate), benzylcellulose–polystyrene, and cellulose acetate–poly(vinyl acetate) block copolymers by vigorous grinding of the polymers, plasticised with the monomer, in the absence of atmospheric oxygen[64]. He prepared block copolymers also by swelling cellulose acetates in acrylonitrile[64]. Block copolymers of water-soluble polysaccharides are obtained by repeatedly freezing and thawing out aqueous emulsions of the polymer and monomer[64–66]. Block copolymers can probably be obtained also by the intense mechanical working of thermoplastic cellulose ethers with other thermoplastic polymers (as a result of the combination of macroradicals of the different polymers). In the synthesis of block copolymers by this method, a complicated mixture of products is obtained, containing both homopolymers and block and graft copolymers.

This last fact, the difficulties associated with controlling the composition and size of the blocks, and the impossibility of employing this procedure for modifying ready-made goods have so far prevented the practical realisation of these methods for modifying cellulose and its derivatives.

## 4. Synthesis of Graft Copolymers under the Influence of Radiation

(*a*) Synthesis of graft copolymers by exposure to high-energy particles. When cellulose[67,68], its ethers and esters[69], and other polysaccharides[70] are irradiated with high-energy particles, the main process is degradation. Completely water-soluble products are formed by the exposure of cellulose[68] to a dosage of only ~ 100 Mr. Degradation under the influence of radiation takes place by a free-radical mechanism. The formation of macroradicals of cellulose and its derivatives by the action of high-energy particles can be used to initiate graft copolymerisation. Depending on the conditions, there are four ways in which graft copolymers can be synthesised by this method — (i) simultaneous irradiation of polymer and monomer in the absence of air, (ii) simultaneous irradiation of polymer and monomer in air, (iii) irradiation of the polymer in an inert gas atmosphere with subsequent interaction with the monomer, and (iv) irradiation of the monomer in the presence of air with subsequent interaction with the monomer.

(i) When polymer and monomer are exposed together in the absence of air, graft copolymerisation is initiated by macroradicals of the polymer formed under the influence of the high-energy particles. In the synthesis of graft copolymers of cellulose, macroradicals can be formed either at the end of a chain (by cleavage of the bond between monomeric units in the cellulose macromolecule) or in the middle of a chain[67–69,71].

Rupture of the bond between monomeric units should result in the formation of considerable quantities of block copolymers together with the graft copolymers.

(ii) When polymer and monomer are irradiated together in air, graft copolymerisation is initiated both by macroradicals formed by the direct action of radiation and by macroradicals resulting from the breakdown of peroxy- or hydroperoxy-groups formed by the addition of oxygen to macroradicals obtained in the first stage of irradiation.

When graft copolymers are synthesised by simultaneous irradiation of polymer and monomer, considerable quantities of the homopolymer are formed, since production of polymer macroradicals is accompanied by that of radicals of low molecular weight as a result of exposure of the monomer, and these initiate homopolymerisation[72–84]. One procedure for the simultaneous exposure of polymer and monomer is to irradiate the polymer swollen in the monomer. In this case the homopolymer is formed only on the treated polymer, not in the reaction medium, as is observed when the polymer is irradiated in the monomer solution[85]. One of the most acceptable ways of synthesising graft copolymers by the simultaneous irradiation of polymer and monomer is probably to expose the polymer in the presence of the monomer vapour (vapour-phase copolymerisation)[86,87].

The synthesis of graft copolymers by the irradiation of polymer and monomer together probably involves the formation of strongly branched polymers, since the possibility remains that a macroradical capable of initiating polymerisation will be formed on the grafted chain[88]. Swelling of the cellulosic material is of great importance for the reaction to be efficient, since it increases the rate of diffusion of the monomer. Usmanov and his coworkers investigated the graft copolymerisation of cellulose with acrylonitrile. The reaction was carried out by irradiating

cellulose suspended in a solution of acrylonitrile in water, methanol, or benzene or in pure acrylonitrile. A graft copolymer was obtained only when the cellulose was swollen (no grafting occurred when cellulose was exposed in benzene solution)[72]. Other workers have noted the effect of degree of swelling on rate of graft copolymerisation[71,74,75]. Shapiro and Stannett found that the rate of the graft copolymerisation of cellulose with vinyl monomers is increased by increasing the water content of the reaction medium[74]. Leavitt suggested that the effect of water is not limited to increasing the degree of swelling of the cellulosic material, but involves the generation of OH radicals on irradiation, which split off a hydrogen atom from the cellulose macromolecule to form a cellulose macroradical, as is presumably confirmed by the possibility of the "cross-linking" of water-soluble ethers of cellulose and gelatin in the presence of water. No cross-linking effect is observed when the dried polymers are irradiated[89].

(iii) When cellulose is irradiated in an atmosphere of an inert gas, "long-lived" macroradicals are formed (cellulose which has been exposed in the absence of atmospheric oxygen gives paramagnetic resonance signals for several days after irradiation)[88], which initiate graft copolymerisation on subsequent interaction with a monomer[71,76,90-92]. However, degradation of the cellulose is more intense in this case than on exposure in the presence of a monomer which is an acceptor for free radicals[71].

(iv) When a polymer is irradiated in air, peroxy- or hydroperoxy-groups are formed, which on subsequent heating in the presence of a monomer break down and initiate graft copolymerisation[77,90,91]. Thus exposure of the polymer in the presence of air can be regarded as one way of introducing hydroperoxy-groups; the synthesis of graft copolymers by means of these groups is discussed below. Irradiation of the polymer with subsequent interaction with the monomer has certain technical advantages compared with the above procedure, since it permits the processes of irradiation and of subsequent grafting to be separated.

Wide practical application of methods for synthesising graft copolymers based on the use of ionising irradiation with particles of high energy is made difficult by the absence of methods for eliminating secondary processes resulting in the formation of homopolymer, degradation of the initial polymer, and the production of strongly branched graft copolymers, as well as by the difficulties involved in ensuring the safety of the process.

This last obstacle largely disappears when graft copolymerisation is induced by ultraviolet radiation or by radiation of longer wavelength in the presence of sensitisers. Carrying out grafting by this method enables considerable degradation of the polymer to be eliminated, which, together with its safety, constitutes the advantage of this method of synthesising graft copolymers.

(*b*) Synthesis of graft copolymers by means of low-energy particles. A systematic investigation of graft copolymerisation induced by visible light in the presence of anthraquinonoid dyes as sensitisers have been undertaken by Geacintov[93,94].

The mechanism of graft copolymerisation in the presence of sensitisers is that radiation of a wavelength absorbed by the sensitiser excites its molecule to a state in which it reacts with the polymer, converting the latter into a macroradical which initiates graft copolymerisation. Interaction between the excited sensitiser molecule and the monomer results in the formation of a radical of low molecular weight, which initiates homopolymerisation.

When an anthraquinonoid dye is employed as sensitiser, the mechanism of the process can be represented as follows:

$$AQ^a + h\nu \longrightarrow AQ^{*b}, \quad (10)$$

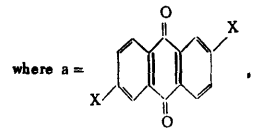
$$AQ^{*b} + \text{Cell}\!>\!\underset{\displaystyle H}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}} \longrightarrow AQH^c\cdot + \text{Cell}\!>\!\overset{\displaystyle OH}{\overset{|}{C}}\cdot, \quad (11)$$

$$\text{Cell}\!>\!\overset{\displaystyle OH}{\overset{|}{C}}\cdot + n CH_2{=}CHR \longrightarrow \text{Cell}\!>\!\overset{\displaystyle OH}{\overset{|}{C}}\!-\!(CH_2\!-\!CHR)_n, \quad (12)$$

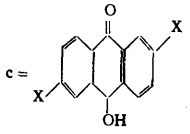
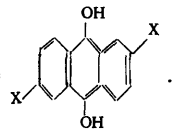
$$AQ^{*b} + CH_2{=}CHR \rightarrow AQH^c\cdot + CH_2{=}\dot{C}R, \quad (13)$$

$$CH_2{=}\dot{C}R + (n-1)\,CH_2{=}CHR \rightarrow (CH_2\!-\!CHR)_n, \quad (14)$$

$$2\,AQH^c\cdot \rightarrow AQH_2^d + AQ^a, \quad (15)$$

where a =  ,

the X being groups which confer on the sensitiser solubility in water ($SO_3Na$) or organic solvents, b is an excited sensitiser molecule,

c =  , d =  .

Such a mechanism is supported by work on related systems using alcohols of low molecular weight[6].

The rate of graft copolymerisation by this method is greater in the presence of air than in an inert gas, since in the presence of oxygen the above reactions are accompanied by the formation of peroxides, hydroperoxides, or both, which break down to form a cellulose macroradical[93].

Graft copolymerisation by this method is carried out under conditions of considerable swelling of the cellulose (in a solution of the monomer in a mixture of dimethylformamide and water or in an aqueous solution of the monomer) with minimum concentrations of the sensitiser (up to 0.01 M). The quantity of monomer grafted on is proportional to the time of exposure and the concentration of the dye.

Geacintov employed the above method to synthesise graft copolymers of cellulose with polyacrylonitrile, poly(vinyl acetate), polystyrene, and poly(methyl methacrylate), employing as starting material regenerated cellulose film, paper, etc.

A considerable amount of homopolymer — cf. reactions (13) and (14) — is formed in all cases of the synthesis of graft copolymers by this method. A further defect of the method is the difficulty of controlling the length and number of graft chains.

5. Synthesis of Graft Copolymers by the Preliminary Introduction of Groups which Break Down to Form Macroradicals

Under certain conditions hydroperoxy(or peroxy)-, diazo-, azonitrile, and diazoamino-groups break down to form radicals capable of initiating the polymerisation of vinyl monomers in contact with them[95-100]. If these groups are chemically combined with a polymer molecule, their decomposition produces macroradicals which initiate graft copolymerisation.

The synthesis of graft copolymers of cellulose and its derivatives is effected only by first introducing hydroperoxy- and diazo-groups into the cellulose macromolecule.

(*a*) Synthesis of graft copolymers of cellulose and its derivatives by the preliminary introduction of hydroperoxy-groups. Hydroperoxy- or peroxy-groups can be introduced into the macromolecule of cellulose and its ethers by treating the polymer with ammonium peroxodisulphate[101], irradiating it with high- and low-energy particles in the presence of air[77,99,102], and also by passing a stream of air through a solution of the cellulose ether containing azoisobutyronitrile[103] or a stream of oxygen or oxygen enriched with ozone[99,100,104,105]. The oxidation of cellulose and its derivatives for the purpose of introducing peroxy- or hydroperoxy-groups is almost always accompanied by considerable degradation of the polymer[102,103,105].

Ozonisation is a method frequently employed in laboratory investigations for introducing hydroperoxy-groups. The rate of accumulation of peroxy- and/or hydroperoxy--groups during ozonisation is increased by the presence of water, although hydrogen peroxide is not formed under the experimental conditions[106].

When a stream of oxygen containing 6% of ozone is passed through a cellulosic material, it is possible after 6 h to introduce 1 peroxy-group per 20 monomeric units. Peroxy-groups introduced into cellulose do not break down at 20° even on storage of the oxidised cellulose for 3 months. Appreciable diminution in the content of available oxygen is observed only at 75–80°; at 100° complete breakdown of peroxy-groups occurs after 2 h.[99]

A systematic investigation of ozonisation and of the properties of oxidised cellulose acetates has been made by Radchenko and his coworkers[105].

When cellulose preparations containing hydroperoxy--groups are heated in the presence of a monomer at 80–100°, the groups break down to form a macroradical, which initiates graft copolymerisation, and a hydroxy--radical, which causes homopolymerisation of the monomer:

$$\text{Cell}-\text{OOH} \rightarrow \text{Cell}-\text{O}^{\cdot} + {}^{\cdot}\text{OH}. \qquad (16)$$

In the presence of metals of variable valency the hydroxy--radical is reduced to a hydroxide ion:

p l l o pe h y lf e xycl l ot r p/d u d l f l l l ht

The preliminary introduction of hydroperoxy-groups and/or peroxy-groups into the polymer has been used to synthesise graft copolymers of cellulose with polyacrylonitrile, polystyrene[99], poly(methyl methacrylate), poly-(vinyl acetate), and polyvinylpyridine, of cellulose nitrates with poly(butyl methacrylate)[102], of benzyl- and ethyl--cellulose with polystyrene, and of carboxymethylcellulose with polyacrylonitrile[92].

This method has the advantages that it makes possible the synthesis of graft copolymers based on almost any derivative of cellulose, the number of grafted chains can be readily varied (by varying the content of available oxygen in the polymer), and the process is comparatively simple to carry out. Among its disadvantages are the formation of a certain amount of homopolymer together with the graft copolymer, and the degradation of the original polymer on oxidation. These defects can be eliminated by using preparations of cellulose containing a small quantity of diazo--groups.

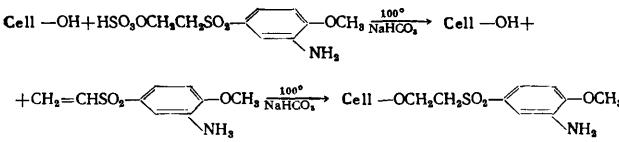
(*b*) Synthesis of graft copolymers by the preliminary introduction of diazo-groups. This method was suggested almost simultaneously and independently by Richards[107] and by Rogovin[108]. According to Richards, aromatic amino-groups can be introduced by treating alkali-cellulose with *p*-amino-ω-chloroacetophenone

$$\text{Cell}-\text{ONa}+\text{ClCH}_2\text{COC}_6\text{H}_4\text{NH}_2 \rightarrow \text{Cell}-\text{OCH}_2\text{COC}_6\text{H}_4\text{NH}_2, \qquad (18)$$

or by heating an aqueous solution of the sodium salt of carboxymethylcellulose with a solution of *p*-aminochloroacetophenone in dimethylformamide:

$$\text{Cell}-\text{OCH}_2\text{COONa}+\text{ClCH}_2\text{COC}_6\text{H}_4\text{NH}_2 \rightarrow \text{Cell}-\text{OCH}_2\text{COOCH}_2\text{COC}_6\text{H}_4\text{NH}_2. \qquad (19)$$

Rogovin et al. proposed a simpler single-stage method for introducing aromatic amino-groups into the cellulose macromolecule. When cellulose is treated in weakly alkaline medium at 100° with a 2-sulphonylethyl sulphate, the sulphate group is split off, and a vinylsulphonyl group is formed which, in the nascent state, adds on to the hydroxy--groups of the cellulose molecule to form a cellulose ether (Michael reaction). To introduce aromatic amino-groups into the cellulose macromolecule, use was made of the water-soluble sulphuric esters of 2-(3-amino-4-methoxyphenylsulphonyl)ethanol and 2-*p*-aminophenylsulphonylethanol. The alkylation of cellulose proceeds according to the scheme




(20)

Diazotisation of the cellulose macromolecule effects the introduction of diazo-groups, which break down on subsequent heating to form a macroradical, which initiates graft

the Cl· radical into a $Cl^-$ ion, and they are probably involved in chain termination by interaction of the growing macroradical with the oxidised form of the metal cation:

$$\text{Cell}-OAr{N_2}Cl+Fe^{2+} \rightarrow \text{Cell}-OAr^{\cdot}+N_2+Cl^-+Fe^{3+}, \quad (22)$$

$$-CH_2-\dot{C}HR+Fe^{3+} \rightarrow -CH=CHR+Fe^{2+}+H^+. \quad (23)$$

In order to synthesise graft copolymers by this method it is sufficient to obtain a cellulose ether having $\gamma = 3-10$. The quantity of polymer grafted depends on the activity of the radical formed, the degree of alkylation, and the nature of the initial monomer [108]. This method has been used to synthesise graft copolymers of cellulose with polyacrylonitrile, poly(vinylidene chloride), poly(methyl methacrylate), and polyacrylic and polyvinylphosphinic acids. In no case is the homopolymer formed [107-114].

It must be noted that the synthesis of graft copolymers by this method always yields coloured products [108]. The probable explanation is that the main reaction of diazotisation of the amino-groups with subsequent formation of a macroradical is accompanied by azo-coupling, in which some of the unchanged amino-groups take part.

In spite of the considerable advantages of this method (the possibility of synthesising graft copolymers from aqueous solutions or aqueous emulsions of the polymer without homopolymer formation, and the ease of regulating the number of graft chains), the necessity of first introducing aromatic amino-groups, with the associated considerable consumption of a relatively expensive compound and the production of coloured materials, prevents the widespread practical application of this method.

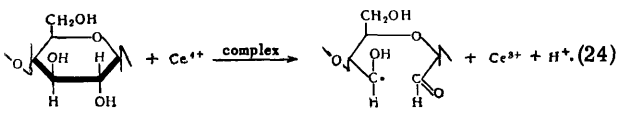
The synthesis of graft copolymers of cellulose and its derivatives on redox systems in which the cellulose or its derivative acts as reducing agent is a considerably more promising method.

### 6. Synthesis of Graft Copolymers on Redox Systems in which the Polymer Acts as Reducing Agent

The principle underlying the synthesis is that the oxidation with some oxidising agents of polymers containing reducing groups involves a stage in which macroradicals are formed; these are capable of initiating the graft copolymerisation of vinyl monomers in contact with them.

This principle was first exploited for the synthesis of graft copolymers by Mino, who proposed a quadrivalent cerium salt as oxidant [115]. This method has been investigated systematically by Japanese workers [116-127] and in our laboratory [128-136]. Work has also been done on the oxidation of compounds of low molecular weight [137-141], as well as of poly(vinyl alcohol) [142] and cellulose [120], with $Ce^{4+}$ ions, and on the polymerisation of vinyl monomers on redox systems formed by an alcohol of low molecular weight with $Ce^{4+}$. [140,143,144]

The initiation of the graft copolymerisation of cellulose by this method takes place according to the scheme




This mechanism of initiation is supported by the following experimental results:

(i) In all cases of the oxidation of alcohols of low and high molecular weight, and of polymerisation by means of alcohol–$Ce^{4+}$ redox systems, a complex of reductant and oxidant is formed, the rate of oxidation being determined by the rate of disproportionation of this complex [140].

(ii) The oxidation of compounds containing a glycol grouping by cerium(IV) salts involves the intermediate formation of free radicals, with cleavage of the bond between the carbon atoms having attached hydroxy-groups [138,140,142].

(iii) Polymers synthesised on the redox system formed by an alcohol of low molecular weight with $Ce^{4+}$ contain a terminal hydroxy-group [145].

(iv) When highly substituted methyl ethers of cellulose containing no free glycol groups are employed as initial polymer, graft copolymers cannot be synthesised, whereas with methylcelluloses of low degree of substitution graft copolymerisation is rapid [131].

Termination of the material chain is achieved in this method mainly by interaction of the growing macroradical with an oxidant cation. This hypothesis is supported by the lack of dependence of reaction velocity on initiator concentration and the almost complete absence of homopolymer formation [115,128,146]. By this method it is possible to vary the number and degree of polymerisation of the graft chains without changing the total quantity of graft component [133].

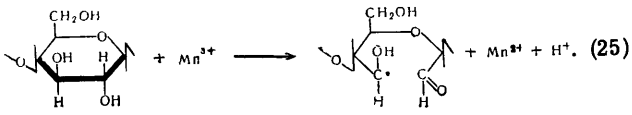
It must be noted that the use of cerium(IV) salts for the synthesis of graft copolymers may cause polymerisation of the monomer even in the absence of a reducing agent. However, polymerisation of the monomer begins after a definite induction period, whereas oxidation of the polymer, and hence initiation of graft copolymerisation, take place without an induction period. Thus by keeping the duration of the synthesis shorter then the induction period it is possible to obtain graft copolymers practically without formation of homopolymer. The synthesis of graft copolymers using cerium(IV) salts is carried out in aqueous solutions or aqueous emulsions of the monomer with minimum amounts of oxidant [128,129]. This method has already been employed to synthesise copolymers of cellulose with polyacrylonitrile [120,121,128,132,147,148], poly(methyl methacrylate) [117,119,133], poly(vinyl acetate) [118], poly(butyl acrylate) [136], polystyrene [122], polyacrylamide [116,148], poly-(2,3-epoxypropyl methacrylate) [123,145], and poly(methyl acrylate) [121,148], and of cellulose nitrates and acetates with poly(methyl acrylate) [130,134].

The appearance of Mino and Kaizerman's paper stimulated attempts to find other redox systems, not involving the use of the scarce and expensive cerium salts.

Japanese workers have proposed the use of potassium permanganate and cobalt(III) salts [127] for the synthesis of graft copolymers of polyvinyl alcohol, starch, and block copolymers containing the terminal hydroxy-groups of a polyethylene glycol, and sodium periodate [149] or cobalt(III) salts [127] for the synthesis of graft copolymers of cellulose. Graft copolymerisation by means of these oxidants is accompanied by the formation of considerable quantities of homopolymer, resulting from oxidation of the monomers with formation of radicals of low molecular weight.

Rogovin and Livshits suggested the use of manganese(III) pyrophosphate [150] for the synthesis of graft copolymers of cellulose, and vanadium(V) compounds [151-154] for modified cellulosic preparations containing small quantities of aromatic amino-groups or aldehyde groups.

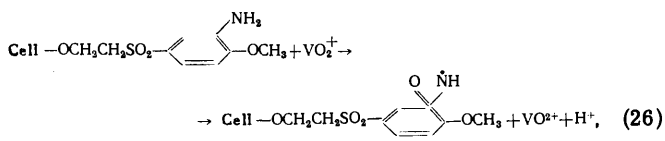
When manganese(III) pyrophosphate is used, initiation of graft copolymerisation is effected, as with cerium(IV) salts, by free-radical oxidation of a glycol group in the cellulose macromolecule [154], and chain termination occurs by interaction between the growing macroradical and an oxidant cation.



(25)

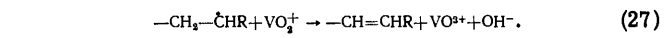
With manganese(III) pyrophosphate as oxidising agent, as with cerium(IV) salts, graft copolymers can be synthesised without homopolymer formation, and also without the use of organic solvents, while the number and length of the graft chains can be readily varied by changing the oxidant concentration. A further advantage of using the pyrophosphate is its ready availability.

In the synthesis of a graft copolymer based on modified cellulose preparations containing aromatic amino-groups — the ether of cellulose and 2-(3-amino-4-methoxyphenylsulphonyl)ethanol — with vanadium(V) compounds as oxidants, initiation of graft copolymerisation is accomplished according to the scheme



(26)

and chain termination is probably represented by the equation



(27)

In the synthesis of graft copolymers of modified cellulose preparations containing aromatic amino-groups or aldehyde groups, with a vanadium(V) compound as oxidant, formation of homopolymer does not occur, however long the contact between oxidising agent and monomer, if the conditions have been chosen correctly, in contrast to what occurs in methods involving the use of $Ce^{4+}$ or $Mn^{3+}$. This together with the ready availability of the oxidising agent constitutes an important advantage of this method, since it enables the process to be carried out continuously using aqueous solutions or emulsions of the monomer. One defect of the method is the necessity of first introducing a small quantity of amino-groups or aldehyde groups into the cellulosic materials. The method is applicable not only to cellulose but also to all other polymers containing these groups.

From this survey of the various methods for synthesising graft copolymers of cellulose and its derivatives we can conclude that the most promising methods are — (1) syntheses of graft copolymers on redox systems in which the polymer acts as reductant, and (2) in several cases chain transfer from initiator radicals.

In spite of the considerable amount of research on the synthesis of graft copolymers of cellulose and its derivatives, several fundamental questions relating to the characterisation and properties of graft copolymers have not yet been settled. Systematic investigations have still not been made to elucidate the effect of the conditions of graft copolymerisation on the length and number of graft chains, and especially on the quantity of cellulose entering into the graft copolymer. The quantity of homopolymer formed from the synthetic compound of high molecular weight has been determined in most published work, but the fact that not all the cellulose macromolecules become incorporated in the graft copolymer has been ignored. The quantity of cellulose homopolymer undoubtedly has an important influence on the properties of the products resulting from grafting. Nor has the effect of the degree of polymerisation and the number of graft chains on the properties of graft copolymers of cellulose and its derivatives been investigated, except in one paper [133]. Carrying out the reaction in a heterogeneous medium, as is almost always the case in grafting to cellulose and its derivatives, results in the production of graft copolymers containing a small number of graft chains of high molecular weight (with degrees of polymerisation up to 30 000), and sometimes, therefore, graft copolymers do not differ in their fundamental properties from mechanical mixtures of the homopolymers. The development of methods yielding graft copolymers having a small number of relatively short graft chains is an urgent task. An investigation of these questions has recently been undertaken in our laboratory.

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Since this paper was submitted to the Editors, several publications have appeared on the synthesis of graft copolymers of cellulose by the radiation method [155-164], by the use of cerium salts [165-171], by chain transfer from initiator radicals [172-174], and by ionic polymerisation [175,176]. Several papers have been published on the properties of graft copolymers of cellulose and its derivatives [168,173,174,176-179].


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# REACTION GAS CHROMATOGRAPHY IN ANALYSIS

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## 1. INTRODUCTION

Gas chromatography is now an effective method for the analysis of organic and inorganic compounds. Fairly frequently, however, particularly in the analysis of complex organic mixtures, the oridinary methods of gas chromatography are unsatisfactory.

The efficiency of gas chromatography as an analytical method can be increased considerably by the simultaneous use of chromatographic separation and chemical reactions. Chemical reactions in gas chromatography can be carried out for different purposes, in particular: (1) the analysis of substances for which direct use of the methods of gas chromatography is impossible (e.g. the analysis of polymers, non-volatile compounds, etc.); (2) the reduction of a difficult analytical problem to a simpler problem which has previously been resolved (e.g. the conversion of alcohols into alkenes or alkanes or esters of nitrous acid, followed by chromatographic analysis of the reaction products); (3) the identification of peaks due to unknown components by the use of group (individual) selective absorbers (e.g. sulphuric acid for the absorption of alkenes from hydrocarbons) or group qualitative reactions; and (4) the simplification of quantitative calculations and increase in the sensitivity and accuracy of analysis by the conversion of all the organic compounds being analysed into one or two simple compounds at the outlet from the separating column (e.g. conversion to carbon dioxide and water or hydrogen with the use of a thermal-conductivity detector).

Thus the use of chemical reactions in gas chromatography is extending appreciably the range of the ordinary chromatographic separation and exhibits a number of specific features. It is therefore appropriate to deal with the use of chemical reactions in gas chromatography as a separate field — reaction gas chromatography. This term was first used by Drawert[1,2], who at first, however, gave a too narrow definition of reaction gas chromatography, restricting himself to the case where the substance being analysed undergoes changes in a reaction vessel placed before the separating column (in order to convert the compounds being analysed into definite compounds whose chromatographic analysis presents no difficulties).

In a later paper, Drawert[3] correctly pointed out that in a wider sense the term "reaction gas chromatography" can be taken to mean the use of chemical reactions together with chromatographic separation. It is necessary only to emphasise that the chemical changes should take place in a single chromatographic scheme. The present review considers only the analytical applications of the combined use of chemical reactions and chromatographic separation. Another important independent field of reaction gas chromatography involves the study of the kinetics and mechanism of chemical reactions under chromatographic conditions. Work on these lines, which is now being successfully developed, was begun by Roginskii and coworkers[4,5].

A promising development is the use of the mathematical methods of the theory of reactions under chromatographic conditions to determine the initial concentration of a substance in a specimen, some components of which undergo chemical changes as a result of chemical reactions in the chromatographic column.

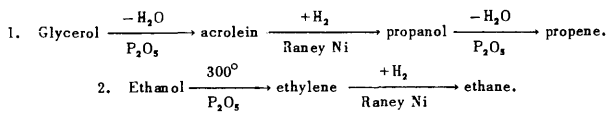
Thus analytical reaction gas chromatography is a form of gas chromatography in which chemical reactions in a single gas-phase chromatographic process are used for analytical purposes. The chemical reactions may take

place in special reaction vessels placed before, after, or directly inside the column or between two chromatographic columns. When a special reaction vessel is introduced into a chromatographic set-up, there is a possibility that the efficiency of separation will be reduced. These fears generally prove groundless, however, since the chromatographic characteristics of the packing of the reaction vessel and column do not generally differ greatly from one another, and the length of the reaction vessel amounts to only a small percentage of the length of the chromatographic column.

No published papers have referred to a decrease in the efficiency of separation. For a quantitative estimate of the decrease in the efficiency using chromatograms obtained with and without a reaction vessel[6], we calculated the number of theoretical plates. The calculation showed that there is no decrease in the efficiency of separation.

Table 1 gives a classification of known reaction gas chromatography procedures according to the given chromatographic set-up (position of reaction vessel) and according to the types of chemical reaction used.

In a number of cases it is convenient to effect different chemical reactions simultaneously in a single analysis by using a multistage reaction vessel. For example, for the determination of alcohol and glycerol in dilute aqueous solutions, Drawert et al.[3] used a complex multistage reaction vessel in which the following chemical changes took place:




The gas-chromatographic determination of the products formed (propene and ethane) presents no difficulties and can be carried out using simpler apparatus than that required for the determination of the original compounds (glycerol and ethanol). The combined use of several chemical reactions has also been described[7]. The fractions leaving the gas chromatograph were oxidised on a platinum catalyst, and the oxidation products were studied by qualitative reactions for sulphur, nitrogen, and halogens. A positive qualitative test indicated the presence of the elements detected in the molecule of the original compound.

TABLE 1. Chemical reactions and chromatographic set-ups*.

| Types of chemical change | Position of reaction vessel in gas-chromatographic set-up | | |
|---|---|---|---|
| | reaction vessel before column | reaction vessel—column | reaction vessel after column |
| Pyrolysis | 10—30, 31—36 | | |
| Hydrogenation and dehydrogenation | 1, 2, 3, 8, 39—43 | | |
| Dehydration and decarboxylation | 2, 3, 39, 40 | | |
| Esterification | 1, 2, 3, 39, 40, 44 | 9 | |
| Saponification | | | 45 |
| Formation of non-volatile compounds | 6, 48, 49, 46 | | 47 |
| Oxidation | 8, 37, 38 | | 52—64 |
| Qualitative reactions | | | 7, 67 |
| Cracking | | | |
| Study of reactions under chromatographic conditions | | 4.5 | 37—39 |
| Reduction | 65, 66 | | |

* The numbers give the literature references.

To detect traces of inorganic gases (carbon monoxide, oxygen, etc.) by means of the highly sensitive flame-ionisation detector, the inorganic gases are converted quantitatively into compounds which can be measured by this detector. An example is the gas-chromatographic method for determining oxygen by means of a flame-ionisation detector after the quantitative conversion of the oxygen to carbon monoxide over carbon and reduction of the carbon monoxide to methane in a current of hydrogen over a nickel catalyst[8].

Different chemical reactions and different set-ups can be used in reaction gas chromatography, depending on the type of problems to be solved. Thus pyrolysis, hydrogenation, dehydration, esterification, and other chemical changes are usually employed for the analysis of non-volatile substances and for the conversion of polar, unstable, or non-volatile substances, which are difficult to study chromatographically, into compounds which are determined more easily. In this case the reaction vessel is generally placed before the chromatographic column.

Reactions involving oxidation, reduction, cracking, and the formation of non-volatile compounds, and also qualitative colour reactions, are often used to simplify quantitative calculations, to increase sensitivity, and for the identification of peaks due to the compounds being studied. In this case the reaction vessel is usually placed after the column, either before the detector or (when qualitative reactions are being carried out) after the detector. In some cases the chromatographic set-up contains no special reaction vessel and the reaction takes place directly in the column. Thus Anders and Mannering[9] introduced acetic or propionic anhydride into a chromatographic column immediately after a specimen of alkaloids and steroids and their derivatives. Under these conditions many of the compounds being analysed formed esters (acetates or propionates) directly in the column.

Thus the aims and purposes of the study determine not only the position of the reaction vessel in the general gas-chromatographic set-up, its shape, and the constructional details, but also the type of chemical reaction used.

The use of various types of chemical reaction in reaction gas chromatography is examined below.

## 2. PYROLYSIS

Pyrolysis is widely used in reaction gas chromatography for the identification of polymers, the study of the composition of copolymers, the identification of individual functional groups (e.g. benzene nuclei) in the molecules of non-volatile compounds, and the identification of isomeric paraffinic hydrocarbons.

A combination of the controlled pyrolysis of non-volatile compounds with gas-chromatographic determination of the product spectrum opens up the possibility of rapid identification of non-volatile compounds.

It has been shown[10-15] that under certain pyrolysis conditions, solid non-volatile substances decompose in a specific fashion and that analysis of the products enables certain conclusions to be reached regarding the structure and composition of the original substances.

The pyrolysis is carried out in a special assembly mounted before the separating column. The substance being studied is deposited beforehand on a metallic (platinum or, less frequently, nichrome) filament, wound to

form a spiral or mesh. After the spiral carrying the substance has been introduced into the gas stream, the spiral is heated rapidly by an electric current. The resulting pyrolysis products pass to the chromatographic column and are recorded by the detector at the outlet from the column.

Fig. 1 shows a typical pyrolysis cell. In some cases[16-19] the pyrolysis is carried out in a tube heated to high temperature.

The use of a special cell for the rapid pyrolysis of non-volatile substances on an incandescent filament has certain advantages over the method involving prolonged pyrolysis in a heated tube: (1) small quantities of the specimen (milli- or micro-grammes) are required for the analysis; (2) the method is rapid; and (3) the part played by secondary reactions in the formation of pyrolysis products is reduced.

The method of depositing the specimen on the filament is determined by the nature of the specimen. Solid soluble substances are deposited in a thin layer from solution on one or two rings in the centre of the spiral, and insoluble substances are deposited in the form of an aqueous suspension. The spiral with the specimen is then dried by means of an infrared lamp until the solvent is completely removed.

It is not always possible to achieve complete removal of the solvent, and the pyrolysis products of the solvent are generally present in the chromatograms together with the pyrolysis products of the substances being studied[20,21].

In another method[13,14,21,22] pyrolysis is carried out in a special boat of inert material (porcelain or quartz), which is brought rapidly into the hot zone. The quantity of volatile products and the weight of residue are found by weighing the boat.

By carrying out the pyrolysis in a boat, it is also possible to control accurately the pyrolysis process, to analyse liquid and solid specimens, and to determine the resulting products chromatographically. The temperature of pyrolysis is varied over a wide range, from 150° to 950°, depending on the nature of the substances being studied. The optimum pyrolysis temperature is found empirically. The temperature dependence of the yield of pyrolysis products from butyl methacrylate (Fig. 2) shows that, under the given conditions of pyrolysis in the boat, the optimum pyrolysis temperature is ~500°.

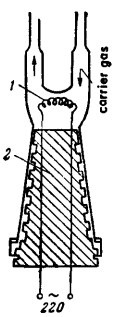



Fig. 1. Pyrolysis cell:
1) nichrome spiral with specimen; 2) Teflon block.

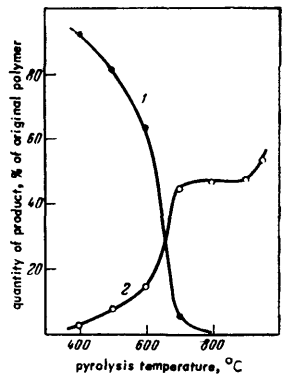



Fig. 2. Dependence of the yield of pyrolysis products from butyl methacrylate on the pyrolysis temperature:
1) butyl methacrylate monomer; 2) gaseous products ($CO + CO_2$).

The method involving pyrolysis can be used successfully to study the structure and composition of solid, liquid, and gaseous substances. For example, in the pyrolysis of polymers of the methyl methacrylate type and other acrylates[14,16,23-25] the original monomers are formed as chief product. The method involving pyrolysis has been used for the analysis of a number of copolymers (of styrene with methyl methacrylate[26] and of ethylene with vinyl acetate and ethyl acrylate[27,28], etc.) and polymers (polyurethane[17], polyethylene, polypropylene[29], etc.). Pyrolysis in gas chromatography has also been used to establish the structure of non-volatile compounds such as natural oils[6-8] and medicinal products[10-12,15,30]. As an example, Fig. 3 gives the chromatograms of the pyrolysis products from natural barbituric acids. It can be seen from Fig. 3 that the compounds of the same class give identical pyrolysis products.

Study of the pyrolysis products from a large number of high-boiling aromatic compounds (~100)[19] showed that a combination of pyrolysis with subsequent chromatographic analysis of the products provides a reliable method for detecting benzene rings in the compounds being analysed,

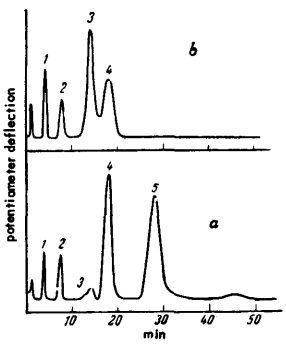


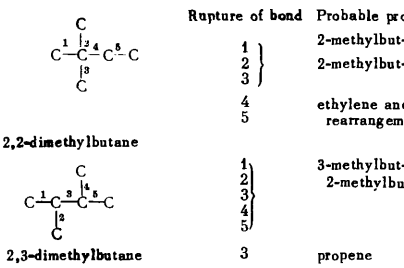

Fig. 3. Chromatograms of the pyrolysis products from the sodium salts of barbituric acid derivatives. Analysis conditions: 30% squalane on Celite 545, 100°:
*a*) luminal, *b*) eudon; 1) benzene; 2) toluene; 3) ethylbenzene; 4) *o*-xylene; 5) propylbenzene.

since the benzene nuclei are not broken down during the thermal decomposition of the substances, and the decomposition products contain aromatic compounds. Thus, for example, in the pyrolysis of benzyl alcohol, benzyl benzoate, and benzyl phenylacetate, the chief products are benzene, toluene, and carbon dioxide (Fig. 4). The pyrolysis was carried out in a short quartz tube filled with chromosorb (~2 g) and connected to the chromatographic column.

Hyden[31] proposed the use of the pyrolysis method for the gas-chromatographic analysis of thermally unstable compounds. For example, in the water–di-t-butyl peroxide system at 310° the peroxide decomposes almost instantaneously and the thermal decomposition products can be used for its qualitative identification. The method can be used for the quantitative analysis of the peroxide, since it has been established that there is a linear relationship between its concentration in the specimen and the area of the peaks due to the decomposition products (see Table in Ref. 31).

Nishi Sueo[32] showed that the method involving pyrolysis can be used for the qualitative and quantitative analysis of carbonyl compounds. The $C_2$–$C_6$ carbonyl compounds are liberated quantitatively from the 2,4-dinitrophenylhydrazones by heating with dicarboxylic acids. A specimen of the dinitrophenylhydrazone being studied is mixed with phthalic acid in the ratio 1 : 10 and introduced into a glass reaction vessel (250 × 0.3 cm) placed directly before the separating column. The dinitrophenylhydrazones of the carbonyl compounds decompose quantitatively at 250° with the liberation of the original compounds, which are then analysed chromatographically.

The use of pyrolysis in reaction gas chromatography is not restricted to the study of the pyrolysis products from polymers and non-volatile compounds. By analysing the pyrolysis products from 2,2- and 2,3-dimethylbutanes, Keulemans and Perry[33] showed that it is possible to identify paraffinic hydrocarbons. The pyrolysis was carried out in an empty quartz tube at 500°. The various possibilities of C–C bond rupture lead us to expect the formation of the following compounds:



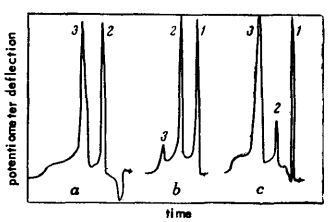




Fig. 4. Chromatogram of pyrolysis products from: *a*) benzyl alcohol; *b*) benzyl benzoate; *c*) benzyl phenylacetate (stationary liquid phase — silicone oil); 1) carbon dioxide; 2) benzene; 3) toluene.

TABLE 2. Chief products of the pyrolysis of 2,2-dimethylbutane (2,2-DMB) and 2,3-dimethylbutane (2,3-DMB).

| Products | Composition, % | |
|---|---|---|
| | 2,2-DMB | 2,3-DMB |
| Propene | 1 | 10 |
| But-1-ene, isobutene | 10 | 3 |
| 3-Methylbut-1-ene | 0 | 0.5 |
| 2-Methylbut-1-ene | 3 | traces |
| 2-Methylbut-2-ene | 11 | 16 |

Data on the composition of the pyrolysis products from the isomeric alkanes 2,2-dimethylbutane and 2,3-dimethylbutane (Table 2) show that the expected products are in fact formed. There is thus a simple relationship between the pyrolysis product and the original compound and this can be used for the identification of the hydrocarbons.

The study of substances by the pyrolysis method is carried out using standard chromatographs fitted with special assemblies for the pyrolysis[34,35] or in specially constructed apparatus[36].

## 3. CRACKING

Hydro-cracking was first used in gas chromatography by Zlatkis and Ridgway[37] to increase the sensitivity and accuracy of quantitative analysis and to simplify analytical calculations. The fractions leaving the separating column undergo cracking to methane and water at 425° in a reaction vessel containing a catalyst (nickel on kieselguhr). The water is absorbed in a special column and the methane is recorded by a thermal-conductivity detector. This method can be used to record various classes of organic compounds: alkanes, alkenes, aldehydes, ketones, alcohols, etc. In particular, the hydro-cracking of chromatographically separated aldehydes to methane has been described[38,39]. It should be noted that when the high-boiling compounds to be analysed are converted into equivalent quantities of methane, it is possible to use simpler and less expensive detector assemblies operating at room temperature.

## 4. HYDROGENATION AND DEHYDROGENATION

It is convenient to use hydrogenation and dehydrogenation reactions for the identification and analysis of compounds which give products whose gas-chromatographic separation has been studied in detail (i.e. for the reduction of an unknown problem to a problem which has already been solved) and also for the determination of impurities. In all cases the resulting hydrogenation and dehydrogenation products have properties which differ sharply from those of the original compounds, and this can be used for the qualitative and quantitative analysis of complex mixtures by comparative calculation based on two chromatograms obtained for the original specimen and the hydrogenated specimen. Thus by carrying out the catalytic hydrogenation of oxygen-containing compounds it is possible to identify ketones, esters, aldehydes, alcohols, and acids in a mixture from the hydrocarbons produced.

Drawert and coworkers[39,40] used hydrogenation to determine small quantities of ethanol in aqueous solutions and in blood. The alcohols were converted into hydrocarbons

by hydrogenation in a short tube filled with catalyst (Raney nickel on kieselguhr in the ratio 1 : 10). The hydrogenation is carried out at 160–200° in a current of hydrogen, which is also used as carrier gas. The above ratio of catalyst and inert carrier is an optimum, since large quantities of nickel above 200° lead to sintering of the catalyst, and when the quantity of nickel is decreased the rate of the hydrogenation also decreases. In the analysis of specimens with a high water content the water is removed from the specimen in a tube which contains $CaH_2$ and is placed after the reaction vessel but before the separating column. This method can be used to determine small quantities of the $C_1$–$C_{10}$ alcohols in aqueous solutions.

In a number of cases, in the analysis of saturated and unsaturated hydrocarbons, hydrogenation is used for the identification of peaks due to alkenes[41], using platinised asbestos as catalyst. The reaction vessel is placed before the column.

Struppe[42] made use of reaction gas chromatography in capillary chromatography. The reaction vessel was an aluminium capillary tube (600.00 × 0.03 cm) whose inner wall was covered with a thin layer of platinum. The catalyst was deposited on the inner walls of the capillary reaction vessel by the usual method for depositing the stationary liquid phase on a capillary column, i.e. the capillary was filled with an ethereal solution of $H_2[PtCl_4]$, the solution was shaken from one end of the tube to the other for 15 min, and the reaction vessel was dried in a current of hydrogen at 150° to reduce the hydrogen chloroplatinate to platinum. The hydrogenation was carried out in a current of hydrogen at 125°. The method was tested by analysing synthetic mixtures of hydrocarbons with boiling points up to 85°. It was shown that mono-, di-, and cyclo-alkenes add on hydrogen rapidly across the double bonds, whereas the carbon structure of aromatic, naphthenic, and cyclic hydrocarbons remains unchanged during hydrogenation under these conditions.

Keulemans and Voge[43] studied the dehydrogenation of naphthenes on a platinum catalyst (platinum–alumina–halogen). It was shown that under the conditions studied, cyclopentanes show different reactivities. In the reaction vessel, placed before the chromatographic column, cyclohexane is converted to benzene, but cyclopentane is unaffected under these conditions. Cyclopentanes undergo aromatisation to a much smaller extent than cyclohexanes and this can be used for the identification of cyclohexane in complex hydrocarbon mixtures.

From these examples, it can be seen that the use of hydrogenation and dehydrogenation provides a useful means of solving a number of analytical problems. The method has a number of disadvantages, however. In particular, the hydrogenation of various alkenes and alkynes containing the same number of carbon atoms in the molecule gives only one alkane, and the dehydrogenation of the *cis–trans*-isomers of cyclohexane derivatives gives only one aromatic hydrocarbon and this makes detailed qualitative analysis and identification of the original compounds difficult. Certain other reactions used in reaction gas chromatography have the same disadvantage.

## 5. DEHYDRATION AND DECARBOXYLATION

Dehydration and decarboxylation have been used successfully to determine alcohols and acids in dilute aqueous solutions. The procedure[2,3] does not require the preliminary separation or concentration of the compounds and solutions. The method can be used to analyse mono- and di-hydric alcohols and acids by separating the hydrocarbons which are formed from the oxygen-containing compounds in a reaction vessel placed directly before the chromatographic column. The reaction vessel consists of a stainless steel tube (10–15 × 0.6–1.0 cm) filled with sterchamol impregnated with phosphoric acid (ratio 2 : 1). The reaction temperature is 250–300°. To remove the water present in the specimen and formed during dehydration, a special drying tube containing calcium hydride is placed between the reaction vessel and the separating column. Monobasic organic acids react with phosphoric acid on heating and are decarboxylated to hydrocarbons; the number of carbon atoms per molecule of the latter is one less than that in the original acid.

Dilute aqueous solutions of glycerol and alcohol have been analysed using a multistage reaction vessel in which, in accordance with the scheme described earlier, the original substances undergo quantitative conversion to propene and ethane, whose gas-chromatographic analysis presents no difficulty.

It should be noted that, in the decarboxylation of each acid, only one product is formed, whereas in the dehydration of secondary alcohols, for example, two alkenes may be formed.

## 6. ESTERIFICATION

Carbonyl compounds, whose determination by ordinary chromatographic methods often presents difficulty, are esterified directly in the column or before the column and are analysed in the form of esters of organic or inorganic acids. Esterification in reaction gas chromatography is also used for the group identification of the individual class of compound in the analysis of complex mixtures.

Drawert and coworkers[1-3,39,40] developed a method for the analysis of alcohols in dilute aqueous solutions in the form of their nitrite esters. The esters are formed in a reaction vessel placed before the chromatographic column in the stream of carrier gas. The water which is present in the specimen and which interferes in the analysis of certain alcohols is absorbed in a drying tube containing calcium hydride. The reaction vessel consists of a stainless steel tube (length 8–12 cm, diameter 10 mm) filled with sterchamol and sodium nitrite (ratio 1 : 1). The nitrite esters are formed at 160–200°. The process of ester formation is improved considerably and takes place quantitatively if the specimen is acidified beforehand with tartaric or oxalic acid. The method was used to determine traces of ethanol (concentration $1 \times 10^{-5}$%) in blood.

Anders and Mannering[9] showed that the introduction of acetic or propionic anhydrides into the chromatographic column several seconds before the introduction of specimens of certain organic compounds, such as primary or secondary amines or compounds containing an alcoholic or phenolic hydroxyl, leads to the direct formation, in the column, of propionates or acetates whose retention times are different from those of the original compounds. Comparison of two chromatograms for the esterified and non-esterified specimens gives the necessary information for the qualitative and quantitative analysis of complex compounds of different classes. The use of this method, which is called[44] "the peak displacement method", makes it possible to determine naphth-1-ol, *p*-phenylphenol, ephedrine,

TABLE 3. The use of esterification in the analysis of some mixtures of compounds*.

| Compound | Column temperature, °C | Volume of 0.5% solution, ml | Without acetic anhydride: retention time, min (area, cm²) | With acetic anhydride: area for esterified compounds, cm² | With acetic anhydride: retention time, min (area of displaced peaks, cm²) |
|---|---|---|---|---|---|
| Amphetamine | 125 | 0.5 | 2.8(70) | 0 | 18.7(4.8) |
| Ephedrine | 125 | 4.0 | 9.2(21.0) | 0 | 63.0(10.8) |
| Naphth-1-ol | 150 | 0.5 | 6.8(6.7) | 3.4 | 9.1(2.0) |
| *p*-Phenylphenol | 150 | 1.0 | 16.3(12.1) | 2.7 | 23.1(6.0) |
| Codeine | 215 | 1.0 | 14.3(18.2) | 16.6 | 20.9(0.3) |
| Morphine | 215 | 6.0 | 16.5(15.8) | 0 | 20.3(22.5) 29.2(11.5) |
| Testosterone | 235 | 1.0 | 12.4(10.4) | 8.6 | 16.8 (0.6) |
| Diosgenin | 250 | 3.0 | 34.7 (68.4) | 11.0 | 47.7 (5.0) |
| Digitoxigenin | 275 | 5.0 | 23.7(21.7) | 6.9 | 28.0 (0.6) |

* 0.5% solutions of each compound were prepared in methanol, ethyl acetate, or tetrahydrofuran.

codeine, and their derivatives at temperatures in the range 125–275°. Table 3 shows that the retention times of the esterified compounds are much higher and this can be used for identification purposes.

## 7. SAPONIFICATION

In the analysis of esters the determination of mixed esters is of interest; this can be carried out by saponification, followed by chromatographic analysis of the alcohols formed.

This method was used successfully by Janak et al.[45] for the identification of esters of malonic acid. The reaction vessel (Fig. 5), placed at the outlet from a laboratory chromatograph with a katharometer, was filled with sterchamol with 40% potassium hydroxide deposited on its surface. Steam from water boiling in flask *D* was passed directly to the reaction vessel. After saponification of the high-boiling ester, a specimen of gas containing the vapour of the corresponding alcohols was collected at the outlet from the reaction vessel. The specimen taken was then introduced into a chromatograph with a flame-ionisation detector, where the alcohols formed on saponification were analysed. As an example, Fig. 6 gives the chromatograms for the products of the saponification of various esters of malonic acid.

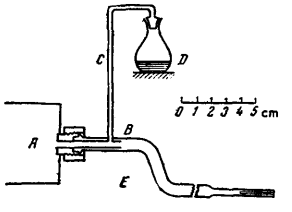



Fig. 5. Assembly for the saponification of ester fractions at the chromatograph outlet: *A*) detector; *B*) reaction vessel; *C*) tube; *D*) flask with boiling water; *E*) reaction vessel thermostat.

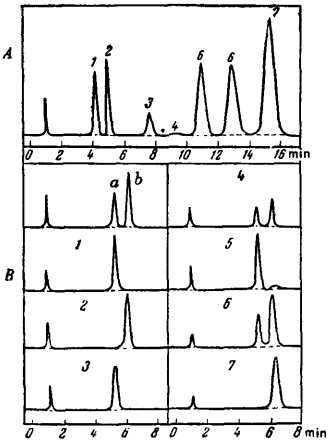



Fig. 6. Identification of esters of malonic acid from the saponification products: *A*) chromatogram of mixture of esters (Apiezon L, 220°); *B*) chromatograms of alcohols in a synthetic mixture [*a*) methanol; *b*) ethanol] and samples of saponified fractions 1–7 (triethanolamine, 60°): 1) methyl phenylacetate; 2) ethyl phenylacetate; 3) dimethyl phenylmalonate; 4) methyl phenylmalonate; 5) dimethyl ethylphenylmalonate + traces of diethyl phenylmalonate; 6) methyl ethyl ethylphenylmalonate; 7) diethyl ethylphenylmalonate.

## 8. FORMATION OF NON-VOLATILE COMPOUNDS

Of considerable importance in the qualitative and quantitative interpretation of the chromatograms of natural hydrocarbon mixtures are the methods of identification in reaction gas chromatography which involve the selective removal of certain classes of compound from the mixture. Thus sulphuric acid forms non-volatile compounds with alkenes. Martin[6] made use of this property of sulphuric acid in a reaction vessel (20.0 × 0.4 cm) filled with silica gel treated with sulphuric acid (2 : 3). The reaction vessel was placed in the gas-chromatographic set-up before the chromatographic column. It was shown that the absorption of monoalkenes, dialkenes, cycloalkenes, and alkynes, up to at least the $C_8$ fraction, takes place quantitatively in a stream of carrier gas in the temperature range 20–50°. The chromatograms given in Fig. 7 characterise fairly clearly the "subtraction method", as described by its author.

Mercury(II) perchlorate can also be used successfully for the selective removal of alkenes from a complex mixture[46]. A reaction vessel (25.0 × 0.8 cm) filled with firebrick moistened with a 1 M solution of mercury(II) perchlorate in 2 M perchloric acid (firebrick : solution ratio = = 1 : 1) is placed before the chromatographic column. Unlike the reaction vessel containing sulphuric acid, the vessel containing mercury(II) perchlorate absorbs only alkenes and does not absorb aromatic hydrocarbons.

The ordinary version of the subtraction method suffers from a number of disadvantages, chief of which are the need to obtain two chromatograms and the low accuracy of the determination for the case of a low concentration of component being removed in a general unresolved chromatographic peak. These disadvantages can be avoided by

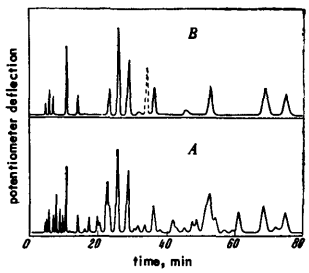



Fig. 7. Chromatograms of petroleum products from catalytic cracking (complex mixture of $C_3$–$C_6$ hydrocarbons); experimental conditions: stationary liquid phase — 10% quinoline on brick; length of column 10.5 m; temperature of column 25°; carrier gas velocity (nitrogen) 60 ml $min^{-1}$; volume of specimen 5 $\mu$l: *A*) without reaction vessel containing $H_2SO_4$; *B*) with reaction vessel containing $H_2SO_4$ (see Table II in Ref. 43 for interpretation of peaks).

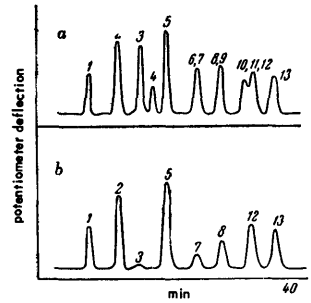



Fig. 8. Chromatograms of mixtures of $C_1$–$C_6$ monobromoalkanes on a column containing Tween 60: *a*) reaction vessel without $AgNO_3$; *b*) reaction vessel containing $AgNO_3$:
1) bromomethane; 2) bromoethane; 3) 2-bromopropane; 4) 2-bromo-2-methylpropane; 5) 1-bromopropane; 6) 2-bromobutane; 7) 1-bromo-2-methylpropane; 8) 1-bromobutane; 9) 2-bromo-2-methylbutane; 10) 2-bromopentane; 11) 3-bromopentane; 12) 1-bromo-3-methylbutane; 13) 1-bromopentane.

using the direct method of determining the individual-group composition of complex mixtures, in which the mixture to be analysed is separated on a chromatographic column, after which only those components of the mixture which are absorbed by the selective absorber of a differential analyser are recorded. This is achieved by placing the selective absorber between the katharometer chambers[47].

Since the analyser should record very low, rapidly-changing concentrations of substances in the chromatographic peaks of different compounds against a background of carrier gas and non-absorbed compounds, and also analyse solid and liquid substances in a gaseous phase, it must satisfy special requirements: (1) the dead space in the absorber should be small, relative to the volume of the carrier gas in which the component being analysed is distributed; (2) it is desirable that the sensitivity of the detector be the same for different compounds; and (3) the absorber should have an appreciable capacity and should absorb rapidly compounds of a definite class.

In addition to group reagents, use is also made of specific reagents reacting with one or a few compounds. For example, water is absorbed using compounds such as Anhydrone, calcium chloride, phosphorus pentoxide, etc.

The method of selective absorption has been used successfully to determine the isomeric bromo-hydrocarbons, 2-bromobutane and 1-bromo-2-methylpropane, which are generally eluted as a single peak in chromatographic analysis. The reaction vessel consisted of a 0.8 cm diameter glass tube filled with various reagents: the first layer (3 cm) consisted of silver nitrate on diatomite (1 : 1), the second (2 cm) consisted of sulphuric acid on diatomite, and the third (1 cm) consisted of disodium phosphate on diatomite. The layers in the reaction vessel were separated from one another by a layer of diatomite brick. The reaction vessel was placed before the separating column. At room temperature, 2-bromobutane is absorbed quantitatively by silver nitrate, whereas 1-bromo-2-methylpropane undergoes almost no reaction with this reagent. By comparing the chromatograms (Fig. 8), it is possible to calculate the concentrations of compounds which are not separated by ordinary gas chromatography.

Gil-Av and Herzberg-Minzly[48] extended the range of the subtraction method by proposing for the identification of peaks due to unknown compounds the use of relatively slow chemical reactions, leading not to complete but merely to partial absorption of the peaks ("the partial subtraction method"). As an example, let us consider the reaction between dienes with conjugated bonds (the components absorbed) and a dienophilic stationary liquid phase — chloromaleic anhydride. The reaction products are non-volatile and remain in the reactor column. The compounds being analysed are identified from the retention volume data and also by quantitative estimation of the rates of the chemical reactions with the stationary liquid phases. For example, the determination of the *cis*- and *trans*-isomers of 1,3-dienes is based on the fact that the *trans*-isomer reacts more rapidly with the dienophilic phase than the *cis*-isomer.

Ray[49] was one of the first to use the method of halogenation, leading to the formation of high-boiling compounds in a gas-chromatographic set-up, for the determination of impurities in ethylene. It was shown that removal of ethylene from the mixture being analysed takes place on a column containing 40% liquid bromine deposited on carbon, as a result of the formation of heavy bromo-derivatives of ethylene. The processes of bromination, adsorption (removal), and subsequent volumetric chromatographic separation of the light impurities were combined in a single instrument. The method made possible the quantitative determination of traces of hydrogen, nitrogen, carbon monoxide, methane, and ethane, present in ethylene in very low concentrations.

In reaction gas chromatography impurities accompanying a given compound are sometimes determined using fillers in the separating columns which "selectively retain" certain compounds. The formation of hydrogen bonds can also be regarded as a chemical reaction. Ackman and Burgher[50] made use of the formation of hydrogen bonds between macromolecular alcohols and the stationary liquid phase in a column to determine these impurities. It was shown that at 180–240° higher aliphatic alcohols are completely absorbed and retained by a separating column containing a polyester phase (diethyleneglycol succinate or

diethyleneglycol succinate containing 2% phosphoric acid) on the carrier. The non-alcoholic impurities in the higher aliphatic alcohols are retained on the polyester phase to an insignificant extent.

It is also of interest to supplement the ordinary method involving the selective absorption of certain compounds by subsequent gas-chromatographic analysis of the resulting non-volatile compounds; for this purpose it is necessary either to alter the temperature conditions of the experiment or to carry out new chemical changes.

## 9. OXIDATION OF ORGANIC COMPOUNDS

The oxidation of organic compounds is used in reaction gas chromatography to increase the sensitivity and accuracy of katharometers, to simplify quantitative calculations on the chromatograms, and also to reduce a complicated analytical problem to a simpler problem which has already been solved. A new method for the analysis of amino--acids was proposed by Zlatkis and Oro[38,51]. The amino--acids are oxidised to volatile aldehydes at 130° in a special reaction vessel placed before the chromatographic column and containing 30% ninhydrin on kieselguhr. The mixture of aldehydes formed was separated on the chromatographic column and passed to a reaction vessel for conversion into methane[37]. This method (where the separating column is placed between two reaction vessels) makes it possible to carry out the quantitative analysis of amino-acids in aqueous solutions at amino-acid concentrations down to $10^{-5}$%. The determination was carried out for a mixture of amino-acids containing alanine, α-amino-n-butyric acid, valine, norvaline, leucine, isoleucine, and norleucine. To improve the sensitivity and accuracy of detection, the fractions leaving the separating column are often oxidised and converted into carbon dioxide and water in a special reaction vessel placed before the detector[52]. Quartz or metallic tubes of different lengths (10–20 cm) and diameters (0.6–1.5 cm), filled with copper oxide wire, are used as reaction vessels. At 700–800° the fractions or individual compounds separated by gas chromatography undergo combustion on copper oxide with the formation of $CO_2$ and $H_2O$. Water is removed, beyond the oxidation reaction vessel, in absorption tubes containing calcium chloride, phosphorus pentoxide, or other effective absorbents.

The increase in sensitivity when the substances are analysed as carbon dioxide is due to the increase in the number of molecules being analysed, since one molecule of original substance gives several molecules of carbon dioxide. For example, the oxidation of one molecule of heptane gives seven molecules of carbon dioxide, so that the sensitivity of detection increases by a factor of 7. A particularly sharp increase in sensitivity (carrier gas nitrogen) is achieved by using a two-stage reaction vessel in which the organic compound fractions are oxidised to $CO_2$ and $H_2O$ and the water is reduced to hydrogen[53]. A tube (30.0 × × 0.4 cm) filled with copper oxide and finely-ground reduced iron is used as reaction vessel. The tube is heated to red heat (700–800°). After leaving the reaction vessel, the gases pass through a short soda lime column to remove carbon dioxide.

The chromatogram given in Fig. 9 shows the increase in sensitivity when various methods of converting the mixture of substances, before the latter reaches the katharometer, are used.

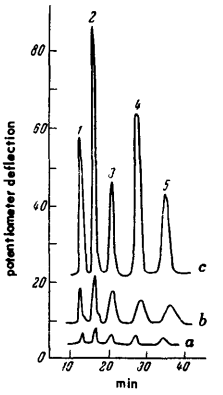



Fig. 9. Change in the sensitivity of the determination of organic compounds when preliminary conversion is used; chromatograms of equal-weight mixtures:
1) cinnamaldehyde; 2) butyl benzoate; 3) coumarin; 4) phenyl propylbutyrate; 5) naphthyl phenyl ketone; experimental conditions: stationary liquid phase — 20% silicone oil on Celite 545; detector — katharometer; carrier gas — nitrogen at 13 ml $min^{-1}$; column temperature 195°; weight of specimen 1 mg;
*a*) without conversion; *b*) conversion into carbon dioxide; *c*) conversion into hydrogen.

TABLE 4. C:H ratio in organic compounds, obtained from the peak areas (standard deviations of values given not greater than 3%; benzene used for calibration).

| Substance | Peak area, $cm^2$ | | Ratio of peak areas ($H_2$:$CO_2$) | C:H ratio | |
|---|---|---|---|---|---|
| | $H_2$ | $CO_2$ | | calculated | observed |
| Benzene | 634 | 140 | 4.53 | 1.00 | 1.00 |
| Cyclohexane | 515 | 55.6 | 9.26 | 2.00 | 2.04 |
| Ethyl ether | 547 | 47.9 | 11.42 | 2.50 | 2.52 |

The oxidation method is used successfully for the elementary analysis of organic compounds[54,55].

A method has been developed[56,57] for the continuous determination of the carbon and hydrogen contents of volatile organic compounds which have previously been separated on a chromatographic column. The conversion is carried out using a two-stage oxidation–reduction reaction vessel (60.0 × 0.6 cm tube) at 725°. After leaving the reaction vessel, the gases were separated on a supplementary column containing acetonylacetone on Celite and detected with a thermal-conductivity detector. The results are shown in Table 4.

In some cases[58,59] quantitative oxidation is used for the continuous radiometric analysis of substances, labelled with $^{14}C$ and $^{3}H$, on leaving the chromatograph. The method involving the detection of the compounds being analysed after their quantitative conversion into $CO_2$ has been used for the analysis of ethane–ethylene and propane–propene fractions[60], phenylchlorosilanes[61], and other purposes[62–64].

## 10. DETERMINATION OF WATER

Water is an important component of many systems to be analysed. In the analysis of specimens containing water, two problems arise: (1) the drying of the specimen, and (2) the quantitative determination of the water, The determination of water by the ordinary chromatographic method presents certain difficulties because of its strongly polar character. In some cases, when the water is present in the specimens in sufficient quantities, it can be determined, for example, on columns containing mono- and poly-ethyleneglycol, but the quantitative estimation of the moisture content of specimens with low water content is extremely difficult. The use of reaction gas chromatography makes it possible to analyse specimens containing down to $2 \times 10^{-4}$% of water[65].

When a reaction vessel containing calcium carbide is placed before the chromatographic column, the water in the mixtures being studied is converted into acetylene, whose determination by gas chromatography presents no difficulty.

If the calcium carbide in the reaction vessel is replaced by calcium hydride, the reaction of $CaH_2$ with water gives hydrogen, which is readily determined by chromatographic analysis. The problem of converting water quantitatively into hydrogen and acetylene in heterogeneous systems is not simple and this operation is a source of experimental error. These sources of experimental error are avoided in a method[66,67] for the determination of traces of water in hydrocarbons, based on the gas-chromatographic determination of the quantity of hydrogen liberated as a result of the reaction between the water dissolved in the liquid specimen under study and a solution of sodium aluminium hydride in the dimethyl ether of diethyleneglycol; the sensitivity of the method is $2 \times 10^{-4}$%.

## 11. QUALITATIVE CHEMICAL REACTIONS

The identification of the components of complex mixtures in gas-chromatographic analysis from retention volume data alone does not always give correct results, since many substances of different classes may have the same retention volumes on the same stationary liquid phase.

Fractions separated chromatographically can be identified by making use of the qualitative chemical reactions of group analysis (Table 5).[68]

The components of the specimen were prepared on an ordinary 1.83 mm analytical column packed with squalene on kieselguhr. Beyond the detector (katharometer) the gas stream was split into five separate streams by means of a special device. Each stream was directed into a tube (diameter 1 cm, height 3.5 cm) filled with a suitable reagent for qualitative functional group analysis. The change in the colour in one of the tubes indicated the class of compound being eluted. For the rapid replacement of the tubes containing the reagents (this is particularly important in the identification of chromatographic peaks with similar retention volumes), the gas stream was directed by means of a three-way tap into one of a series of five tubes. After the compound corresponding to a given chromatographic peak had passed through the tubes containing the five reagents, the gas stream was directed to the next series of tubes.

The composition of the specimens was determined from retention volume data and the results of the qualitative functional group analysis. Each substance was determined by comparing the corrected retention volume with the calibration graph for the corresponding homologous series. Since the plot of log $V$ versus $n$, where $V$ is the retention volume and $n$ the number of carbon atoms in the compound, is linear for two compounds, it is possible to construct this graph when the retention volumes are known.

As an example of the determination of the composition of a complex mixture, let us consider the chromatogram and the results of qualitative analysis given in Fig. 10. Although the chromatogram consists of five peaks, ten compounds were identified. In particular, the first peak corresponds to two compounds — ethanol and propan-2-one.

Thus by using the reagents for qualitative group analysis in chromatography, it is possible to detect substances of a definite class of compound in the fractions leaving the chromatographic column.

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The above examples are evidence of the wide scope and the rapid development of reaction gas chromatography as

TABLE 5. Characteristics of reagents for functional group analysis.

| Type of compound | Reagent | Characteristics of positive test; colour of solution or precipitate | Minimum sensitivity, mg | Compounds detected |
|---|---|---|---|---|
| Alcohols | $K_2Cr_2O_7$–$HNO_3$ | pale blue | 20 | $C_1$–$C_8$ |
| | cerium nitrite | amber | 100 | $C_1$–$C_8$ |
| Aldehydes | 2,4-DNPH | yellow precipitate | 20 | $C_1$–$C_6$ |
| | Schiff's reagent | pink | 50 | |
| Ketones | 2,4-DNPH | yellow precipitate | 20 | $C_3$–$C_8$ (methyl-ketones) |
| Esters | Fe hydroxamate | red | 40 | $C_1$–$C_8$ (acetates) |
| Thiols | Na nitroprusside | red | 50 | |
| | isatin | green | 100 | $C_1$–$C_9$ |
| | $Pb(OAc)_2$ | yellow precipitate | 100 | |
| Sulphides | Na nitroprusside | red | 50 | $C_2$–$C_{12}$ |
| Amines | Ginsberg's reagent | orange | 100 | $C_1$–$C_4$ |
| | Na nitroprusside | red, 1° | 50 | $C_1$–$C_4$ |
| | | pale blue, 2° | 50 | $C_1$–$C_4$ diethyl and dipentyl |
| Nitriles | Fe hydroxamate–propyleneglycol | red | 40 | $C_2$–$C_5$ |
| Aromatic | HCHO–$H_2SO_4$ | wine red | 20 | $C_6H_6$–$C_{10}H_{14}$ |
| Aliphatic | HCHO–$H_2SO_4$ | ditto | 40 | $(C_2H_6)$? |
| Halogeno-derivatives | alcoholic $AgNO_3$ solution | white precipitate | 20 | $C_1$–$C_5$ |

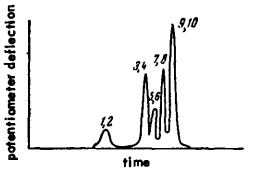



Fig. 10. Identification of compounds in a complex 10-component mixture; experimental conditions: 125°; carrier gas velocity 50 ml $min^{-1}$; volume of specimen 2.0 $\mu$l:
*a*) alcohol and ketone, ROH, RCOR′; *b*) ketone and ester, RCOR′, RCOOR′; *c*) thiol, RSH; *d*) aldehyde, alcohol, aromatic hydrocarbon, RCHO, ROH, ArR; *e*) aldehyde and aromatic hydrocarbon, RCHO, ArR.

an analytical method. The development of analytical reaction gas chromatography is taking place in two directions: (1) the development of new methods which make it possible to extend the methods of gas chromatography to the analysis of compounds which cannot be analysed by the ordinary form of gas chromatography (e.g. the analysis of polymers, salts of organic acids, etc.); (2) the development of simple convenient practical methods for the analysis of specific systems (particularly in biochemical studies) whose analysis requires complex and expensive equipment (capillary chromatography, electron-capture detectors, etc.). These methods are of particular importance for carrying out specific analyses in industry and in the laboratory.

Thus the introduction of a new "variable" (chemical reactions) into gas chromatography has led to the creation of a promising new form of chromatography – reaction gas chromatography. The skilful use of this "variable" will undoubtedly have a positive influence on the development of practical gas-chromatographic methods for the analysis of a wide variety of mixtures.


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# THE STRUCTURE OF COMPLEXONES AND THEIR COMPLEX-FORMING POWER

N. M. Dyatlova and R. P. Lastovskii

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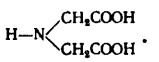
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## I. INTRODUCTION

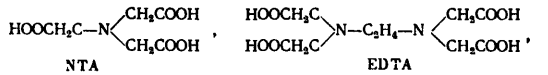
The increasing importance of complex compounds in different fields of theoretical research and, particularly, in practical applications, has led to the rapid developement of the chemistry of multidentate reagents. The complexones form some of the most interesting and promising compounds of this type [1-7].

The term complexone is usually applied to compounds that contain at least one iminodiacetate group $-N(CH_2COOH)_2$, linked to various aliphatic or aromatic substituents by residues of acetic or alkyliminodiacetic acid. At present a series of complexones are also known which are derivatives of iminodipropionic acid, and also aminomethyl--phosphonic and -sulphonic acids [8-17].

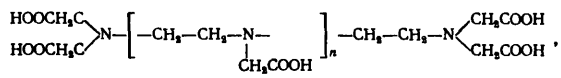
The simplest representative of this class of compounds is iminodiacetic acid:



Nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), and other polyethylenepolyaminepolyacetic acids may be regarded as its structural analogues:



NTA EDTA



where $n = 0, 1, 2\ldots$

These compounds were first mentioned in 1936 when NTA, EDTA, and their salts were patented by I. G. Farbenindustrie and put on the world market under the names Trilon A† and Trilon B‡ as compounds suitable for water

† At present also marketed under the names: Complexone I, Chelaton I, and Titriplex I [these refer to NTA (Ed. of Translation)].

‡ At present also marketed under the names: Complexone III, Chelaton III, Sequestrene, Versene, Irgalon, Titriplex III, Nervanid [most of these refer to the dihydrate of the disodium salt of EDTA, EDTA itself being known as Complexone II, etc. (Ed. of Translation)].

softening. The subsequent work of Schwarzenbach[3,4,18-20] on the determination of the physicochemical constants of the complexones, and on the kinetics and mechanism of their reactions with cations, opened great possibilities for the use of these compounds and provided fruitful ground for the creation of a whole series of new complexones. At the present time there are more than 200 complexones.

These multidentate chelating agents, which created unlimited possibilities for modification of the properties of the central atom and ligands by the formation of highly stable water-soluble complexes, found wide use in many branches of science and technology; this is shown by the tremendous number of publications and patents that have appeared in both Soviet and non-Russian literature.

The introduction of complexones into analytical chemistry opened great possibilities in volumetric[2-7,18-24], gravimetric[2-7,18,19,25-30], colorimetric[2,3,6,7,18,19,31-37], polarographic[2,3,6,7,18,19,38-42], amperometric[6,7,18,19,43,44], and other methods of analysis[6,7,18-20,45-50]. By the use of these compounds the simplest methods of determining cations occurring in difficult combinations without preliminary separation could be developed.

In order to show more clearly the importance of complexones in analysis, it is sufficient to note that at the present time over 60 elements of Mendeleev's Table (practically all the cations and many anions) can be determined by direct or indirect methods with the aid of complexones. These compounds indeed form the nucleus of modern volumetric analysis, which means of analytical chemistry as a whole. The complexones are no less important in the purification and preparation of various elements and compounds. One of the most difficult tasks, the separation of the rare-earth elements, has now been solved by the use of complexones[51-62].

The complexones are of great importance in biology and medicine. These compounds are quite effective in removing toxic metals from the body, including radioactive isotopes and their fission products[63-67]. They are also used for removing radioactive compounds from various contaminated surfaces[68-74]. By the use of complexones and complexonates in some branches of agriculture, the metal content of the soil can be regulated and chlorosis of plants can be prevented[75-78]. Moreover complexones have been widely used in the textile, leather, food, and paper industries, in the production of metals, varnishes, paints, and rubbers, and in the purification of petroleum, wax, fats, etc.[8,9,49]

The number of papers on the use of complexones is very large. Most of them have been summarised and presented as monographs and reviews[2-8].

Problems connected with the study of the effect of the structure of these multidentate chelating agents on their complexing properties, and also on the kinetics and mechanism of their interaction, are dealt with practically only in the original literature. In this connection we consider it expedient to devote the present article to these important questions with a preliminary examination of the fundamental principles of chelate formation.

## II. PROPERTIES OF COMPLEXONES AND PRINCIPLES OF CHELATE FORMATION

Complexones are multidentate chelate-forming reagents. The term "chelate" was proposed by Morgan[79] to denote those cyclic structures that are formed as a result of the union of a cation with two or more donor groups belonging to one molecule of complexing agent. The same is derived from the Greek word "χιλη" which denotes a claw (from which another name for these compounds "clawlike" is derived). This type of ring formation can, of course, only be formed by polyfunctional reagents which can replace more than one position in the coordination sphere of the metal[80-85]. In this connection we distinguish bi-, ter-, quadri-, and multi-dentate complexing agents; these can form one, two, three, and more chelate rings with the metal ion.

Iminodiacetic acid is an example of a terdentate, NTA of a quadridentate, and EDTA of a sexidentate complex-forming agent.

The normal complexes are formed as a result of the interaction of a cation with the completely dissociated anion of the complexone, or in the extreme case, when only betaine hydrogen is present in it. For example, EDTA (denoted below by $H_4Y$) forms a complex by the reaction

$$M_{aq}^{n+} + Y^{4-} \rightleftarrows MY^{n-4} + aq.$$

In an acid medium a weakly basic hydrogen complex may be formed, and in an alkaline medium a hydroxo-complex. In solution the formation of compounds of this kind proceeds in the following manner. When the complexone is introduced into the solution conditions are created for competition between water molecules of the hydration shell of the cation and molecules introduced into the solution by the chelating agent. The necessary conditions for displacing water from the aquo-complex are: a higher donor power of the ligand groups bonding with the metal; a suitable pH value of the solution; and a sufficiently convenient structure of the chelating agent, for otherwise steric hindrance makes coordination impossible.

The competing complexing agent (Y), satisfying these requirements is, under suitable conditions, capable of displacing water from the coordination sphere of the aquo-complex ($M_{aq}$) with the formation of a new complex (MY). The stability of the complexes formed in solution may be denoted by the equilibrium constant (the formation or stability constant):

$$K = \frac{a_{MY}}{a_M a_Y},$$

where $a$ is the activity of compounds taking part in the reaction (the charge is omitted in the formula).

The inverse quantity, the instability constant, is often used[2,3,4,78-85,86]. This quantitative characteristic, indicating the magnitude of the displacement of equilibrium in the direction of complex formation, is derived from the law of mass action, without taking account of successive replacement of the coordination positions in the aquo-complex and the possibility of the formation of several intermediate complexes. At constant ionic strength, concentration ("apparent") stability constants of the complex may be successfully used; these are derived from the equation

$$K_{MY} = \frac{[MY]}{[M][Y]}.$$

These constants show the ratio between the concentrations of ion bound in the complex and the free ion of the metal for every given concentration of the complexing agent.

High thermodynamic stability is an outstanding property of chelate compounds. This is mainly due to the spatially favourable arrangement of complexing groups, leading to the possibility of using in the complex all donor atoms of the ligand, both oxygen and nitrogen, with fairly large polarisability [3,87-90].

EDTA is an ideal example of compounds of this type. This complexone is a universal sexidentate reagent, capable of fully saturating the coordination capacity of most cations, thereby creating the optimal variant of an intra--complex compound with the maximal number of five--membered rings and comparatively little spatial stress.

However, it should be mentioned that there are cases when not all groups of the ligand capable of coordination take part in the formation of rings of a given chelate; as a result less stable compounds are formed. This may be explained by too large a strain on the rings with maximal use of chelate groups capable of coordination, or by the large volume of the coordinating groups, often preventing the achievement of the maximal coordination number of the ions. Phenomena of this kind are undoubtedly connected with the geometrical structure of the internal ligand contour of the chelating agent, and also with the nature of the donor atoms and the central metal ion. Cases are known in which multidentate reagents do not occupy all possible coordination positions in the internal sphere of the complex [3,91-93]. This is mainly observed with small cations and also with some metal ions that form complex compounds with a planar structure. Moreover, the presence in the solution of other donor atoms firmly bound to the cation also leads to a number of cases of incomplete substitution of its coordinating positions by the chelating agent.

The chelate compounds are usually more stable than their non-chelate analogues. In the general case, the equilibrium constant of the substitution reaction

$$ML_n + mY \rightleftarrows MY_m + nL, \qquad (1)$$

where $n$, the number of unidentate ligands replaced by $m$ related multidentate ligands (occupying the same number of coordination positions), is greater than unity. Schwarzenbach called this increased stability that arises through the formation of a ring the "chelate" effect [94,95]. This effect is so general that isolated cases of a negative value of $\log K$ of substitution may be explained either by the complete absence of chelate rings or by a hypothesis about their strain.

Most authors [86,96-100] connect the chelate effect with a greater increase in entropy in reactions in which chelate compounds are formed than in reactions connected with the addition of some simple ligands. Many attempts have been made to determine the entropy change for this effect. Calvin and Bailes proposed that the positive entropy change for the equilibrium substitution, Reaction (1), is mainly due to a gain in translational entropy; however, the effect is observed much less frequently than would be expected from this hypothesis [101]. Martell noted that the value of $\Delta S$ for a number of complexonates increases with increasing number of donor atoms and with decreasing radius of the cation [96]. He also found that the dependence of $\Delta S$ on the number of coordinating acetate groups is linear. Schwarzenbach proposed that the entropy contribution to the chelate effect is related to ring closure and in the main does not depend on the nature of the metal ion or on the bonding atom of the ligand [94]; the greatest chelate effect is observed in the formation of the smallest ring free from strain, which usually consists of five members in a saturated ring and of six members in an unsaturated ring. Adamson [102] considers that the chelate effect is more apparent than real; it is to a large degree a packing effect, which appears as configurational entropy. However, it should be noted that since the chelate effect is expressed by the difference between the logarithms of the stability constants of the chelate complex and the complex with simple ligands of the same type, there is a correlation between factors affecting the stability of the complexes formed and a ring effect. In this connection, the unequal changes of these two constants with a change in the concentration of the complexing agent for a different number of ligands should be taken into account. The value of the stability constant of a simple complex by $n$ ligands (L) given by the equation

$$K_{ML_n} = \frac{[ML_n]}{[M][L]^n},$$

changes with change in concentration of the complexing agent much faster than in the case of chelate formation, expressed by the equation:

$$K_{MY} = \frac{[MY]}{[M][Y]};$$

therefore the standard state of the reacting compounds is usually taken as a 1 M solution of the completely hydrated ions or molecules.

Another important characteristic of the complexing reaction is the kinetics of the process [2,3,85]. Although practically the same quantities (charge, size, and stereochemical configuration, electronegativity, polarisability of the central metal ion and ligands) enter into the factors affecting the rate of reaction and the stability of the complexes formed, it has been stated in the literature [85] that these two quantities are not correlated, that is, the stability of the complexes does not characterise their kinetic behaviour in formation or substitution reactions. A low rate of displacement does not inevitably mean a high stabilisation of the bond. A few studies in the complexone field have shown that the whole process of interaction of the metal with complexones is subject to the same kinetic laws; the exchange proceeds both by a second-order reaction (direct exchange between metal and complex) and by a first-order reaction (dissociation of various protonated complexes) [103-105].

Protonation of the ligand reduces the electron density at the metal bond and increases the rate of dissociation of this bond. For example, HCd(EDTA) dissociates 20 times faster than Cd(EDTA), that is, aquation appears to be catalysed by acids. The formation of complexes of the external shell type Fe(EDTA) is practically instantaneous; the formation of complexes of the internal shell type, in which there is at least one electron on each $d$-shell — for example, Cr(EDTA) and Co(EDTA) — proceeds incomparably slower [103]. Therefore, in compounds of this type the formation and decomposition of the complexes are essential kinetic factors equivalent to the effect of electronic structure. The formation of complexes with cyclohex-1,2-ylenebis(iminodiacetic acid) is somewhat slower [2,3,106], which is probably connected with rigid fixation at a definite distance and the corresponding directional alignment of the complexing groups.

A considerably larger number of investigations have been devoted to the substitution reactions of complexes, in which the central metal ion or a ligand is exchanged. Many complexes enter into exchanges with free metal ions with measurable velocity; very often the exchange proceeds in several stages, sometimes with partial opening of the

chelate ring and the formation of new metal–ligand bonds; in all cases the mechanism of the exchange reaction and the constants for the rate of formation of complexes depend on pH[3,85]. Cation-exchange reactions of most complexonates of NTA and EDTA[103] are practically instantaneous, but the reactions of complexonates of cyclohex-1,2-ylenebis(iminodiacetic acid) are much slower (10 to 100 times). Thus, establishment of the equilibrium

$$FeY^- + Th^{4+} \rightleftarrows ThY + Fe^{3+}$$

takes several days[106] but displacement of nickel from cyclohex-1,2-ylenebis(iminodiacetate) by other cations in general does not reach equilibrium in a measurable time. Of particular interest are the rates of oxidation-reduction processes, and in particular between two oxidation states of the same element in the complex. These reactions are practically instantaneous. Thus, the rate of the exchange reaction $[Co(EDTA)]^{2-}$–$[Co(EDTA)]^-$ is $4 \times 10^{-7}$ mole$^{-1}$ s$^{-1}$ and that for the reaction $[Fe(EDTA)]^{2-}$–$[Fe(EDTA)]^-$ exceeds $1 \times 10^{-3}$ mole$^{-1}$ s$^{-1}$.

Summarising, one should note that this side of the question of complex formation, which is important in practice and interesting from a theoretical standpoint, has been studied insufficiently; it is therefore not always possible to compare results obtained and to give basic interpretations of observed facts.

## III. THE EFFECT OF THE STRUCTURE OF COMPLEXONES ON THEIR COMPLEXING POWER

The question of the relation between the structure of chelating compounds and their reactivity is a very important and topical one from both the practical and the theoretical viewpoints. A knowledge of the fundamental physical constants and the variety of factors that affect complex formation, forms a definite scientific base, which has already made the use of complexones possible not only in a number of problems in analytical chemistry, but also in finding new fields of application for these compounds. This knowledge has been used to solve some most important problems in the national economy and has given rise to promising possibilities of further development.

The theoretical side of the problem is also of undoubted importance; complexones are multidentate reagents[99] that form stable complex compounds with practically all cations and, for this reason, if some degree of selectivity is to be conferred on them, a special structure of the molecule is necessary, account being taken of electronic structure, nature of the coordinating atoms, and the stereochemistry of the complexes. All studies connected with the elucidation of the principles of change in the complexing action of complexones are very valuable contributions to the setting up of a theory of organic reagents. Furthermore, these principles make possible theoretical predictions, which in a number of cases permit the synthesis of new complexones with predetermined properties.

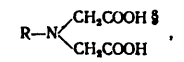
Modifications of the complexone molecule have been carried out in the following main directions:

(1) introduction into the complexone molecule of various substituents not taking part in complex formation but affecting the basicity of the coordinating nitrogen of the iminodiacetate grouping; (2) increasing the denticity of the chelating agent by introducing into the complexone molecule heteroatoms and iminoacetate and characteristic analytical groupings that tend to form complexes with certain elements; (3) changing the geometry of the internal ligand contour.

The following Sections of this review will be devoted to this aspect of the problem.

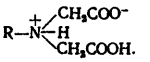
### 1. The Effect of the Basicity of the Nitrogen of the Iminodiacetate Group

One of the main factors affecting the complexing power of complexones is the basicity of the nitrogen atom of the iminodiacetate groups. This effect has been well studied on derivatives of iminodiacetic acid, which is the simplest structural model of complexones. At the present time a considerable number of compounds with the general formula:



have been synthesised, where R represents various aliphatic, aromatic, or alicyclic substituents containing functional and non-functional groups[107-118]. Data on the complexing properties of these compounds are collected in Table 1.

The first three vertical columns of Table 1 contain values of the acid dissociation constants of the complexones. In accordance with the views of Schwarzenbach, the betaine structure is ascribed to all these acids[18,108-115]:



The betaine structure of these compounds also explains the high value of the negative logarithm of the dissociation constant for the first hydrogen atom, the mobility of which depends on the basicity of the nitrogen atom linked to it. The basicity of the nitrogen atom in turn changes with the inductive effect of substituents R linked to nitrogen. When hydrogen in the iminodiacetic acid group is replaced by the $CH_3$ group, the basic properties of the nitrogen are increased as a result of the positive inductive effect of the $CH_3$ group. If one, or particularly two, phenyl groups are introduced into the methyl group the basicity of the nitrogen decreases somewhat due to the comparatively strong electron-acceptor properties of these groups. In the case of aniline, the electron pair of the nitrogen is displaced towards the benzene nucleus, which leads to a still greater weakening of the basic properties of the nitrogen.

A definite relation between the mobility of the betaine proton and the coordinating power of the nitrogen atom would therefore be expected. In fact, for complexones containing alkyl, alkylaryl, and alicyclic radicals a simple linear relationship is observed between the basicity of the nitrogen, as expressed by the acid dissociation constant of the last proton, and its coordinating power (Fig. 1).

As Fig. 1 shows, the introduction of alkyl and alkylaryl radicals increases the complexing power of the complexones, and, on the contrary, when the phenyl radical is a direct neighbour, the complexing power of the iminodiacetic acid group is lowered.

§ In future the iminodiacetate group $-N\langle^{CH_2COOH}_{CH_2COOH}$ will be denoted by the symbol $-N\langle$.

TABLE 1. Negative logarithms of dissociation constants and stability constants of complexes of iminodiacetic acid and its derivatives.

| Complexone | Formula | pK dissociation | | | $pK_{MY}$ | | | | | | | | | | | | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $pK_1$ | $pK_2$ | $pK_3$ | $Mg^{++}$ | $Ca^{++}$ | $Sr^{++}$ | $Ba^{++}$ | $Mn^{++}$ | $Fe^{++}$ | $Co^{++}$ | $Ni^{++}$ | $Cu^{++}$ | $Zn^{++}$ | $Cd^{++}$ | $Pb^{++}$ | $Hg^{++}$ | |
| Iminodiacetic acid | HN(CH$_2$–N) | 9.12 | 2.54 | — | 3.86 | 3.41 | — | 1.67 | — | — | 6.9 | 8.2 | 10.3 | 7.0 | 5.4 | — | — | 111,114,116 |
| Methyliminodiacetic acid | CH$_3$N(CH$_2$–N) | 9.65 | 2.12 | | 3.44 | 3.75 | 2.85 | 2.59 | 5.40 | 6.65 | 7.62 | 8.73 | 11.09 | 7.65 | 6.77 | 8.02 | 5.47 | 110,114,115 |
| *N*(3,3-Dimethylbutyl)-iminodiacetic acid | CH$_3$–C(CH$_3$)$_2$–CH$_2$–CH$_2$–N(CH$_2$–N) | 10.24 | 2.4 | | 3.60 | 3.68 | 2.70 | 2.41 | 5.55 | — | 7.78 | 8.70 | 11.49 | 7.92 | 7.12 | 8.16 | 5.91 | 114 |
| 2-Hydroxyethyliminodiacetic acid | HO–CH$_2$–CH$_2$–N(CH$_2$–N) | 8.72 | 2.2 | | 3.44 | 4.63 | 3.77 | 3.42 | 5.55 | 6.78 | 7.90 | 9.28 | 11.86 | 8.33 | 7.52 | 9.41 | 5.48 | 114 |
| 2-Mercaptoethyliminodiacetic acid | HS–CH$_2$–CH$_2$–N(CH$_2$–N) | 10.79 | 8.17 | 2.14 | 3.32 | 4.88 | 3.62 | 3.55 | 9.32 | 11.72 | 14.67 | 13.75 | — | 15.92 | 16.72 | 17.03 | 16.16 | 114 |
| 2-Methoxyethyliminodiacetic acid | CH$_3$O–CH$_2$–CH$_2$–N(CH$_2$–N) | 8.96 | 2.2 | | 4.31 | 4.53 | 3.84 | 3.56 | 5.53 | 6.81 | 7.96 | 9.39 | 12.24 | 8.43 | 7.53 | 9.49 | 5.94 | 114 |
| 2-Methylthioethyliminodiacetic acid | CH$_3$S–CH$_2$–CH$_2$–N(CH$_2$–N) | 8.91 | 2.1 | | 3.02 | 3.34 | 2.71 | 2.62 | 5.10 | 7.12 | 8.51 | 10.0 | 12.63 | 8.28 | 7.89 | 9.12 | 8.01 | 114 |
| 2-Aminoethyliminodiacetic acid | H$_2$N–CH$_2$–CH$_2$–N(CH$_2$–N) | 11.05 | 5.58 | | 4.58 | 4.63 | 3.55 | 3.19 | 7.71 | 9.81 | 11.78 | 13.73 | 15.90 | 11.93 | 10.58 | 12.22 | 9.75 | 114 |
| Nitrilotriacetic acid | HOOC–CH$_2$–N(CH$_2$–N) | 9.73 | 2.49 | 1.89 | 5.41 | 6.41 | 4.98 | 4.82 | 7.44 | 8.83 | 10.38 | 11.53 | 12.96 | 10.67 | 9.83 | 11.39 | — | 108,112,113 |
| Nitrilotriacetic acid monoamide | O=C(H$_2$N)–CH$_2$–N(CH$_2$–N) | 6.60 | 2.30 | | 2.47 | 3.96 | 3.03 | 2.88 | 4.93 | — | 6.91 | 8.02 | 9.68 | 7.30 | 7.08 | 8.40 | 3.82 | 114 |
| Nitrilotriacetic acid mononitrile | N≡C–CH$_2$–N(CH$_2$–N) | 4.34 | 3.06 | | 1.86 | 2.75 | 2.15 | 1.98 | 3.50 | — | 5.38 | 6.20 | 7.45 | 5.80 | 4.43 | — | 2.40 | 114 |
| 2-(Trimethylammonio)-ethyliminodiacetic acid | (CH$_3$)$_3$N$^+$–CH$_2$–CH$_2$–N(CH$_2$–N) | 5.45 | 2.32 | | 1.42 | 1.88 | 1.22 | 1.34 | 2.87 | — | 5.51 | 6.00 | 7.73 | 5.34 | 4.62 | 5.40 | 2.77 | 114 |
| *N*-[2-(2-Ethoxycarbonylamine(ethyl)]iminodiacetic acid | C$_2$H$_5$O–C(=O)–NH–CH$_2$–CH$_2$–N(CH$_2$–N) | 8.57 | 2.20 | | 2.68 | 2.99 | 2.14 | 2.00 | 4.60 | — | 6.71 | 7.94 | 10.50 | 6.86 | 5.86 | 7.25 | 4.50 | 114 |
| 2,2′,3″-Nitrilodiaceticpropionic acid | HOOC–CH$_2$–CH$_2$–N(CH$_2$–N) | 9.66 | — | | 5.28 | 5.04 | 3.87 | 3.40 | — | — | — | — | — | — | — | — | — | 114 |
| Taurine-*N*-diacetic acid | $^-$O$_3$S–CH$_2$–CH$_2$–N(CH$_2$–N) | 8.16 | 2.28 | 1.90 | 3.48 | 4.15 | 3.26 | 3.01 | — | — | — | — | — | — | — | — | — | 110 |
| *N*-Phosphonomethyliminodiacetic acid | $^-$HO$_3$P–CH$_2$–N(CH$_2$–N) | 10.70 | 5.57 | 2,25<br>2.00 | 6.28 | 7.18 | 5.59 | 5.35 | — | — | — | — | — | — | — | — | — | 107,110 |
| *N*-2-Phosphoethyliminodiacetic acid | $^-$HO$_3$P–CH$_2$–CH$_2$–N(CH$_2$–N) | 6.54<br>10.46 | 27.45<br>7.00 | 2.0<br>2.74 | 6.38 | 5.44 | 4.10 | 3.64 | — | — | — | — | — | — | — | — | — | 107,110 |
| Phenyliminodiacetic acid | C$_6$H$_5$–N(CH$_2$–N) | 5.18<br>4.96 | 2.40<br>2.51 | | 1.15 | 1.5 | — | — | 1.58 | 2.01 | 2.90 | 3.53 | 6.57 | 3.22 | 2.16 | 3.49 | — | 107,109,117 |
| *o*-Sulphophenyliminodiacetic acid | HO$_3$S–C$_6$H$_4$–N(CH$_2$–N) | 6.29 | 3.10 | 1,0 | 2.68 | 4.57 | 3.50 | 3.48 | — | — | — | — | — | — | — | — | — | 109 |
| *m*-Sulphophenyliminodiacetic acid | HO$_3$S–C$_6$H$_4$–N(CH$_2$–N) | 4.78 | 2.36 | 1 | 1.26 | 1.26 | — | — | — | — | — | — | — | — | — | — | — | 109 |
| *p*-Sulphophenyliminodiacetic acid | HO$_3$S–C$_6$H$_4$–N(CH$_2$–N) | 4.54 | 2.31 | 1 | 1.15 | 0.95 | — | — | — | — | — | — | — | — | — | — | — | 109 |
| *o*-Carboxyphenyliminodiacetic acid | HOOC–C$_6$H$_4$–N(CH$_2$–N) | 7.75 | 2.98 | 2,35 | 3.91 | 5.06 | 3.91 | 3.57 | — | — | — | — | — | — | — | — | — | 109,116 |
| *m*-Carboxyphenyliminodiacetic acid | HOOC–C$_6$H$_4$–N(CH$_2$–N) | 5.10 | 4.06 | 2.40 | 1.38 | 1.46 | 1.0 | 1.0 | — | — | — | — | — | — | — | — | — | 109 |
| *p*-Carboxyphenyliminodiacetic acid | HOOC–C$_6$H$_4$–N(CH$_2$–N) | 5.20 | 4.28 | 2.31 | 1.30 | 1.30 | 1.0 | 1.0 | — | — | — | — | — | — | — | — | — | 109 |

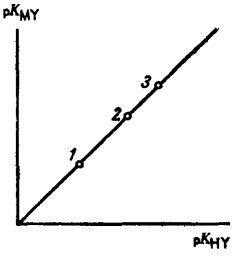


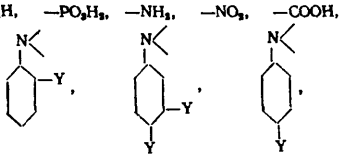

Fig. 1. Dependence of the coordinating power of the nitrogen on its basicity, expressed as an acid dissociation constant of the last betaine proton:
1) benzyliminodiacetic acid; 2) cyclohexyliminodiacetic acid; 3) methyliminodiacetic acid.

More complex relationships are observed when various functional substituents are introduced into the hydrocarbon radical of iminodiacetic acid.

Schwarzenbach [110-114] studied derivatives of iminodiacetic acid and anilinediacetic acid with the general formulae:

X–CH$_2$–N(CH$_2$–N), X–CH$_2$–CH$_2$–N(CH$_2$–N),

where X = –SO$_3$H, –PO$_3$H$_2$, –NH$_2$, –NO$_2$, –COOH, –OH.

and 

where Y = –SO$_3$H, –COOH.

The introduction of similar substituents on iminodiacetic and phenyliminodiacetic acid has a twofold effect on the complexing power of the compounds. On the one hand, the basicity of the imino-nitrogen changes because of the electrostatic effect of the substituents; on the other hand, the complexing power of the compounds changes because of the tendency of some of the substituents introduced to form additional rings. The latter factor mainly affects $\alpha$-derivatives of alkylaminodiacetic acid and *ortho*-derivatives of phenyliminodiacetic acid [109]. For ligands of this kind, containing several types of group capable of coordinating, the linear dependence between the basicity of the nitrogen and coordinating power only holds approximately; the dependence holds only for a number of ligands of similar structure that form the same number of chelate rings of the same size and having the same $\pi$ bonding tendency. If there is no steric hindrance, then the change in free energy (enthalpy) shifts in parallel with the values of p$K$ for $HY^-$ (in water). A greater or lesser deviation from linear dependence between p$K$(MY) and p$K$($HY^-$) is probably due to enthalpy or entropy effects, or to both.

A comparison of various oxygen-containing donors indicates that the stability of the bond practically always increases with increasing basicity of nitrogen, although the relation is not always linear.

## 2. The Effect of Functional-Analytical Groupings and Heteroatoms on the Complexing Power of Complexones

The question of the selectivity of the chelating agent for a given cation is of great interest. One way in which this selectivity can be achieved is by the introduction into the complexing molecule of characteristic functional groupings with a definite specificity; this often leads to the required analytical effect. The presence of these groupings in the complexone, without changing the main reaction mechanism, often promotes a clearer development of the analytical effect, and is favourably reflected in the character of the final product.

The introduction into the complexone molecule of hetero-atoms — sulphur, nitrogen, oxygen — capable of coordinating with a metal to form a new ring, has a similar action. The nature of the donor atom plays the main part in increasing the selectivity.

The effect of the introduction of various groupings on the complexing power of the complexone in the aliphatic series has been studied in detail on derivatives of iminodiacetic acid with the general formula $X-CH_2-N<$ [110,114,115,117,118]. Different substituents have different effects on the complexing power.

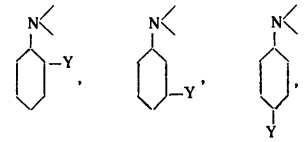
The nitrogen, oxygen, sulphur, and phosphorus atoms of aliphatically bound groups, $-OH$, $-OCH_3$, $-SH$, $-SCH_3$, $-PO_3H$, $-SO_3H$, $-NH_2$, form a coordinate bond with metals and this considerably increases the stability of the complexes. The maximal effect is observed when the substituent is in the $\alpha$-position to the nitrogen of the iminodiacetate group. In the case of the $\beta$-position the stabilising effect is much weaker. The complexone acquires a definite selectivity depending on the grouping introduced and the nature of the donor atom. Many workers have noted a specificity for iron in complexones containing hydroxyethyl groups [120-126]; this has been utilised in a number of practical problems.

Complexones containing a mercapto-group sulphur atom and an amino-group show a great tendency to form complexes with heavy metals [114]. Sulphur in *NNS*-mercaptoethylaminotriacetic acid shows the same activity [127]. The presence in this compound of an additional complex-forming group makes it more selective than iminodiacetic acid. It has been shown that this complexone is selective with regard to the rare-earth elements; it forms complexes with only four cations out of 14. Moreover, complexes of different stability with the cations of copper and lead, cadmium and zinc, and cobalt, nickel, and zinc may be used for the separation of these metals.

The group of ethyl carbamate, the nitrile group, the positively charged amino-group, and the trimethylammonium group show practically no tendency to coordination; their effect on the stability of complexes is only connected with the change in the basicity of the coordinating nitrogen.

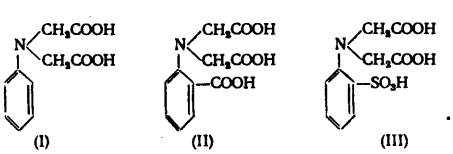
Uramildiacetic acid [perhydro-2,4,6-trioxopyrimidine--5-iminodiacetic acid (Ed. of Translation)], which forms stable complexes, is of considerable interest. The great basicity of the nitrogen atom, and evidently, the presence of a barbituric acid residue greatly increases the stability of complexes formed with uramildiacetic acid [128]. The stability of the complexes increases in the order Ba, Sr, Ca, Mg. The remaining derivatives of the alkyliminodiacetic acids shown in Table 1 are not now widely used and are mainly of theoretical interest.

Schwarzenbach studied the effect of the introduction of substituents into complexones of the aromatic series, using derivatives of anilinediacetic acid [109]:

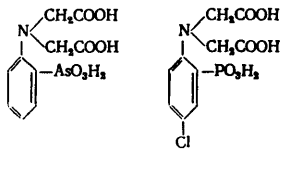


where Y = $-SO_3H$, $-COOH$. The introduction of carboxylic and sulpho-groups *ortho*, *para*, and *meta* to the iminodiacetate grouping has different effects, on the complexing power of the complexone.

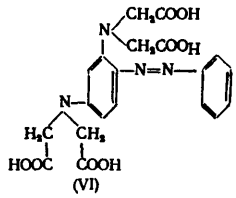
Substituents in the *meta*-, and *para*-positions have no material effect on the basicity of the iminodiacetate group nitrogen and the stability of the complexes formed. Substituents in the *ortho*-position greatly increase the complexing power; the effect of the substituent on the complexing power is in the same order as in the aliphatic series, that is, $-COOH > -SO_3H$. We have continued investigations in this direction, studying the effect of the introduction of arsonic, phosphonic, and azo-groups *ortho* to the iminodiacetate group of the benzene ring, on complexing power; as is well known, these groups comprise the analytical groupings of many valuable reagents. With this object 2-arsonophenyliminodiacetic acid (IV) [129], 4-chloro-2-phosphorophenyliminodiacetic acid (V), and chrysoidinetetraacetic acid [azobenzene-2,4-bis(iminodiacetic acid) (Ed. of Translation)] (VI) [130] have been synthesised and investigated. The complexing properties of these compounds were compared with the properties of phenyliminodiacetic (I), 2-carboxyphenyliminodiacetic (II), and 2-sulphophenyliminodiacetic (III) acids



(I) (II) (III)



(IV) (V)



(VI)

The stability of the complexes formed were recorded on the basis of the displacement of the half-wave potential $\Delta E_{1/2}$ = = $E_{1/2}$ (I, II, III, ...) - $E_{1/2}$ (without complexone) (Table 2).

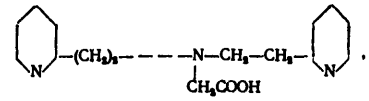
The results obtained showed that the introduction of these groupings increases the complexing properties of phenyliminodiacetic acid, makes the complexone more specific and thus more interesting from a practical point of view. Thus, 2-arsonophenyliminodiacetic acid forms stable complexes with lead and cobalt. This enables lead to be determined polarographically in the presence of copper and bismuth, and cobalt to be determined complexometrically. The presence of the phosphonic acid group enables cations to be determined when present together (Cu, Pb, Cd, As, Zn, Mo) in an acid medium.

The combination in the chrysoidinetetraacetic acid complexone molecule of azo- and iminodiacetate groupings increases the specificity of this compound compared with *m*-phenylenebis(iminodiacetic acid). The presence of a polarographically active azo-group in this complexone enables arsenic, manganese, and aluminium to be determined polarographically and amperometrically.

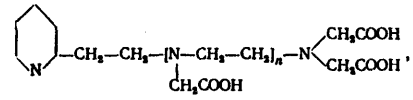
The effect of the groupings enumerated above in the *ortho*-position in phenyliminodiacetic acid is determined both by the electrostatic influence of the substituent and by its direct participation in the formation of the complex.

Following the success achieved in the field of analytical reagents, we made other attempts to increase the specificity of complexones by the introduction of special analytical grouping into the skeleton of polyaminecarboxylic acids.

The introduction of pyridine and quinoline nuclei with their marked tendency to bind transition metals (especially Co and Ni) and also some heavy metals (U, V, Pb, Zn, etc.) in stable complexes led to the creation of new complexones selective for heavy metals[9]. Thus, for Co and Ni the complexone

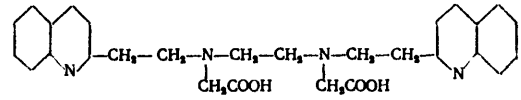


and for Pb, V, Zn, and U the complexone



where $n$ = 1–3, have been proposed.

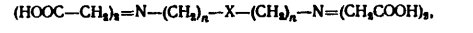
In a number of compounds the pyridine ring was replaced by the quinoline ring:



These examples, as well as some others, bridge the gap between special reagents for cations and complexones, and to a certain extent enable the theoretical prerequisites developed in the field of organic reagents to be applied to the effect of the structure of the complexones on their specificity.

The complexing power of a complexone is affected to at least an equal degree by the inclusion of the heteroatoms oxygen, sulphur, and nitrogen in the hydrocarbon chain of its molecule.

The part played by the heteroatom in complexones of the aliphatic series has been studied on compounds of the general formula [131]:



where for $n = 2$, X = —O—, —S—, —S'—S—, —N(CH$_3$)—;

for $n = 3$–4, X = —O—.



where X = —O—, —S—, —N(CH$_3$)—.

TABLE 2. Half-wave potentials of cations in the absence and presence of (I), (II), (III), (IV), (V), and (VI), measured relative to the saturated calomel electrode.

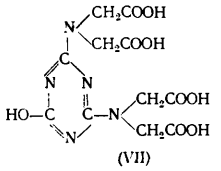
| Cations | pH 2.5 | | | | | | | pH 9.3 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $E_{1/2}$ without complexone | $E_{1/2}$ with complexone | | | | | | $E_{1/2}$ without complexone | $E_{1/2}$ with complexone | | | | | |
| | | (I) | (II) | (III) | (IV) | (V) | (VI) | | (I) | (II) | (III) | (IV) | (V) | (VI) |
| $Pb^{2+}$ | —0.38 | —0.42 | —0.47 | —0.44 | —0.52 | —0.42 | —0.58 | —0.18 | —0.36 | —0.49 | —0.44 | —1.0 | — | 0.9 |
| $Cu^{2+}$ | +0.02 | —0.04 | —0.28 | —0.2 | vanishes | —0.02 | —0.02 | —0.29<br>—0.54 | —0.54 | —0.4 | —0.31 | —0.68 | —0.30 | —0.29 |
| $Ca^{2+}$ | —0.60 | —0.61 | —0.65 | —0.66 | —0.70 | —0.61 | —0.74 | —0.66 | —0.68 | —0.69 | —0.69 | —0.8 | —0.92 | —0.69 |
| $As^{III}$ | —0.80 | —1.05 | —1.13 | —1.10 | —0.27<br>vanishes | —0.90 | vanishes | — | — | — | — | —1.05 | —1.72 | —1.71 |
| $Zn^{2+}$ | —1.01 | —1.09 | —1.08 | —1.08 | —1.24 | —1.07 | —1.12 | —1.14 | —1.28 | —1.28 | —1.20 | —1.20 | — | —1.02 |
| $Ni^{2+}$ | —0.96 | —1.04 | —1.08 | — | —1.24 | vanishes | —1.00 | —0.91 | —0.88 | —1.06 | —1.06 | vanishes | —1.14 | —0.98 |
| $Co^{2+}$ | —1.12 | —1.32 | — | —1.22 | —1.22 | vanishes | —1.15 | —1.01 | — | —1.24 | —1.22 | vanishes | —1.66 | —1.10 |
| $Mn^{2+}$ | — | —1.01 | — | — | —0.43 | vanishes | vanishes | —1.58 | —0.1 | —1.66 | —1.64 | — | — | —1.54 |
| $Mo^{VI}$ | —0.44 | —0.64 | —0.44 | —0.78 | —0.41<br>vanishes | —0.52 | —0.7 | — | — | — | — | — | — | — |
| $Ti^{IV}$ | —0.65<br>—0.97 | —0.68<br>—1.01 | —0.69<br>—1.01 | —0.70<br>—1.10 | —0.68<br>vanishes | —0.47<br>— | —0.48 | —0.48 | — | — | — | — | —0.50 | —0.48 |

It has been shown that the introduction into the complexone molecule of the heteroatoms N, O, S, which tend to coordinate with metals, leads to an increase in the complexing power of these complexones. Participation in complex formation of the additional N, O, or S atoms confers some specificity on the complexone molecules in relation to certain metal cations [16,132]. Thus, for the alkaline earth cations the relative order of stability is O > N > S; for the transition elements with almost completely filled *d* orbitals the order of stability is N > S > O. With the rare-earth elements the complexing power increases in the order S < N < O.

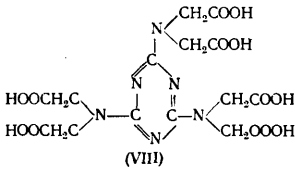
Van Uitert and Fernelius attempted to explain phenomena of this kind by considering the effective electronegativities of hybrid bonds of the ligand and the metal ion [133].

The studies of Izalt, Fernelius, and Block in this field agree with the ligand field theory [134]. Thus, cations especially sensitive to ligand field stabilisation form the most stable compounds with donor atoms that cause large ligand field splitting and conversely.

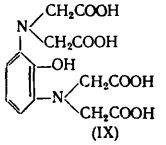
The effect of a heteroatom is also shown in cyclic compounds. This was studied on complexones of the triazine series [135,136] and on derivatives of benzthiazole and aminothiazole [137]. The properties of 2-hydroxy-1,3,5-triazin--4,6-diylbis(iminodiacetic acid) (VII), and 1,3,5-triazin--2,4,6-triyltris(iminodiacetic acid) (VIII), containing the 1,3,5-triazine ring are compared in Table 3 with the properties of *m*-phenylenebis(iminodiacetic acid) (IX). The instability constants of the complexes of (VII) and (VIII) are in all cases greater than the constant for compound (IX); moreover (VIII) has a tendency to form more stable complexes than (VII).



(VII)

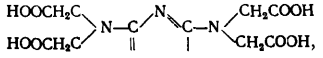


(VIII)



(IX)

A characteristic of (VII) and (VIII) is the presence of the same grouping



which is capable of forming complexes with metal cations.

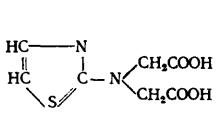
TABLE 3. Logarithms of stability constants of cations with complexones at pH 2.5.

| Cations | (VII) | (VIII) | (IX) |
|---|---|---|---|
| $Pb^{2+}$ | 4.75 | 5.08 | 3.73 |
| $Cu^{2+}$ | 3.78 | 4.07 | 3.36 |
| $As^{3+}$ | 5.08 | 6.10 | 5.01 |
| $Zn^{2+}$ | 6.70 | 7.10 | 3.40 |
| $La^{III}$ | 5.08 | 5.56 | 3.05 |
| $Ti^{IV}$ | 3.89 | 4.22 | — |

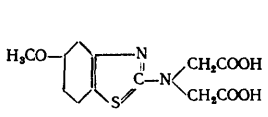
It is natural to suppose that the nitrogen of the triazine ring participates in complex formation. It is this that leads to an increase in the complexing power of (VII) and (VIII) compared with (IX).

The increase in the complexing power of (VIII) compared with (VII) may be ascribed to symmetry in the molecule (three iminodiacetic acid groups), leading to easier formation of complexes, sometimes with a large number of rings.

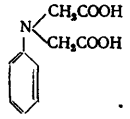
The complexing properties of 1,3-thiazol-2-yliminodiacetic acid (X) and 5-methoxybenzothiazol-2-yliminodiacetic acid (XI), containing two heteroatoms, nitrogen and sulphur, were studied [137] by the polarographic method of displacement of half-wave potentials; these compounds showed a reduction in analytical activity against a series of cations in comparison with a complexone containing an aromatic ring (phenyliminodiacetic acid) (XII):



(X)



(XI)



(XII)

Table 4 shows that (XII) forms weak complexes with nearly all the cations mentioned, while (X) and (XI) behave differently.

In the acid range, pH 2.5–4.4, these complexones form complexes only with Cu, Mo, As, Pb, and Co; in the alkaline range they form complexes with Co, Sb, Pb, Zn, and As, which indicates that they have some specificity. The reduction in analytical activity is probably due to the spatial proximity of the heterocyclic sulphur and nitrogen atoms, which considerably reduces the basic properties of the iminodiacetate nitrogen. The introduction of functional groups and heteroatoms into the complexone molecule is one way of obtaining complexones with a selective action.

### 3. The Effect of Replacing Carboxymethyl Groups on the Nitrogen Atom by Other Groupings

Apart from complexones with a changed composition of radicals on the iminodiacetate group, a number of compounds have been described in which acetic acid residues on the nitrogen atom are replaced by other groups [138-140].

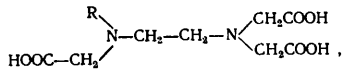
TABLE 4. Half-wave potentials of cations in the presence of (X) and (XI) in comparison with (XII).

| Cations | pH 2.7 | | | | pH 9.4 | | | |
|---|---|---|---|---|---|---|---|---|
| | $E_{1/2}$ without complexone | $E_{1/2}$ with (X) | $E_{1/2}$ with (XI) | $E_{1/2}$ with (XII) | $E_{1/2}$ without complexone | $E_{1/2}$ with (X) | $E_{1/2}$ with (XI) | $E_{1/2}$ with (XII) |
| $Pb^{2+}$ | −0.38 | −0.42 | −0.42 | −0.42 | — | −0.72 | — | −0.36 |
| $Cu^{2+}$ | +0.02 | −0.02 | −0.1 | −0.04 | −0.29<br>−0.54 | — | −0.3<br>−0.6 | −0.54 |
| $Bi^{3+}$ | −0.00 | −0.01 | −0.09 | −0.10 | — | — | — | −0.43 |
| $Cd^{2+}$ | −0.60 | −0.60 | −0.60 | −0.61 | −0.66 | −0.68 | −0.66 | −0.68 |
| $Tl^{+}$ | −0.46 | −0.46 | −0.46 | −0.43 | −0.48 | −0.48 | −0.48 | −0.50 |
| $As^{3+}$ | −0.80 | −1.12 | −0.88 | −1.05 | −1.71 | −1.70 | −1.31 | not repr. |
| $Sb^{3+}$ | −0.19 | −0.88 | −0.19 | −0.2 | — | −1.02 | −0.82 | −0.67 |
| $Zn^{2+}$ | −1.06 | −1.06 | −1.04 | −1.09 | −1.14 | −1.20 | −1.26 | −1.28 |
| $Ni^{2+}$ | −0.96 | −1.16 | −1.04 | −1.04 | −0.91 | −0.94 | −1.10 | −0.88 |
| $Co^{2+}$ | −1.12 | — | −1.20 | −1.32 | −1.10 | −1.18 | −1.20 | — |
| $Mn^{2+}$ | — | — | — | −0.01 | −1.58 | −1.54 | −1.58 | −0.10 |
| $Mo^{VI}$ | −0.44 | −0.54 | −0.54 | −0.64 | — | — | — | −0.38 |

Complexones in which the carboxyl groups are completely or partially replaced by residues of sulphonic, arsonic, or phosphonic acids or by hydroxyalkyl groups are of definite interest. Experimental results in papers by Schwarzenbach [110], Kabachnik [17,141,142], and others on complexones with phosphonic groupings and comparison of their properties with those of the corresponding aminocarboxylic and aminosulphonic acids indicate that the greatest effect is obtained when two types of complexing groups are present on the nitrogen of the complexone. As our investigations showed, with some cations *NN'*-bisphosphonomethylethylenebis(aminoacetic acid) forms more stable complexes than the corresponding analogues containing only carboxymethyl or phosphonomethyl groups [141].

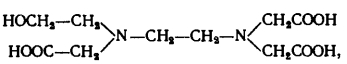
A certain selectivity in compounds of this type should be noted. It was shown by Kabachnik and his coworkers [141,142] that, apart from diethylenetriaminepentaacetic acid, the most powerful complexing agents for rare-earth ions are methylphosphonic acid and *NN'*-bisphosphonomethylethylenebis(aminoacetic acid); these complexing agents are recommended for removing the rare-earth elements from the body. Manecke and Gergs have pointed out the selectivity of ethylenediamine-*NN'*-bisethylarsonic acid for copper [143].

Bruno and coworkers [138] have studied *N*-substituted *NN'N'*-ethylenediaminetriacetic acids of the type:



where R = n-butyl, n-octyl, n-dodecyl, cyclohexyl, or benzyl. Replacement of the carboxymethyl group by these radicals leads to the changes in the properties of EDTA shown in Table 5.

With copper the *N*-benzyl derivative gives a less stable complex than EDTA and a more stable one than the *N*-butyl and *N*-octyl derivatives. *N*-Cyclohexylethylenediaminetriacetic acid forms the weakest complex with copper, and *NN'*-dicyclohexylethylenebis(aminoacetic acid) does not form such complexes at all. With calcium these acids behave as weak complexing agents. However, the *N*-benzyl derivative forms the most stable complexes. Replacement of the $-CH_2COOH$ group in the complexone molecule by hydroxyalkyl groups gave compounds capable of complexing iron in a moderately alkaline medium [9,144]. *N*-(2-Hydroxyethyl)ethylenediaminetriacetic acid:



the trisodium salt of *N*-(2-hydroxypropyl)ethylenediaminetriacetic acid:

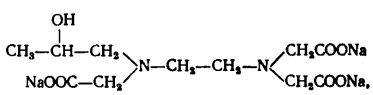
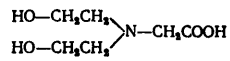


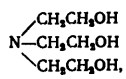
TABLE 5. Complexing power of *N*-substituted ethylenediaminetetraacetic acids.

| R | Dissociation constants of acids | | | pK | |
|---|---|---|---|---|---|
| | $pK_1$ | $pK_2$ | $pK_3$ | $Cu^{2+}$ | $Co^{2+}$ |
| Butyl | 1.8 | 6.64 | 10.04 | 12.7 | 1.6 |
| Cyclohexyl | 1.6 | 6.47 | 10.15 | 11.5 | 1.7 |
| Octyl | 1.9 | 6.53 | 9.76 | 12.5 | — |
| Benzyl | 1.9 | 5.10 | 9.84 | 16.8 | 6.7 |
| Dodecyl | 2.0 | 6.56 | 9.77 | — | — |

and *NN*-di-(2-hydroxyethyl)aminoacetic acid:



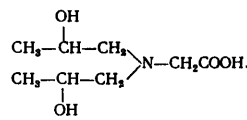
are examples of compounds of this type. The last compound has a characteristic tendency to form a complex with the $Fe^{3+}$ ion, in the same way as the structurally similar triethanolamine:



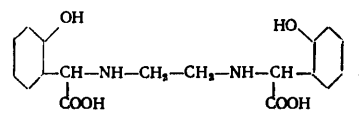
which, as is well known, is a very powerful complexing agent for the $Fe^{3+}$ ion.

It should be noted that the alkaline earth ions do not form complexes with dihydroxyethylglycine; this compound cannot therefore be used alone for removing the hardness from water and it is generally employed as a mixture with EDTA.

It has been shown that, in contrast to *NN*-di-(2-hydroxyethyl)aminoacetic acid, *NN*-di-(2-hydroxypropyl)aminoacetic acid does not form stable complexes with iron:



This is probably due to steric factors when the hydroxyethyl groups in the complexone molecule are replaced by hydroxypropyl groups. Ethylenebis[amino-(*o*-hydroxyphenyl)acetic acid] is the most specific complexone for tervalent iron; this compound contains the hydroxyphenyl grouping which is characteristic for complex formation with $Fe^{3+}$:



The instability constant of this complex with iron is $10^{-35}$, that is, one of the smallest ever measured for complexes in aqueous solution.

Data on the stability of complexes with some metal ions are given in Table 6.

Thus, the introduction into the complexone molecule skeleton of groupings containing hydroxyalkyl or hydroxyaryl groups led, as would be expected, to the formation of complexones specific for the $Fe^{3+}$ ion [139-145].

TABLE 6. Stability constants of ethylenebis-[amino-(*o*-hydroxyphenyl)acetic acid] with some metals.

| Metal ion | $pK_{MH_2Z}$ | $pK_{MHZ}$ | $pK_{MZ}$ |
|---|---|---|---|
| $Cu^{2+}$ | 15 | 20 | 24 |
| $Ni^{2+}$ | 11.4 | 15.6 | 19.7 |
| $Zn^{2+}$ | 9.3 | 12.9 | 16.9 |
| $Cd^{2+}$ | 7.8 | 10.1 | 13.1 |
| $Mg^{2+}$ | 2.9 | 5.2 | 8.0 |
| $Ca^{2+}$ | 1.7 | 4.8 | 7.2 |
| $Fe^{3+}$ | — | — | 35 |

4. The Effect of Increasing Denticity When Additional Iminoacetic Acid Groups Are Introduced into the Complexone Molecule

The effect of increasing the denticity without changing the fundamental structure of the complexone has been studied on analogously constructed polyethylenepolyaminepolycarboxylic acids [146-149]: diethylenetriaminepentaacetic acid (DTPA), triethylenetetraaminehexaacetic acid (TTHA), and tetraethylenepentaaminehexaacetic acid (TPHA).

A study of their complexing properties, determination of dissociation and stability constants of their complexes with a number of metals (Table 7) and also comparison of the results obtained with corresponding values for NTA and EDTA have shown that the stability of the complexes for practically all cations increases from nitrilotriacetates to diethylenetriaminepentaacetates (DTPA) and then falls with triethylenetetraaminehexaacetates (TTHA) and tetraethylenepentaaminehexaacetates (TPHA) (Figs. 2, 3, 4).

However, it should be noted that a change in the denticity has a different effect on the instability constants of complexes of different metals.

Potentially, the octo-, deca-, and dodeca-dentate character of these polyethylenepolyaminepolyacetic acids, differing by steric accessibility of the coordinating groups, can ensure full saturation of the coordination capacity of such elements as thorium, aluminium, molybdenum, and the rare-earth elements with a coordination number of 8. The number of rings linked with one metal cation then increases

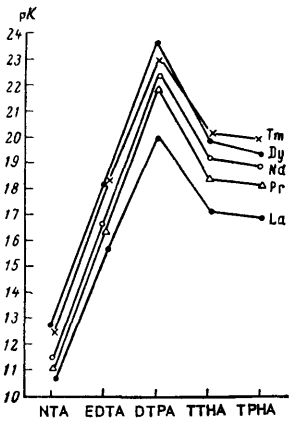



Fig. 2. Dependence of the stability of complexes of the rare-earth elements (p$K$) on the denticity of the complexone.

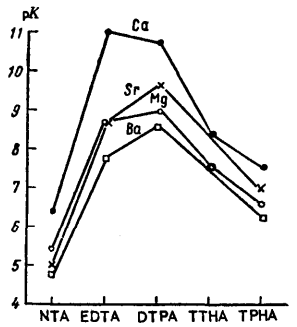



Fig. 3. Dependence of the stability of Ca, Mg, Ba, and Sr complexes on the denticity of the complexone.

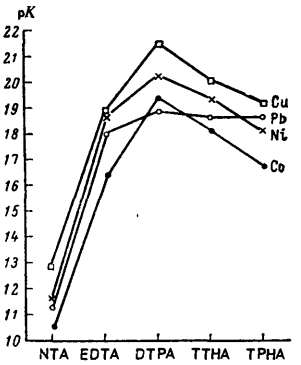



Fig. 4. Dependence of the stability of Ni, Co, Cu, and Pb complexes on the denticity of the complexone.

to 7, and in addition the stability of the complexes formed increases in comparison with that of the ethylenediaminetetraacetates. The comparatively small reduction in the stability of the complexes in the series DTPA, TTHA, and TPHA is probably connected with the change in basicity of the coordinating nitrogen atoms of the iminodiacetate groupings and the possibility of the formation of associated complexes.

For Mg, Ca, Sr, Ba with TTHA and TPHA the formation of complexes of the type $M_2Y$ is characteristic; this accounts for the observed fall in stability and the position of the constants between the corresponding values of

TABLE 7. Logarithms of stability constants of complexes of some metals with polyethylenepolyaminepolyacetic acids [146-149].

| Complexone | p$K$ dissociation | | | | | | p$K_{MY}$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | p$K_1$ | p$K_2$ | p$K_3$ | p$K_4$ | p$K_5$ | p$K_6$ | Ca | Mg | Zn | Cu | Mn | $Fe^{2+}$ | $Fe^{3+}$ |
| Diethylenetriaminepentaacetic acid | 1.79 | 2.56 | 4.42 | 8.76 | 10.42 | — | 10.71 | 9.03 | 18.55 | 21.53 | 15.60 | 15.97 | 27.50 |
| Triethylenetetraminehexaacetic acid | — | 2.64 | 4.08 | 6.26 | 9.67 | 10.82 | 8.40 | 7.62 | 17.4* | 20.1 | 14.62 | 15.32 | 26.20 |
| Tetraethylenepentaminehexaacetic acid | — | 2.73 | 3.82 | 5.56 | 8.88 | 9.95 | 7.51 | 6.61 | 17.80 | 19.20 | 14.0 | 13.6 | 26.4 |

nitrilotriacetates and ethylenediaminetetraacetates. For such elements as Co, Ni, Cu, Zn, and Pb, the formation of associated complexes of the 3 : 2 type is also characteristic: this probably gives rise to five rings on each complexing cation. The equality in the stability of these complexes with the corresponding ethylenediaminetetraacetates therefore becomes clear. This kind of increase in denticity of complexing agents without change in structure and without disturbance of the optimal symmetry of chelating groups is thus effective for voluminous cations with high coordination capacity. This may be explained by the possibility of forming additional rings; the optimum variant in the structure of a multidentate complexone is still DTPA. Further increase in the denticity by introducing additional acetate groups into the complexone molecule, does not, as a rule, lead to significant stabilisation of the complexes, but rather to increased selectivity. However, because of the very rapid formation and the high stability of complexes of multivalent cations, these complexones could be successfully used in analytical chemistry to mask interfering impurities and for the determination of a number of cations by physicochemical methods.

## 5. The Effect of Steric Factors on the Stability of the Complexes Formed

Analysis of the structure of chelate rings is of great importance in evaluating the effect of the structure of organic chelating agents on their complexing properties and on increased selectivity in the determination of elements. Alkaline earth and rare-earth elements with constant valency and varying atomic volume are ideal systems for this kind of investigation. The effect on complex formation of such stereochemical factors as ligand isomerism, conformation, distance between the main complexing groups, and the arrangement of the chelate rings may be examined in complexones containing two iminodiacetate groups, such as ethylenediaminetetraacetic acid, cyclohex-1,2-ylenebis(iminodiacetic acid), and cyclopent-1,2-ylenebis(iminodiacetic acid).

The most typical representatives of this group of compounds are EDTA and cyclohex-1,2-ylenebis(iminodiacetic acid) (CHDTA). These compounds with a definite stereochemical configuration differ from one another in the distances between the atoms of nitrogen and their arrangement in relation to the framework of the molecule [150-153]. A study of the chelates of these compounds in the solid state by infrared spectroscopy and thermal analysis permitted elucidation of the nature of the bonds and a precise establishment of coordination numbers for different metals. The ionic bond with carboxyl groups is characteristic of alkaline earth, doubly-charged and some triply-charged cations; the covalent bond is characteristic of transition metals of higher valency and lead.

In most cases these compounds behave as sexi- or quinque-dentate chelating agents, and only in the case of palladium and platinum as bi- and quadri-dentate agents. The presence of two residues of iminodiacetic acid and the close arrangement of the nitrogen atoms ensure a high complexing power in these compounds [11-14,95,143-145].

It follows from Table 8 that *trans*-cyclohex-1,2-ylene- and *trans*-cyclopent-1,2-ylene-bis(iminodiacetic acids) are stronger complexing agents for alkaline earth metals than the corresponding *cis*-analogues and EDTA. However, it should be noted that the stability of the complexes does not increase proportionally with the decrease in the distance between the nitrogen atoms in the ligand molecule. The change in the stability constants of the complexes takes place in the following order: *trans*-CHDTA > *trans*-CPDTA > > *cis*-CHDTA, while the distance between the complexing $-N(CH_2COOH)_2$ groupings decreases in a different order: *cis*-CHDTA ≤ *trans*-CHDTA ≤ *trans*-CPDTA. The reduced stability of alkaline earth metal chelates with *cis*-CHDTA is due to steric hindrance in the chelating reaction:

TABLE 8. Logarithms of the stability constants (p$K$) of complexes of the alkaline earth elements with ethylenediaminetetraacetic acid and cyclohex-1,2-ylene- and cyclopent-1,2-ylene-bis(iminodiacetic acid) [150-153].

| Complexone | Distance between complexing groups, Å | p$K_1$ | p$K_2$ | p$K_3$ | p$K_4$ | p$K_{MY}$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Mg | Ca | Sr | Ba |
| Ethylenediaminetetraacetic acid | — | 2.67 | 2.79 | 6.16 | 10.26 | 8.69 | 10.59 | 8.63 | 7.76 |
| *cis*-Cyclohex-1,2-ylenebis(iminodiacetic acid) | 2.0 | 2.44 | 3.50 | 5.21 | 10.70 | 8.32 | 9.45 | 7.33 | 8.00 |
| *trans*-Cyclohex-1,2-ylenebis(iminodiacetic acid) | 2.2 | 2.43 | 3.52 | 6.12 | 11.76 | 10.32 | 12.50 | 10.69 | — |
| *trans*-Cyclopent-1,2-ylenebis(iminodiacetic acid) | 2.6 | 2.40 | 3.30 | 7.56 | 10.80 | 9.05 | 11.08 | 9.49 | 7.7 |

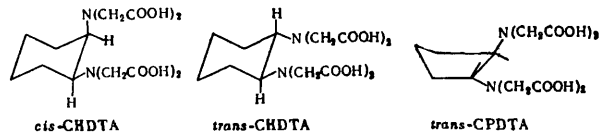



Fig. 5. Models of cyclohex-1,2-ylenebis(iminodiacetic acid) and cyclopent-1,2-ylenebis(iminodiacetic acid).

As the models show (Fig. 5) the *trans*-forms of CHDTA and CPDTA have the maximal number of equatorial substituents. With such an arrangement of ligand groups, the metal–chelate rings are in the same plane as the alicyclic radicals, which leads to a favourable geometrical structure for the molecule. In *cis*-CHDTA the axial hydrogen atoms of the cyclohexane ring prevent free rotation of the carboxymethyl groups, and the plane of the chelate ring is at an acute angle to the plane of the hydrocarbon ring. The steric hindrance produced by this kind of structure of chelating agent in *cis*-compounds and the lack of coplanarity due to it lead to great strain in the complexes formed and to a reduction in their stability.

It is interesting to note that complexes formed by *trans*-CPDTA are more stable than the corresponding compounds with EDTA in spite of the fact that the distance between the iminodiacetate groups in the active form of EDTA is less than the corresponding distance in *trans*-CPDTA. The reduced stability of complexes of EDTA compared with those of CPDTA is connected with the necessity of expending additional energy for converting form (I) into form (II) (Fig. 6), which is capable of forming chelates with metal ions. Moreover, the five condensed chelate rings when EDTA is used as a sexidentate agent form a greatly warped octahedron around the central metal atom with great deformation in the $-N(CH_2)_2N-$ chelate ring plane, in which there are two –N–CO–O– rings at angles deviating greatly

from the normal values [154]. All this produces additional strain in the cyclic structure and also leads to a reduction in the expected stability of the complexes with EDTA. In *trans*-CPDTA the nitrogen atoms are spatially fixed by the cyclopentane ring, which excludes the necessity of expending energy in rotation, and the structure is less strained:

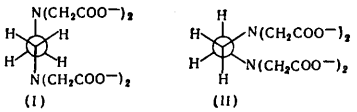


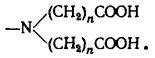

Fig. 6. Models of the two forms of EDTA.

Thus, in these compounds the predominating factor affecting the stability of compounds formed is the mutual arrangement of the ligand groups in the contour of the chelating agent, capable of forming complex structures with more or less strain. However, it should be noted that there are a number of compounds where the decisive part is played by the distance between the complexing groups.

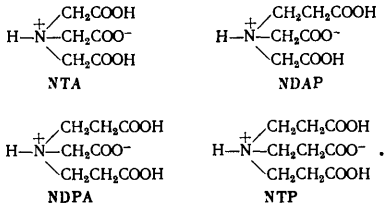
When the distance between the nitrogen atoms is significantly increased, their mutual interaction is weakened and a decrease is observed in the complexing power of the complexone; this is clearly shown by the homologues of EDTA: tri-, tetra-, penta-, etc. polymethylenediaminetetraacetic acids [155-160] (Table 9).

Data on stability constants show that when $n = 2$, with EDTA, the stabilisation produced by the formation of a ring is at a maximum. When the length of the chain of methylene groups (the quantity $n$) increases, the stability due to ring formation disappears and is even replaced by a weak destabilisation effect. This may be explained in the following way: rings with more than seven members are not formed, and when complexones containing four, five, and more hydrocarbon atoms interact with metal ions, the di(carboxymethyl)amino-groups act independently, forming complexes of the composition $M_2Y$. Analogous results were obtained by Schwarzenbach and Ackermann [111] in studying the isomeric cyclohexylenebis(iminodiacetates). The 1,3- and 1,4-derivatives form significantly less stable complexes than 1,2-CHDTA and show a tendency to coordinate with two metal cations and not to form a closed ring. All these results again emphasise the special stability of five-membered rings. However, it should be noted that an increase in the length of the polymethylene bridge in homologues of EDTA ($n = 6$ or 8) promotes the development of specificity in the complex; this specificity is expressed, for example, in increased stability of the complexes with silver and mercury. This is explained by a linear arrangement of valencies in these cations. As the ring increases in size its strain decreases, probably because of bending of the *sp* orbitals of the metal ion.

The distance between the carboxyl group and the nitrogen atom also has a considerable effect on the complexing power of the complexone:



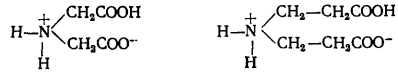

A study of this phenomenon [122] was carried out on a number of derivatives and homologues of iminodiacetic acid and ethylenediaminetetraacetic acid. The following series was investigated: nitrilotriacetic acid (NTA), nitrilodiaceticpropionic acid (NDAP), nitriloaceticdipropionic acid (NDPA), and nitrilotripropionic acid (NTP) (Table 10):




The value of the dissociation constant $pK_3$, and therefore the basicity of the nitrogen, decreases in the order NTA > NDAP = NDPA > NTP.

The stability of the complexes of most metals decreases in the same order as the basicity of the nitrogen atom: NTA > NDAP > NDPA > NTP; the replacement of one or two acetate groups by propionate groups only slightly reduces the stability. A possible explanation is that the propionate group in NDAP and NDPA forms six-membered rings with Cu, Ni, Co, and Zn which are more suitably arranged in space than the five-membered ring in the case of NTA and set up less strain over the whole molecule of complex.

Iminodiacetic acid and iminodipropionic acid:




are similar in structure to the four acids considered [116]. The value of the stability constant of iminodipropionic acid complexes is two orders less than the value of the constant for iminodiacetic acid complexes.

TABLE 9. Logarithms of the stability constants of complexes of the alkaline earth metals with polymethylenediaminetetraacetic acids [109,131,155-160].

| Complexone | pK of dissociation | | | | $pK_{MY}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $pK_1$ | $pK_2$ | $pK_3$ | $pK_4$ | Mg | Ca | Sr | Ba | Na |
| Ethylenediaminetetraacetic acid | 10.26 | 6.16 | 2.67 | — | 8.69 | 10.59 | 8.63 | 7.76 | 1.66 |
| Trimethylenediaminetetraacetic acid | 10.27 | 7.90 | 2.67 | 2.00 | 6.66 | 7.12 | 5.18 | 4.24 | — |
| Tetramethylenediaminetetraacetic acid | 10.45 | 9.07 | 2.66 | 1.90 | 3.44 | 5.05 | 2.80 | 2.40 | — |
| Pentamethylenediaminetetraacetic acid | 10.48 | 9.50 | 2.7 | 2.2 | 3.63 | 4.62 | 2.72 | 2.38 | — |

TABLE 10. Logarithms of the stability constants of metals with NTA, NDAP, NDPA, and NTP. [108-113,122]

| Complexone | pK of dissociation | | | $pK_{MY}$ | | | | |
|---|---|---|---|---|---|---|---|---|
| | $pK_1$ | $pK_2$ | $pK_3$ | Co | Ni | Cu | Zn | Cd |
| Nitrilotriacetic acid | 1.89 | 2.49 | 9.73 | 10.38 | 11.53 | 12.96 | 11.67 | 9.83 |
| Nitrilodiaceticpropionic acid | 2.10 | 3.69 | 9.66 | 7.9 | 9.0 | 11.6 | 7.9 | 5.6 |
| Nitriloaceticdipropionic acid | 3.25 | 3.98 | 9.67 | 7.9 | 9.1 | 11.9 | 8.0 | 5.6 |
| Nitrilotripropionic acid | 3.67 | 4.24 | 9.30 | 4.8 | 5.8 | 9.1 | 5.3 | 3.4 |

A number of derivatives of ethylenediaminediacetic acid (EDDA) in which the acetate groups were replaced by propionate groups were investigated with the object of studying the effect of the distance of nitrogen from the carboxyl group on the complexing power of the complexone.

Comparison of the complexing power of ethylenediaminepolycarboxylic acids with various doubly-charged cations showed that the replacement of one acetate group of EDTA by a propionate group lowers the $pK_{Me}$ by approximately 3–4 units. This effect is much greater with tetrapropionic acids. Symmetrical replacement of two propionate groups in these compounds by acetate groups increases the $pK_{Me}$ in general by 6–7 units. It is clear from the examples given that acetate groups form more stable chelate structures than propionate groups and therefore in this case increasing the distance of the carboxyl group from the nitrogen atom leads to a decrease in the stability of the complexone complexes with most cations. However, it should be noted that there is some selectivity with regard to copper, which may be explained by the planar structure of the complex formed.

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It follows from the foregoing that the synthesis of complexing agents with the maximum possible affinity for metal ions and the development of selective reagents differing as much as possible from one another and having specific complex properties are important problems in coordination chemistry.

After the synthesis and application of such complexes as ethylenediaminetetraacetic acid and cyclohex-1,2-ylenebis-(iminodiacetic acid), the first problem could be considered to be practically solved, but the second is still far from solution.

Ethylenediaminetetraacetic acid appears to be an ideal structural example of a multidentate reagent in its effectiveness in coordinating metal ions. Attempts to make some kind of change in the structure of EDTA which would be expected to increase its complexing power appreciably have, in the main, not given good results; in some cases they showed an effect with only certain groups of elements. Replacement of some acetic acid residues by propionic acid, or of the ethylene bridge joining the two nitrogen atoms by trimethylene, that is, increasing some of the five-membered chelate rings in the EDTA complexes to six-membered rings, reduces the stability of the complexes, although it would seem that this modification of the EDTA molecule should lead to a considerable reduction in the strain which is observed in condensed chelate rings of a complex, particularly in the $-N-(CH_2)_2-N$ plane, and also to stabilisation of the complexes. The behaviour of the oxygen atom of the phosphonic acid group as a ligand atom in ethylenediamine- and 1,2-diaminecyclohexane-tetraacetic acid was also studied. It was found that complexes of completely phosphorylated analogues are more selective, but in many instances less stable than the corresponding carboxyl compounds. This appears to be connected with insufficient use of the complexing atoms of the ligand carrying two negative charges, because of the great expenditure of energy when charged particles approach at the time of coordination. Complexes of beryllium, germanium, and copper, which are highly stable, are exceptions.

Closing of the alicyclic ring in CHDTA, which reduced the free rotation of the amino-group in the ligand and formed an additional ring in the structure, led to an increase in the stability of practically all chelates by 2–3 $pK$ units. Combination in the complexone of two types of grouping on the nitrogen — *NN'*-bisphosphonomethylethylenebis(aminoacetic acid) — increased the stability only of the complexes with certain cations.

In going from EDTA to DTPA, with its greater denticity, there is an increase in affinity for highly charged (3+, 4+) metal ions, while the stability of the complexes with Ca and Mg remains practically unchanged. Further increase in the denticity by introduction of additional iminoacetate groups (TTHA and TPHA) into the molecule leads to stabilisation of complexes formed with cations with the maximal coordination number (rare-earth elements, Th). The special structure of the complex molecule achieved by the introduction of heteroatoms and functional groups, by changing the distance between the iminodiacetate groups, and also between nitrogen and the carboxyl groups, by replacement of the carboxymethyl group by hydroxyethyl and phosphonomethyl groups, or by increasing the electron density of the whole system and destroying the electron density of individual links, as has been shown above, leads to the development of selective complexing agents, but not always to an increase in stability of the complexes formed.

The examples given above thus confirm that in most cases modification of the EDTA molecule leads to some specific activity and only sometimes to a slight increase in the stability of the complexes formed. In this connection, it is desirable that further work on the synthesis and application of complexones should deal with selectivisation linked to both a deeper study of compounds already described in the literature and to the development of complexones and complexing indicators with a specific action.

High selectivity in chelate formation, especially in the case of multidentate reagents is achieved rarely in practice and then only with comparative difficulty. However, the great amount of material in the literature on this subject enables syntheses of complexones with definite properties to be postulated.

According to Schwarzenbach, suitable selectivity of the complex can only be achieved by a special structure of the multidentate ion, account being taken of the maximal geometrical relationship of the internal ligand contour and of the cation. However, such a relationship, besides increasing the stability of chelates with a group of related ions, will hardly increase the selectivity because of the tendency of the ligand to take up a number of conformations and to become deformed to adapt itself to the requirements of other ions. Moreover, the geometric conditions of complex formation for one metal and a given chelate ligand may be close to the conditions for a number of other cations and the same ligand; as a result, the stability of complexes with elements of closely related physical and chemical properties is simply increased. Another way of achieving selectivity is much more promising; this consists in the development of multidentate reagents with the minimum permissible geometric correspondence for a given cation and complete lack of correspondence to the requirements of all other cations [161-163]. This type of variant may be brought about by increasing the rigidity of the system, by limiting free rotation of individual links by steric hindrance, and, finally, by the creation of unusual geometric arrangements of donor atoms with disturbed electron density, achieved by including a weak electron-donor group in the multidentate chelate system. This leads to spatial distortion of the ligand field and to selective action in the reagent. In the creation of model compounds of this type, account must be taken of the

geometric structure of the reagent and chelate molecules, the magnitude of the valency angles and interatomic distances, the change in these parameters under the influence of substituents and other factors, the limits of these changes, the primary coordination of the metal atom, possible distortion of this coordination, the nature of the chemical bond, steric factors, and intramolecular and intermolecular interactions. Besides, in the synthesis of complexones with selectively acting groups, it is desirable to take account of the mobility of the second ligand with regard to the size of the metal ion, so that the distance between the combining atoms corresponds to this volume; this kind of calculation of steric stabilisation increases the selective effect and the stability of the complex. From this point of view complexones would be of great interest if they were capable of reacting with elements of small atomic radius (Be, B, Ti, Ge, Nb, Ta, V, Cr) and high charge, with the rare-earth elements, and also with As, Sb, Sn, Mo, and with anions. Since Be, B, Ti, Ge, and other ions virtually do not coordinate with nitrogen, and the carboxyl groups of the complexones are apparently too voluminous for small cations, complexes of the polyphosphonic or polyarsonic acid type with partial replacement of the acetate groups by amino- and sulpho-groups, and also polyphenols of the pyrocatechol type, or derivatives of 1,8-dihydroxynaphthalene, would be interesting.

For elements that form thio-salts, that is, Sb, As, Sn, Mo, W, and for some platinum metals definite success would be expected from complexones containing mercapto--group sulphur as ligands, which coordinate selectively with these elements. In our opinion, further investigations into the synthesis and detailed study of complexones containing the heteroatoms O, N, S, Se, P, and As appear promising. Investigation of the complexing power of these compounds over a wide pH range, and also in organic solvents, will permit elucidation of the function of these elements in complexones. Moreover, the different nature of the coordinating ligands will increase the stability of these compounds. The preparation of complexones containing arsino- or phosphino-diacetic acids is of undoubted practical and theoretical interest. Since As and P have stronger donor properties than nitrogen, because of the formation of double bonds with metals containing *d* electrons that do not participate in hybrid bond formation, the new complexones will probably form stable complexes with metals of Groups VIII and IB of the Periodic System.

In conclusion, we shall note that the development of complexes capable of binding anions is of great importance. According to Schwarzenbach[4], for this purpose, instead of the nucleophilic atoms, N, O, and S, it would be necessary to introduce electrophilic groups into the molecule; these groups should be capable of coordinating with negatively charged ions. The mercury atom is an electrophilic atom which might be fixed on the framework of the molecule. These compounds would bind halide and other ions.

Studies in the field of the kinetics and mechanism of interaction of complex molecules consisting of different complexing agents and cations would be of undoubted theoretical and practical interest. These complicated systems could potentially form bimetallic and mixed complexes with fundamentally new properties. Moreover, the elucidation of the relative effects of different factors on the kinetics and mechanism of interaction will permit the deliberate direction of reactions and create the necessary conditions for the determination and separation of different cations.


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# THE "COAL–METHANE" NATURAL EQUILIBRIUM SYSTEM AND METHODS FOR STUDYING IT

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## 1. METHANE–COAL DEPOSITS

Deposits of ordinary coal and lignite constitute a gas-producing region of the Earth's crust which is unique and of great practical importance.

The principal components of the gases of coal seams are carbon dioxide, nitrogen, and methane. The appearance of carbon dioxide in coal seams is linked with the oxidation of the coal by oxygen, the metamorphism of the rocks, the migration of the products of the activity of living creatures in the soil layer, and the migration of atmospheric carbon dioxide. The nitrogen has only an atmospheric origin, and the methane is a product of the metamorphism of coal.

The gas phase is not in a quiescent state in the depths of the coalfields: the gases from the metamorphism of coal and rocks move upwards the terrestrial surface, and the gases of atmospheric origin and from biochemical processes move in the opposite direction. The existence of

two steady flows leads to the establishment of dynamic equilibrium between them. Individual gaseous zones will separate out[1] in stable equilibrium in the coal seams and some or others of the components will predominate: a nitrogen–carbon dioxide zone; a zone of nitrogenous gases; a nitrogen–methane zone; and a zone of methane gases.

The present gas-bearing capacity of the coal seams depends on the local geological conditions as well as on the gas-dynamical processes; these conditions include the different coals in the bed and the degree of subsidence of the seams, the presence in them of geological disturbances and outcrops, differences in the gas permeability of the coals and rocks, the action of the infiltrating waters, etc.; all this can assist or impede the migration of coal gases to the day surface.

During the formation of ordinary coal of an average degree of metamorphism, approximately one-quarter of the total organic mass is converted into methane. In the further conversion of the coal into anthracite, another 10% of its total mass is transferred to the gas phase[2].

However, in contemporary coal seams this quantity of methane is not observed. Mining workers find that the methane which is now encountered in coal seams is only about 1 wt.% of the coal mass[2].

The solubility of methane is low; consequently the infiltration water carries very little methane with it. There has been hardly any chemical reaction of the methane with the rocks in the lithosphere, since at the temperatures at which coal formation takes place methane is inert and does not react with either acid or with basic rocks.

For methane, there is only one path for leaving the coal seam — diffusion into the atmosphere; however, if the quantity of methane evolved throughout the whole time of existence of the coal deposits is calculated and the stocks of methane remaining bound with the coal are subtracted, then it appears that 0.02–0.03% of the atmosphere should consist of methane, even without taking into account possible sources of methane other than coal formation (volcanoes, natural gases, petroleum wells, surface decay of plants, etc.). Nevertheless, methane is not detected in the atmosphere in any appreciable amounts.

The most probable hypothesis concerns the oxidation of the methane in those layers of the gaseous envelope of the Earth's crust where there is an appreciable amount of ozone and also in lightning discharges, in which the methane is oxidised to carbon dioxide, by-passing the stages of formaldehyde and carbon monoxide.

However, the quantity of methane which saturates the coal seams in their present condition is so great that the coal deposits can be considered as methane–coal deposits. The methane of the coal seams is often considered only as a hazard in coal mining, but then natural gases should also be considered only as secondary fossil fuel, the exploitation of which is a sideline in petroleum engineering.

The volume of gas liberated from coal in coal mines increases each year; the maximal methane liberation is already approaching 100 $m^3$ (in some instances 300 $m^3$) per tonne of coal mined; the total calorific value of this gas equals 15% or more of that of the coal[3,4]. Therefore in calculating reserves and appraising coal deposits it is necessary to consider them as complex deposits of solid and gaseous fuel and accordingly plan the complex working of both fossil fuels. A coal mine now becomes a producer of not only coal but also the more valuable (in calorific value and convenience of use) fuel — firedamp, the energy of which has until now been lost in flushing it out by a ventilation stream.

TABLE 1. Quantity of methane released from all the mines of a country, $10^6$ $m^3$ $d^{-1}$.

| | | | |
|---|---|---|---|
| USA | 11.0 | Japan | 2.8 |
| Federal Republic of Germany | 8.5 | Belgium | 2.6 |
| | | Czechoslovakia | 1.2 |
| England | 8.0 | Poland | 1.0 |
| USSR | 7.0 | Netherlands | 0.4 |
| France | 3.0 | | |

The reserves of methane in coal seams of industrial importance (on conversion into conventional fuel) occupy the second place (after coal) among fuel sources and are seven times greater than the investigated reserves of natural gas[4].

The firedamp released each year in English coal mines is equivalent to $23 \times 10^8$ kcal, or $13 \times 10^6$ tonnes of good-quality coal[2].

Lidin and Airuni's table (Table 1), which relates to the beginning of 1962, gives an idea of the quantity of methane liberated in the main coal-mining countries in the working of coal deposits.

With the liberation (as subsidiary to coal mining) of such large quantities of methane ($2.5 \times 10^9$ $m^3$ $a^{-1}$ for the USSR) it is impossible to evade the question of the use of this gas in the national economy.

Of course, not all the methane of coal deposits can be used, in view of its low concentration in the ventilation stream, but in the artificial harnessing of the methane, which in ever-increasing degree is being developed here and abroad, firedamp is used as illuminating gas, an industrial and motor fuel, and a chemical raw material.

In the USSR it is planned[3] to increase the recovery of firedamp from $250 \times 10^6$ $m^3$ in 1961 to $1 \times 10^9$ $m^3$ $a^{-1}$ for 1965.

The problem of the recovery of metamorphic methane from coal has, apart from the increase in energy reserves, also another, no less important, side. Because of the explosiveness of oxygen–methane mixtures, firedamp has always threatened the lives of miners, who have considered it their chief enemy and obstacle in work.

In the contemporary development of seams of the most valuable coking coals the depth of mining operations is rapidly increasing and in addition the quantity of gas which is liberated with each tonne of coal mined is also increasing.

In the USSR, up to 1 January 1960 84% of all the coal mined was worked by underground operations and in that over 66% of all pits were gas-bearing, and 30% belonged to the supercategory, that is, to those in which more than 15 $m^3$ gas per tonne of coal mined were liberated in separate regions[5].

Creating safe conditions of work for miners and increasing the profitability of coal deposits are the two sides of the same question, which boils down to how to make coal a competitive source of energy in comparison with natural gas, petroleum, water power, and nuclear energy.

For a scientific and practical solution of these problems, a detailed and thorough study of the natural equilibrium of the "coal–methane" system which exists in most of coal seams being worked is necessary.

## 2. METHODS OF STUDYING THE "COAL–GAS" NATURAL SYSTEM

Study of the structure of coal was started in the 1830's and undertaken by the methods of "classical" chemistry, which achieved much in the study of the chemical nature and composition of the fossil coals and also in establishing the chemistry of the processes in various stages of coal formation. These methods seemed useless when the investigation came to hypotheses about the fine structure and the constitution of the surface of coal, a study of which is necessary for the modern technology of its mining and utilisation.

Over the last 15–20 years a coal science has been formulated[6,7] which united chemico-analytical methods of studying coal with the modern approaches of exact sciences. Both in the USSR and abroad, extensive geological, petrographic, physical, chemical, mechanical, and physicochemical investigations of coal as a source of energy, a metallurgical and chemical raw material, and a medium in which people have to work underground, have been carried out.

An attempt can be made now to present a general picture of the methods for studying fossil coals and to show the utility of each method of investigation. Like every classification of natural phenomena and the sciences of studying them, this scheme has a great element of complexity.

In the geology of coal deposits, by *coal* is meant a solid, combustible, sedimentary rock of plant origin, containing mineral impurities[8].

In the petrology of coal the unit being studied is the coal seam, determinable as a compact stratification, consisting of coal blocks, different in the degree of the chemical modification of the vegetable residues, and also of mineral inclusions and intercalations[9].

In coal petrography, the principal method of investigation of which is optical microscopy, coal is seen as a heterogeneous substance consisting of various petrographic components, which differ from one another in colour, physicomechanical and optical properties, and degree of retention of the plant structure[10].

Physicochemical methods of investigation increase the resolution by three orders of magnitude in comparison with optical microscopy, that is, to $10^{-7}$ cm; they permit the state and area of the surface of fossil coals, their porous structure, and the size distribution of the pores to be studied.

From the viewpoint of the physical chemistry of fossil coals, coal is a highly porous natural sorbent.

Colloidal investigations of coal do not increase the resolution in the study of structure but give a new approach to ideas about coals. In the initial stages of coal formation the coal substance is a heterogeneous, highly disperse system, which consists of the products of conversion of the plant residues, dispersed in water, and possessing aggregate stability.

Such a system can arise by two paths: (1) by dispersion of a coarsely dispersed multi-phase system, or (2) from a single-phase system, by enlargement of the molecules and their aggregates. Both these methods of formation of colloidal systems took place at the time of the peat and lignite stages of coal formation[11].

Ordinary coals are also colloids of the second type, that is, high-molecular-weight systems in which both the disperse phase and the dispersion medium are in the solid state[12].

In the metamorphism of such solid systems there occur the stages of swelling, dispersion, formation of colloidal systems, their aging, and breakdown.

The heterogeneous nature of coal-chemical reactions in which natural coals participate, the non-uniform participation in these reactions of different reactive groups of coals[13] leads to ideas about their macromolecular structure; coal appears to be a three-dimensional polymer in which plane polycyclic networks of atoms of aromatic carbon are linked to one another by side-chains (phenol, hydroxyl, quinone ether, etc. side-chains)[14,15].

Physical methods penetrate deepest of all into the structure of coal. Studies by X-ray diffraction gives information about the dimensions of the polycyclic elements of the macromolecules. Infrared spectroscopy determines the different forms of C–H bonds and the quantitative relation between aromatic and aliphatic compounds.

Thanks to the use of physical methods it has been shown that during metamorphism the coal substance is converted into carboid, in which the plane polycyclic networks of carbon atoms are turned round, tending to be arranged in small piles; some of the electrons of the carbon atoms thereby enter into the space between the atomic layers and bring about an increase in the electrical and thermal conductivities[11].

The eight listed main approaches to coal are different in terminology and methods of investigation, degree of penetration in the structure of coal and possible practical use of their concepts for studying the nature of the "coal–gas" natural system.

The conditions of agglomeration in which the coal deposits were created determine the quantity of gas retained in the seams; the presence of various petrographic micro-components of coals gives the different sorption capacities of coals with the same degree of metamorphism; the mechanical and geological properties of the coal colloids are linked with the different degree of gas-saturation of the coal; the quantitative relation between cyclic condensed nuclei and aliphatic side groups is determined by the degree of natural activity of coals as sorbents; the degree of ordering of the graphite lattice leads to the disappearance of the sorption properties in fossil coals, etc.

The study of the "coal–gas" system is based mainly on physicochemical investigations, but it is unthinkable without geology, petrology, and petrography, colloid science, and coal chemistry and physics.

## 3. COAL AS A COMPONENT OF THE "COAL–GAS" SYSTEM

The properties of coal as a highly porous sorbent are determined by the range of structural sizes, which differ by at least five orders of magnitude (from $10^{-3}$ to $10^{-8}$ cm).

To discriminate between such a large number of structural elements it is necessary to classify coal structures according to their nature and dimensions.

In coal it is possible to distinguish: (1) a molecular structure, determining the chemical nature and reactivity

of the coal, and (2) a disperse (colloidal) structure determining the behaviour of coal in non-chemical processes.

It is possible to discriminate between the rather complex molecular structure of coal only if the classification is continued further and the molecular structure is divided into two, which can be studied by different methods: (a) low-molecular, and (b) polymeric or macromolecular structure.

These three principal structures of coal (molecular, macromolecular, and colloidal) mainly determine its behaviour on reaction with gases.

On the one hand these border on coarser dispersoids (petrographic components and plant residues), and on the other, atomic structures.

(a) Molecular Structure of Coal.

The molecular structure of fossil coals is characterised by the carbon atoms being situated at the vertices of regular hexagons [16]. The carbon skeleton is based on hexagonal systems of cyclic construction, the different orientation of which determines the character of the molecular structure of the coals.

In the metamorphism of mineral coals there is a carbonisation of the substance, that is, an increase in the carbon content relative to the oxygen and hydrogen and also to the "secondary" elements (nitrogen, sulphur, etc.).

However, X-ray investigations of coals destroyed the conception of them as a molecularly homogeneous system in which on moving along the metamorphic series there is only an increase in the number of identical bricks. The coal substance appeared heteromolecular.

The X-ray investigations revealed two types of molecular structures in fossil coals: disordered, which cause general scattering of the X-rays, and more ordered, which cause their diffraction in a definite direction [17].

The more ordered parts of the structure are layers of hexagons; the number of condensed rings in such two--dimensional lattice is from four to ten [6]; with metamorphism, the diameter of these plates of hexagonal-cyclic structure increases from 7 to 16 Å; most of them are orientated at random with respect to one another and do not form a regular graphitic three-dimensional lattice; the maximal number of regularly orientated layers varies from three to ten for coals having an equal stage of metamorphism [18]. The diffraction of X-rays by coals varies for the coals in a metamorphic series (Fig. 1) and differs significantly from the diffraction which is characteristic for graphite [7,19].

Hence there are no graphitic crystals in coals, but only those elements from which the crystals can be formed under appropriate conditions of temperature and pressure. These rudiments of future crystalline structures (crystallites) are the nuclei of the molecular structure of the coal substance.

The framework of graphite-like crystallites is connected together by side groups — unique bridges. These side groups are the most disordered part of the molecular structure, which bring about the general scattering of X-rays. The side radicals of aliphatic structure can contain (in addition to carbon) hydrogen and oxygen, and even sulphur, nitrogen, and other elements. The destructive breakdown of coal when heated in the absence of air leads first to the detachment of unstable side groups; the rest are consolidated into coarse aggregates with an increase in the carbon content and a decrease in the yield of volatile products.

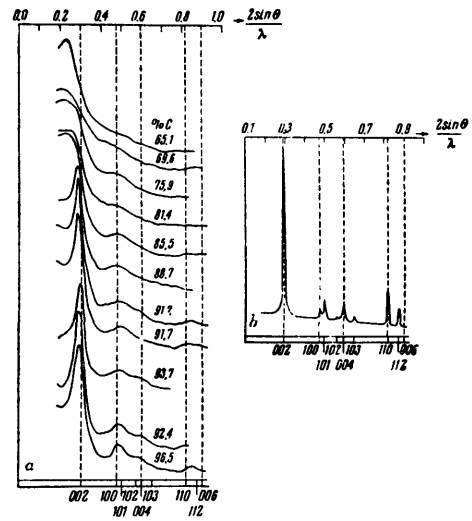



Fig. 1. Photometric trace of X-ray diagrams of: *a*) coal; *b*) graphite.

The nuclei of the polycyclic layers and the side aliphatic groups which connect the nuclei, together form the primary molecular structure of the coal. Hirsch [18] proposed a similar structural model of coal.

The mechanism of the formation of gases from the coal substance, which take place in the bowels of the Earth's crust, is connected with the detachment of the side groups. Gas formation is brought about by homolytic reactions, which proceed in the weakest parts of the molecular structure, that is, at the points of attachment of the side groups to the hexagonal graphite-like layers.

Whereas 82.6 kcal mole$^{-1}$ is required for the rupture of the bond between the carbon atoms in the $C_2H_6$ molecule, only 10–12 kcal mole$^{-1}$ is needed to break a bond between carbon atoms where each is connected with three aromatic rings.

(b) Macromolecular Structure of Coals

In many respects coal is reminiscent of artificial polycondensed resins. The physical and chemical properties of coals are not constant, but change within definite limits; coals are involatile and do not have definite melting or freezing points; the solubility of coals varies with the amount of solvent and the duration of heating, in that coals swell in solvents; vitrification is observed instead of crystallisation in coals; coals are subject to slow plastic deformation and this is highly sensitive to temperature; in the plastic state coals exhibit high viscosity.

In the process of metamorphism fossil coals are subject to polymerisation, which leads to the creation for them of a special amorphous state with a dual nature to the molecular structure, which consists of crystallites and amorphous parts.

Intramolecular reactions (dehydration, decarboxylation, etc.) are characteristic only for the lignite stages of coal

formation; the main processes in the metamorphism of ordinary coals are intermolecular condensations, that is, a growth of the molecule of the coal substance, with an increase in the carbon content from 75 to 95%. For such reactions to take place a definite activation temperature and intermolecular contact are necessary, the latter being achieved in the coal seams owing to the pressure of the overlying rocks.

In the metamorphism of ordinary coals, the polymerisation of their molecular structure proceeds mainly by detachment of side chains; condensed polycyclic layers approach within ~ 3.5 Å in this process; the coal substance acquires the property of a carboid with a characteristic black colour, and electrical and thermal conductivity; starting from the coking coals stage aromatic properties gradually disappear, since the coals are neither nitrated nor sulphonated, that is, they do not give the reactions typical of aromatic compounds [11].

In the detachment of side groups, chemical valencies are left at the place of their removal unsaturated; this facilitates the condensation of the molecular structure.

The primary molecular structure, consisting of nuclei and side groups, forms particles, which serve as elements of a second-order structure [20]. During this, gigantic macromolecules, polymeric in nature, are formed in the coal substance. In the macromolecules of coals, close-range order is observed only within the limits of each crystallite in the form of a two-dimensional lattice. Beyond the limits of the crystallites this order does not exist. The crystallites — small orientated fragments — fasten the coal polymers, like hoops, and make the whole system stable (Fig. 2). Each crystallite is turned somewhat relative to the next, the direction of the rotations being purely random [21].

Natural coals belong to a group of solid polymers whose importance in biology and technology is very great (rubber, cellulose, albumins, plastics, etc.). In solid polymers up to 60% of the material is in an amorphous state, whereas in low-molecular-weight substances the amorphous phase disappears completely during crystallisation [22].

In low-molecular-weight substances crystallisation sharply changes their structure and thermodynamic properties; this is because the whole amorphous mass is reconstructed into crystals with sharp surfaces of separation. In polymers, however, like natural coals, the ordered and disordered parts of the structure are indivisible; the crystallites contain only a small number of atoms, sufficient to diffract X-rays but insufficient to change the thermodynamic properties of the substance.

At the end of the last century, coal chemists made many attempts to devise structural-chemical hypotheses about the macromolecules of ordinary coals and lignites and represent them by formulae [23], but not one of these attempts led to the creation of a generally acceptable model. This is explained by the difficulties of reaching agreement between the concepts of organic chemistry and the results of the physical investigation. Kasatochkin's model [19] gave the most successful representation of the dual nature of the coal macromolecules (Fig. 3).

Van Krevelen's model [7] was devised on the basis of investigations of the optical and mechanical properties and the elemental composition of coals. In this model, which is based on the concepts of organic chemistry, cells of the cyclic parts of the structure are isolated. Such parts are not precisely the same as one another — as is observed in linear polymers with regular repetition of the monomer unit [24]. The value of the model lies in the concept of the existence of "nuclei" and side chains in the macromolecules of the coal substance.

The molecular weight of the macromolecules of the polymers varies within very wide limits — from $10^3$ to $10^6$. Other authors usually give lower values for the macromolecules of the coal substance. On the basis of his statistical structural analysis of coals, van Krevelen considers [24] that as the carbon content rises from 81.5 to 96.0%, the number of rings in the ordered layers increases from four to ten, and the molecular weight rises from $0.5 \times 10^3$ to $1.25 \times 10^3$.

Whitaker [25] in determining the molecular weight by an osmometric method obtained values of $9 \times 10^3$–$12 \times 10^3$ for the products of the thermal dissolution of coals in ethylenediamine.

Probably the most correct ideas [26] are that coal exists as a monolithic aggregate system and has an infinite molecular weight, like a crystal of indefinite size.

### (c) Colloidal Structure of Coal

The colloidal (disperse) structure of the coal substance is coarser than the atomic, molecular, and macromole-

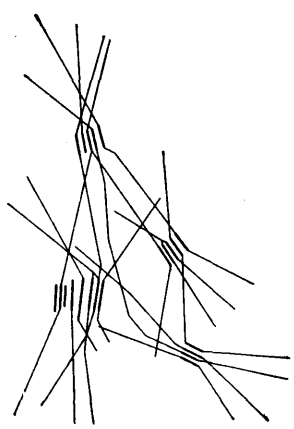


Fig. 2. Macromolecules of a polymeric character (after P. P. Kobeko).

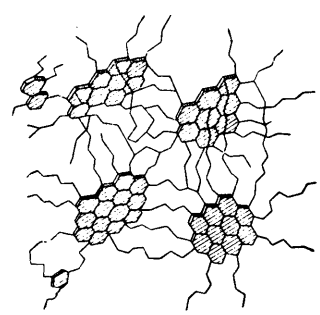


Fig. 3. Macromolecules of coal (after V. I. Kasatochkin).

cular structures. Even at the peat bog stage the aggregates of particles of humus and sapropelite materials acquire such large dimensions that they begin to show colloidal properties.

A complex colloidal structure is superimposed on the molecular structure of the coal substance, distorts its properties, and gives the coal a special quality which determines its behaviour as a component of the "coal–gas" system. The colloidal properties for different coals can differ markedly from one another, even when there is a very great similarity in their molecular composition [20]. The colloidal structure of the coal substance relates to particles with dimensions of $10^{-5}$ to $10^{-7}$ cm, pores and capillaries, with their associated capillary forces, inhomogeneous parts of the surface (where surface forces play the principal part), etc.

Coal colloids occupy a special position, since they can be assigned to both the main types of colloid: disperse heterogeneous systems and high-molecular-weight systems, which are formed by an increase in the size of the macromolecule or the formation of polymers. This explains why during the course of the long process of coal formation the structure and properties of the coal colloids changed sharply.

In the first stage, which can be considered to be mainly biochemical, the plant residues become peat at the bottom of the bog; during this, colloidal hydrosols (that is, disperse heterogeneous systems of the first type) were formed.

Then the hydrosols lost their aggregate stability and conglomeration of the colloidal particles began. The hydrosols were converted into hydrogels — a reticular three-dimensional structure of rigid colloidal particles and capillaries filled with water (peats and earthy lignites). Such gels occupy a position intermediate between liquid colloids and solid polymers.

In the second stage of coal formation (geochemical) the elastic gels were converted into solid polymers owing to the increase in size of the macromolecules of the coal substance (second type of colloidal systems).

In the early stages of coal formation water is the disperse medium; in subsequent stages it was mechanically absorbed by the cells of the hydrogel; in the metamorphic stages of ordinary coals water in the free state almost disappears. The remaining water is held either by close-acting adsorption forces or exists in ordinary coals as a thin film of liquid water, held by adhesion forces. In such a state the water has already lost the properties of a solvent or a dispersion medium.

In further metamorphism, which is accompanied by further loss of water and compaction of the molecular structure, particles of the second order (macromolecules) form still coarser aggregates — elements of a disperse structure of the third order. The coal is converted into a three-dimensional solid polymer. The colloidal properties of such a polymer are already determined not so much by the particle sizes as by the presence of a large boundary with a considerable free surface energy.

The compaction of the molecular structure of coals is accompanied by the detachment of side groups; during this, vacancies are formed in the molecular structure of the coal substance. The forces of molecular attraction tend to compress these vacancies and bring about shrinkage of the coal [20]. However, coals, being three-dimensional polymers with partly ordered packets of a two-dimensional crystalline lattice, are characterised by low elastic limits and rather large moduli of elasticity (up to $15 \times 10^{10}$ dyn $cm^{-2}$). [2] Therefore the coal substance resists compression and the vacancies in it are retained to a considerable degree. This is assisted by the vacancies containing gases formed in the detachment of side groups, conditions being such that migration from the seam is prevented. Ultraporosity appears in the coals, which determines the high sorption activity of the fossil coals and creates a real basis for the prolonged existence in the coal seams of a "coal–gas" system.

Pores in coals are often considered as vacancies, the walls of which serve as the usual phase boundaries, but the surface of the ultrapores, thanks to their small size, is at the limit of disappearance of the phase and does not possess the features of a microscopic surface [20,22]. Calculation of the internal surface of the pores from the sorption by coals of gases which are condensed on phase surfaces is uncertain because of the above reasons.

Usually, in speaking of the colloidal structure of coals the term "micelle" is employed to denote the colloidal particles. The term "micelle of coal substance" has a double meaning.

In a state of colloidal hydrosol a coal micelle, as in the case of all other sols, consists of a central nucleus of a solid substance and, surrounding the nucleus, an electrical double layer of solvated ions; the first layer of stabilising ions is adsorbed on the surface of the central nucleus. The system as a whole is electrically neutral.

A second concept of the micelle of coal is more frequently encountered: this relates to its state in the form of a solid three-dimensional polymer. In this concept the micelle of coal substance should represent a complex of macromolecules, that is, a structural unit of the third order in relation to the molecules and macromolecules. This is colloidal particle ($10^{-5}$–$10^{-7}$ cm) with a phase boundary and a partly ordered structure (crystallites or nuclei of macromolecules). The chain of separate macromolecules forms a more or less spherical micelle, either by the bending of macromolecules and their accumulation in the form of bundles, bound by cross-linking or by radial packing of the macromolecules with later formation of cross-links between them [12].

From determinations of the heats of wetting of coals in methanol, Bangham and coworkers [27] found the internal surface of coals to be 20–200 $m^2 g^{-1}$ and calculated from this the following micelle diameters: 230 Å for gas coals and 2500 Å for coking coals.

The colloidal properties of the solid polymer appear particularly distinctly in what is petrographically the most homogeneous component of coal — vitrain. The parent substance of vitrain is a hydrogel of peat seams, which owing to syneresis has lost part of its water, hardened, and become non-elastic.

## 4. GAS AS A COMPONENT OF THE "COAL–GAS" SYSTEM

The role of the gaseous component of the "coal–gas" system existing in coal seams is determined by its origin, by the qualitative and quantitative composition of the gas mixture saturating the seam and the forces which bind the gas to the coal.

The gases which are formed at the various stages of carbonisation almost completely leave the coal seams,

migrating by various paths to the surface. Coverings packed by subsequent rock beds hinder the migration of gases and create conditions for their accumulation; the comparatively short (from a geological viewpoint) interval of time was insufficient for the coal seams to give off the gases which were formed in the later stages of regional metamorphism and originated in tectonic processes [24,25].

Different geological conditions in the coal seams and geochemical processes accompanying the metamorphism of coals lead to different gas contents in the seams, gas compositions, and zonalities in their vertical distributions. The processes of intraseam migration of gases do not obliterate the non-uniformity in their distribution in the seam, which is associated with the genesis of the gases [28,29]. Coal deposits have a gas zonality (Fig. 4) in which the zone boundaries vary for different deposits and even for different parts of the same deposit.

Ideas about the zonal distribution of the gases in coal allow the main components of the coal seam gases and their proportion in the various zones to be distinguished and show how these ratios vary in different seams and at different depths.

For small deposits, attempts have been made to speak of the mean composition of the gas which saturates the coal seams within the scale of the deposit concerned; with all their tentativeness, such data give some illustration of which gases are held in the seams in their present state and within what concentration limits.

For example, Coppens [30], from analyses of 50 specimens of gas, from 63 Belgian pits, sampled in the zone of methane gases found the compositions of the gases of the Belgian deposits given in Table 2.

Below the zone of gas ventilation the main component of the coal seam gases is methane.

The problem of the origin of carbon dioxide cannot be considered solved. According to Graham [31], gas formation in the carbonisation of plant residues proceeds through the following stages: initially, when the carbon concentration is rising from 65 to 79%, predominantly $CO_2$ is liberated; during the subsequent rise in the carbon concentration from 79 to 85.8%, $CO_2$, $H_2O$, and $CH_4$ are liberated, the volume of the $CO_2$ being twice that of the methane; during the increase in carbon concentration to 88%, the amount of $CH_4$ formed increases; and at 92.3% carbon, methane is already the principal product; above 92.3%, only methane is liberated.

The experiments of Bergius [32] on the artificial carbonisation of peat are indirect confirmation of the predominant

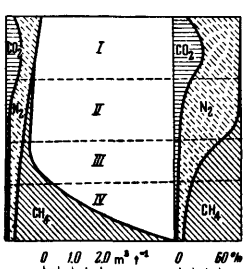



Fig. 4. Gas zonality of coal deposits (after G. D. Lidin).

TABLE 2. Composition of the gases of the Belgian coal seams.

| | $CH_4$ | $C_2H_6$ (+ higher hydrocarbons) | $H_2$ | $CO_2$ | $N_2$(+Ar) | He(+Ne) |
|---|---|---|---|---|---|---|
| Minimal content | 92.9 | 0.02 | 0.000 | 0.03 | 0.0 | 0.001 |
| Maximal content | 99.6 | 2.79 | 0.235 | 3.38 | 6.1 | 0.330 |
| Mean content | 97.3 | 0.47 | 0.044 | 0.74 | 1.5 | 0.044 |

formation of $CO_2$ in the various stages of carbonisation. During the heating of dry peat, Bergius obtained so-called "lignite" containing 75.4% C. In heating 10 g peat, 1110 ml gas containing $CO_2$ 88.1, $CH_4$ 8.4, $H_2$ 2.2%, etc. was evolved. In further experiments on the carbonisation of this "lignite" at pressures up to 6000 atm, Bergius obtained a product with 89% C; the gas liberated contained $CH_4$ 70–80, $CO_2$ 8–11%.

The carbon dioxide formed in the various stages of carbonisation left the coal seams by escaping into the atmosphere, disolving in the seam waters, and reacting with the containing rocks, forming carbonates.

The carbon dioxide which is contained in the coal seams of today has various but different origins: (1) juvenile carbon dioxide (frequently of volcanic origin) penetrates into the coal seams from sources situated below them [24,32]; (2) carbon dioxide which is the final product of deep oxidation of coals, to which lignites are particularly susceptible, which explains, for example, the high concentration of $CO_2$ in the sub-Moscow basin [33].

Hence for contemporary coal seams $CH_4$ is an endogenic gaseous component and $CO_2$ an exogenic.

Ideas about the local penetration of higher hydrocarbons — homologues of methane — into coal seams from petroleum deposits or petroleum-formed substances are still unproved. Other suggestions about the formation of higher hydrocarbons together with methane in the metamorphism of coal and their loss during subsequent natural degassing of the seam are more probable.

The amounts of methane formed throughout the carbonisation process significantly increase the quantities of gas which are now observed in the coal seams. According to Lidin [1], the amount of methane formed during the change from lignite to long-flame coal reaches 30–40 $m^3\ t^{-1}$, that to fat coals 70–80, to lean coals 120–150, and to semi-anthracite up to 200 $m^3\ t^{-1}$. Patteisky [34] considers that these quantities are higher (300–350 $m^3\ t^{-1}$ on conversion into fatty coals) and Vidal [35] gives figures of up to 1300 $m^3\ t^{-1}$ (for anthracites).

In the peat stage of coal formation, when the coal macromolecules originated and the hydrosols were formed, conditions did not yet exist for the creation of an equilibrium system with gaseous components; the gases being liberated in the coal formation reactions escaped.

In subsequent stages, when the hydrosols were converted into hydrogels, which were then subjected to syneresis and lost water, cavities of various dimensions were formed in them. A porous structure was created in the coals; this structure was qualitatively and quantitatively modified both during the conversion of peat into lignite and during the conversion of lignite into ordinary coal.

In the porous structure of fossil coals there appeared forces bonding the coal with the gas which made possible the creation and retention up to the present of the natural equilibrium of the "gas–coal" system. The valence bonds between the carbon atoms in the hexagonal-cyclic parts of the coal macromolecule are characterised by close action and large bonding forces ($\sim 10^2$ kcal mole$^{-1}$); the forces bonding the cyclic part of the molecules with the side chains have an energy an order of magnitude less ($10^1$ kcal mole$^{-1}$); the van der Waals forces which bond the coal substance with the gases have a bond energy again a whole order of magnitude less ($10^0$ kcal mole$^{-1}$), but are characterised by a comparatively large sphere of influence, non-specificivity, and additivity.

The van der Waals forces, which determine the sorption capacity of fossil coals with respect to gases, begin to appear noticeably when water is lost from the coals during metamorphism and side-groups are removed, which screened the sorption surface of the coal.

Hence, as a result of the physical and physicochemical processes taking place throughout the genesis, diagenesis, and metamorphism of coals, there was created in them the specific structure which conferred on the coals the properties of active natural sorbents and was the prerequisite for setting up the "gas–coal" natural system.

A thorough study of such a system has great significance for theoretical and practical problems in not only the mining, but also the utilisation of coals, since in many instances one should now speak not of coal, but of methane–coal deposits.

Study of the "gas–coal" system includes a series of problems, the most important of which are: study of the form of the bond of the coal with the absorbed gases, the sorption and collector properties of coal, the physical and physicochemical conditions of equilibrium of the system at various depths and in different geological circumstances, the conditions of the shift in the equilibrium in the system during changes in pressure, temperature, mechanical influences, etc.


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# SYNTHESES INVOLVING REACTIONS OF PEROXIDE COMPOUNDS WITH SALTS OF TRANSITION METALS IN SOLUTION

L. S. Boguslavskaya

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Oxidation–reduction systems comprising peroxides and salts of metals of variable valency are well known as vinylic polymerisation initiators and are widely used in the production of many interesting low-molecular compounds. The free radicals produced in such systems can react with the solvents, or can dimerise, disproportionate or be oxidised or reduced by the metal ions; and under the influence of the metal salts the peroxides themselves can undergo heterolytic rearrangements or catalysed heterolytic reaction with the solvents. These various processes produce various products.

The object of this paper is to provide, without any pretence at complete exhaustiveness, a review of these reactions, intensive study of which has, in recent years, opened new possibilities for organic synthesis and made a substantial contribution towards the chemistry of free radicals in solution.

## 1. THE $H_2O_2$–$Fe^{2+}$ SYSTEM (FENTON'S REAGENT)

This system has been much investigated since its discovery in 1894. Its use as polymerisation initiator in the oxidation of aliphatic compounds and the hydroxylation of aromatic compounds has been reviewed by Semenov [1] and Walling [2].

The accepted mechanism is that proposed by Haber and Weiss, according to which the active particle produced in the system is a free hydroxyl radical:

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\cdot} + HO^- + Fe^{3+}. \quad (1)$$

In the absence of an organic substrate, the latter can undergo the following series of reactions:

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^-, \quad (2)$$

$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}, \quad (3)$$

$$HO_2^{\cdot} + H_2O_2 \rightarrow HO^{\cdot} + H_2O + O_2, \quad (4)$$

$$HO_2^{\cdot} + H_2O \rightarrow H_3O^+ + O_2^-, \quad (5)$$

$$O_2^- + H_2O_2 \rightarrow {}^-OH + {}^{\cdot}OH + O_2. \quad (6)$$

In 1958 Coffman and coworkers [3] used Fenton's reagent for the production of bifunctional compounds from unifunctional, according to the reactions†

$$RH + {}^{\cdot}OH \rightarrow R^{\cdot} + H_2O, \quad (7)$$

$$2R^{\cdot} \rightarrow R{-}R. \quad (8)$$

The dilution and pH were selected so as to produce the dimeric compounds as the main reaction products in good yield, the reaction being conducted at room temperature by adding aqueous solutions of equimolar quantities of hydrogen peroxide and iron(II) sulphate to an excess of the aliphatic compound (as an aqueous solution or emulsion). The reaction is not a chain reaction — each mole of reacted aliphatic compound requires one mole of hydroxyl radical. This method was used for the dehydrodimerisation of lower aliphatic carboxylic acids, nitriles, amides, amines, alcohols, and ketones.

The attack of the hydroxyl radicals on the molecule of the aliphatic compound is not specific [3]: the hydroxyl abstracts hydrogen not only from the position $\alpha$ to the functional group, but from more distant positions also; as a result a series of bifunctional isomers is obtained, the yield sometimes reaching 60% (calculated on the hydrogen peroxide).

For example, the reaction of propionitrile with Fenton's reagent gives a mixture of approximately equal amounts of adipodinitrile, $\alpha\alpha'$-dimethylsuccinodinitriles, and $\alpha$-methylglutarodinitrile (total yield 60%). Acetic acid gives a low yield (4%) of succinic acid. Individual dehydrodimers are only obtained when the C–H bonds in the starting material are all equivalent; thus trimethylacetic acid gives $\alpha\alpha\alpha'\alpha'$-tetramethylsuccinic acid (37% yield), and t-butyl alcohol gives $\alpha\alpha\alpha'\alpha'$-tetramethylbutane-1,4-diol (36% yield).

The applicability of the method is limited by the requirements that the starting material should have a suitable solubility in water and should not undergo oxidative decomposition. Best results are obtained at pH 2 and at a dilution of 1 g-mole $H_2O_2$ to 2 litres water.

Comparison of their experimental results with literature data on the activity of chlorine atoms in reaction with propionic and butyric acid [4,5] led Coffman and coworkers to infer that free hydroxyl radicals and atomic chlorine exhibit a similar strength of attack on C–H bonds.

The carbonyl group deactivates the $\alpha$-position in carboxylic acids in respect of attack by the hydroxyl radical; according to their data the C–H bonds in pivalic acid $(CH_3)_3CCOOH$ are nine times as reactive as in acetic acid.

Razuvaev and Boguslavskaya investigated the reaction of methyl esters of aliphatic carboxylic acids and alkyl acetates with Fenton's reagent under the conditions of the Coffman synthesis [6–9], and obtained dimeric and oligomeric esters and oxidation products of the starting esters.

The dehydrodimers of the methyl esters are mixtures of the dimethyl esters of isomeric dicarboxylic acids; those of the alkyl acetates are glycol diacetates. The yields of dimers and oligomers sometimes reach 60% (based on $H_2O_2$) or 70% (based on starting ester). For example, the reaction of methyl isobutyrate with Fenton's reagent gave the following products, the percentage yields, based on $H_2O_2$ and reacted ester respectively, being given in parentheses: dimethyl $\alpha\alpha'$-dimethyladipate (12, 14), dimethyl $\alpha\alpha\alpha'$-trimethylglutarate (14, 17), dimethyl $\alpha\alpha\alpha'\alpha'$-tetramethylsuccinate (2, 2.5), oligomers (trimers and tetramers) of methyl isobutyrate (29, 35), monomethyl esters of $C_8$-dicarboxylic acids (2, 2.5), acetone (-, 2), and isobutyric acid (-, 24) [reactions (9)–(15)]. Similarly, isopropyl acetate gave 1,4-dimethylbutane-1,4-diol (11, 28), oligomers of isopropyl acetate (6, 14), acetone, and acetic acid (-, 58) [reactions (16)–(20)].

In the reaction of esters containing chains of several carbon atoms in the alcohol and acid parts of the molecule, mixed dehydrodimers are formed. These are obtained by dimerisation of radicals formed as a result of attack by hydroxyl on the alcohol and acid parts of the ester molecule. Thus ethyl propionate gives diethyl adipate, diethyl $\alpha\alpha'$-dimethylsuccinate, ethyl 5-propionylhydroxyvalerate and ethyl 2-methyl-4-propionylhydroxybutyrate, with

† Abstraction of hydrogen initially bonded to carbon.

traces of unidentified dimers (total yield 21% on the initial ester).

The processes occurring in the reaction of esters with Fenton's reagent are shown in the following series of reactions:

*Methyl esters (example: methyl isobutyrate)*

$$CH_3CH(CH_3)COOCH_3 + \cdot OH \rightarrow \begin{cases} CH_2C(CH_3)COOCH_3 & (I) \\ CH_2CH(CH_3)COOCH_3 & (II) \\ CH_3CH(CH_3)COOCH_2 & (III), \end{cases} \quad (9)$$

$$2\,(I) \rightarrow (CH_3)_2CCOOCH_3\,|\,(CH_3)_2CCOOCH_3, \quad (10)$$

$$(I) + (II) \rightarrow C(CH_3)_2COOCH_3\,|\,CH_3CH(CH_3)COOCH_3$$

$$2\,(II) \rightarrow CH_3CH(CH_3)COOCH_3\,|\,CH_3CH(CH_3)COOCH_3,$$

$$(CH_3)_2C(OO)COOCH_3 + \cdot OH \xrightarrow[[H_2O_2]]{} (CH_3)_2CCOOCH_3 \rightarrow (CH_3)_2C{=}O, \quad (11)$$

$$CH_3CH(CH_3)COOCH_3 + \cdot OH \xrightarrow[[H_2O_2]]{} CH_2CH(CH_3)COOCH_2OH \rightarrow CH_2CH(CH_3)COOH \quad (12),$$

$$CH_3CH(CH_3)COOCH_3\,|\,CH_3CH(CH_3)COOCH_3 + \cdot OH \rightarrow \begin{cases} \dot{C}HCH(CH_3)COOCH_3\,|\,CH_3CH(CH_3)COOCH_3 & (A) \\ CH_2\dot{C}(CH_3)COOCH_3\,|\,CH_2CH(CH_3)COOCH_3 & (B) \\ CH_2CH(CH_3)COOCH_3\,|\,CH_2{-}CHCOOCH_3\,|\,\dot{C}H_2 & (C) \\ CH_2CH(CH_3)COOCH_3\,|\,CH_2CH(CH_2)COO\dot{C}H_2 & (D), \end{cases} \quad (13)$$

$$(A), (B), (C), (D) + (I), (II), (III) \rightarrow \text{trimers, tetramers, and higher oligomers,} \quad (14)$$

$$(D) + \cdot OH \xrightarrow[[H_2O_2]]{} CH_2CH(CH_3)COOCH_3\,|\,CH_2CH(CH_2)COOCH_2OH \rightarrow CH_2CH(CH_3)COOCH_3\,|\,CH_2CH(CH_2)COOH, \quad (15)$$

*Alkyl acetates (example: isopropyl acetate)*

$$CH_3CH(CH_3)OCOCH_3 + \cdot OH \rightarrow \begin{cases} CH_2\dot{C}(CH_3)OCOCH_3 & (IV), \\ \cdot CH_2CH(CH_3)OCOCH_3 & (V), \end{cases} \quad (16)$$

$$2\,(V) \rightarrow CH_3CH(CH_3)OCOCH_3\,|\,CH_3CH(CH_3)OCOCH_3, \quad (17)$$

$$(IV) + \cdot OH \xrightarrow[[H_2O_2]]{} CH_3C(CH_3)OCOCH_3 \rightarrow (CH_3)_2C{=}O, \quad (18)$$

$$CH_3CH(CH_3)OCOCH_3\,|\,CH_3CH(CH_3)OCOCH_3 + \cdot OH \rightarrow \begin{cases} \dot{C}HCH(CH_3)OCOCH_3\,|\,CH_3CH(CH_3)OCOCH_3 & (E) \\ CH_3CH(CH_3)OCOCH_3\,|\,CHCHOCOCH_3\,|\,\cdot CH_3 & (F) \\ CH_3\dot{C}(CH_3)OCOCH_3\,|\,CH_3CH(CH_3)OCOCH_3 & (G), \end{cases} \quad (19)$$

$$(E), (F), (G) + (V) \rightarrow \text{trimers, tetramers, and higher oligomers} \quad (20)$$

The oligomers are a complex mixture of structural isomers.

Under identical reaction conditions, the maximal yield of dimers and oligomers of methyl esters is obtained with methyl isobutyrate, and that of dimers and oligomers of alkyl acetates with n-propyl acetate (Figs. 1 and 2).

The presence of a large quantity of oligomers makes it difficult to calculate the positions of free-radical attack; however, with methyl isobutyrate an approximate calculation shows that the $\alpha$-position is more reactive than the $\beta$-position.

Complex-forming metal ions ($Fe^{3+}$, $Ni^{2+}$, $Co^{2+}$, $Mn^{2+}$) form complexes with the free alkyl radicals, and so decrease their ability to react and hence favour dimerisation[10]. When $Fe^{3+}$ is used as complex-forming ion, the addition of NaF, which binds $Fe^{3+}$ into a stable complex, produces a considerable decrease in the quantity of dimer formed.

Razuvaev and Boguslavskaya investigated the influence of additions of equimolar amounts of various metal salts on the reaction of aliphatic esters with Fenton's reagent. Addition of Ni, Co, or Mn salts or NaF have no substantial effect on the yield or composition of the products. In the presence of an equimolar amount of NaCl there is practically no dehydrodimerisation of the esters; chlorinated derivatives of the initial esters are produced in small amounts. Chloride ions are known to reduce the rate of oxidation with Fenton's reagent[11,12]:

$$\cdot OH + Cl^- + H^+ \rightarrow Cl\cdot + H_2O. \quad (21)$$

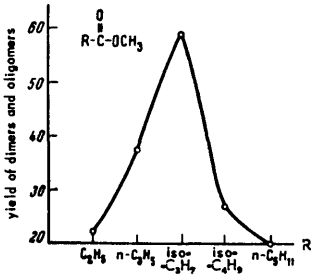



Fig. 1. Yield of dimers and oligomers of esters $RCOOCH_3$ as a function of the size and structure of the radical R.

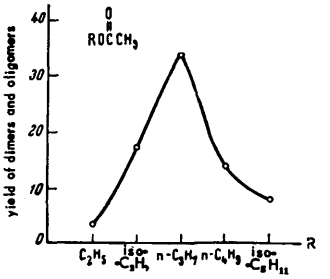



Fig. 2. Yield of dimers and oligomers of esters $ROCOCH_3$ as a function of the size and structure of the radical R.

An equimolar amount of $CuSO_4$ also suppresses the dehydrodimerisation of esters practically completely. It is known that $Cu^{2+}$ can oxidise alkyl radicals [13,14]:

$$R^{\cdot}+M^{+n} \rightarrow \begin{cases} \text{alkene} + M^{+n-1} + H^+ \\ R^+ + M^{+n-1} \end{cases}, \quad (22)$$

$$R^+ + H_2O \rightarrow ROH + H^+, \quad (23)$$

The addition of $CuSO_4$, for example, to the system methyl butyrate–$FeSO_4$–$H_2O_2$ would therefore be expected to produce esters of unsaturated and hydroxy-acids (or their further oxidation products: aldehydo- and keto--acids), but these products have not been observed. Small amounts of unsaturated esters are formed in the absence of $CuSO_4$ as well as in its presence. The considerable decrease in the yield of dimers is probably due to the reduced equilibrium concentration of hydroxyl radicals in the presence of excess of $Cu^{2+}$:

$$Cu^{2+} + H_2O_2 \rightleftarrows Cu^+ + HO_2^{\cdot} + H^+ \text{ (see Semenov[1])}. \quad (24)$$

The reaction of various amines and ethers with Fenton's reagent has been investigated [15]; the corresponding dehydrodimers are produced in very low yields (0.5–10%), *NN'*-diethylbutenediamine is obtained from diethylamine (yield ~ 10%) and *NN'*-diethyl-*NN'*-diphenylbutenediamine from ethylaniline (yield < 10%).

Addition of 1,3-dienes to the $Fe^{2+}$–$H_2O_2$– substrate system produces addition dimers [16,17]:

$$RH + {\cdot}OH \rightarrow R^{\cdot} + H_2O,$$
$$R^{\cdot} + M \rightarrow RM^{\cdot}, \quad (25)$$
$$2RM^{\cdot} \rightarrow RMMR, \quad (26)$$

where M is a molecule of the 1,3-diene. These dimers are straight-chain (H) and branched-chain (J), (K) compounds produced by 1,4- and 1,2-addition to the diene:

$$R(CH_2{-}CH{=}CHCH_2)_2R; \quad RCH_2CH{=}CHCH_2\underset{\displaystyle CH{=}CH_2}{\underset{|}{C}}HCH_2R; \quad RCH_2\underset{\displaystyle CH{=}CH_2}{\underset{|}{C}}HCH_2R.$$
$$\text{(H)} \qquad \text{(J)} \qquad \text{(K)}$$

Addition dimerisation is favoured by adding equivalent amounts of the iron(II) salt, $H_2O_2$, and the diene simultaneously to a large excess of the substrate in water at -5° to 0° at a definite pH.

Substrates used have been carboxylic acids, alcohols, ketones, esters, acetaldehyde, propionitrile, and cyclohexylamine. Butadiene has been the main diene used, but chloroprene, isoprene, cyclopentadiene, acrylonitrile, and maleic acid have also been employed. The yield of addition dimers has reached 70–77% in some cases. The yield of products containing more than two butadiene units in the molecule is less than 10%.

The production of dichlorinated conjugated dienes by addition dimerisation has been patented [18]; thus butadiene reacts with the radicals produced in the $H_2O_2$–$FeCl_2$ system in solution in acetone to give $(ClC_4H_6)_2$. A new method for the addition of two azide groups to alkenes using Fenton's reagent has been developed [19]:

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\cdot} + HO^- + Fe^{3+},$$
$$HO^{\cdot} + (FeN_3)^{2+} \rightarrow (FeOH)^{2+} + N_3^{\cdot}, \quad (27)$$

$$N_3^{\cdot} + \underset{|}{\overset{|}{C}}{=}\underset{|}{\overset{|}{C}} \rightarrow N_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{\cdot}, \quad (28)$$

$$N_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{\cdot} + (FeN_3)^{2+} \rightarrow N_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}N_3. \quad (29)$$

This reaction has been used with styrene, butadiene, hex-1-ene, cyclohexene, etc.

Of interest is the novel synthesis of carboxylic acids by passing carbon monoxide into a $Fe^{2+}$–$H_2O_2$– substrate system [20]:

$$RH + CO + H_2O_2 \xrightarrow{Fe^{2+}} RCOOH + H_2O. \quad (30)$$

The formation of the acids is accompanied by dimerisation of the radicals R· into RR; thus t-butyl alcohol has given the carboxylation product (β-hydroxyisovaleric acid) and the dehydrodimerisation product (ααα'α'-tetramethylbutane-1,4-diol) in yields of 0.23 and 0.33 g-mole per mole $H_2O_2$ respectively.

The carboxylation proceeds at room temperature by introducing $H_2O_2$, $FeSO_4$, and CO simultaneously into a vigorously stirred mixture containing an excess of the organic reactant. The optimal $H_2O_2$ : $FeSO_4$ ratio and CO pressure is selected for each organic reactant. In some cases carboxylation takes place at atmospheric pressure. The following mechanism has been suggested:

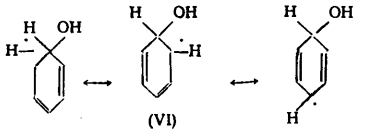
$$HO{\cdot} + RH \rightarrow R{\cdot} + H_2O,$$
$$R^{\cdot} + CO \rightarrow RC{=}O, \quad (31)$$
$$RC{=}O + Fe^{3+} \rightarrow \overset{+}{R}C{=}O + Fe^{2+}, \quad (32)$$
$$\overset{+}{R}C{=}O + \bar{O}H \rightarrow RCOOH. \quad (33)$$

If the reaction medium contains NaF, which binds $Fe^{3+}$ into a stable complex, the yield of carboxylation products is markedly reduced.

Aromatic compounds are oxidised by Fenton's reagent by a non-chain mechanism [21–23]; hydroxylation occurs, and, with benzene and toluene, dehydrodimerisation also. The total yield of reaction products (based on $H_2O_2$) is always very low (< 5%). Merz and Waters have suggested the following mechanism [22]:

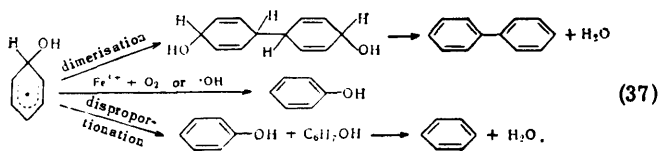
$$ArH + {\cdot}OH \rightarrow Ar^{\cdot} + H_2C, \quad (34)$$
$$2Ar^{\cdot} \rightarrow Ar{-}Ar, \quad (35)$$
$$Ar^{\cdot} + {\cdot}OH \rightarrow ArOH. \quad (36)$$

The oxidation of benzene and toluene by Fenton's reagent has recently been investigated in some detail [24]. The oxidation of benzene produces phenol and biphenyl. The formation of $C_6H_5^{\cdot}$ radicals is excluded, because of the absence of any isotope effect in the analogous oxidation of deuterobenzene. In the suggested mechanism, a hydroxyl radical first adds on to benzene to form the resonance--stabilised adduct (VI):



(VI)

which then dimerises, disproportionates, or is oxidised to produce the final products (phenol, biphenyl, and benzene):



(37)

It is difficult to evaluate the importance of each step in the overall process, but an important characteristic is that the relative amount of phenol produced is decreased by excluding $Fe^{3+}$ (by adding fluoride) and oxygen.

In the oxidation of toluene, which apparently also proceeds by way of the analogous intermediate adduct (as well as by oxidation of the $-CH_3$ group), the following compounds have been obtained, in the indicated relative percentage contents: benzyl alcohol and benzaldehyde (38.3), benzoic acid (18), 1,2-diphenylethane (30.5), phenol (2.9), *o*-cresol (3), *m*-cresol (0.2), *p*-cresol (1), *o*-hydroxybenzaldehyde (3.2), diphenylmethane (1), and bi-*o*-tolyl (2.1).

Brodskii and Vysotskaya[25] used $^{18}O$ to investigate the mechanism of hydroxylation of phenol with Fenton's reagent, and showed that the oxygen in the resulting pyrocatechol comes from the hydrogen peroxide. They conclude that free hydroxyl radicals do not participate in the hydroxylation.

The same conclusion was reached by Hamilton and Friedman[26], who studied the hydroxylation of anisole with Fenton's reagent. They suppose the hydroxylation to proceed by a type of electrophilic substitution.

Cier and Nofre[27] investigated the mechanism of hydroxylation of benzoic acid and *N*-acylanilines in aqueous solution with hydrogen peroxide in the presence of transition metal ions in their lower valency state, and found the activity of the metals to fall in the series $Fe^{2+} > Co^{2+} > Cu^{+} > Mn^{2+}$. Addition of ascorbic acid increases the activity of the systems and changes the order of reactivity: $Cu^{+} > Co^{2+} > Fe^{2+} > Mn^{2+}$. Complexing agents such as ethylenediaminetetraacetic acid activate or inhibit the reaction, depending on their nature and the metal ion. The hydroxylation of benzoic acid gives *o*-, *m*-, and *p*-hydroxybenzoic acids, and is accompanied by partial decarboxylation. The carboxy-group orientates the entering OH group in the ratio $o:m:p = 9:6:5$. For *N*-acylaniline this ratio is 11 : 5 : 4. A free-radical mechanism is accepted for the hydroxylation, and the analogy is pointed out between the reactions studied and biochemical hydroxylation in an organism. The action of a modified Fenton's reagent on purine[28] and pyrimidine bases[29] has been studied, to provide a model for the indirect action of ionising radiations on fundamental biochemical molecules in aqueous media. To increase the catalytic action of the $Fe^{2+}$ ion, it was chelated with sodium pyrophosphate, which allowed the Fenton's reagent to be used at pH 7. The purine bases reacted to the extent of 0.5–1%, and hydroxylation of the pyrimidine bases took place with a yield of approximately 1–6.5%.

In the presence of iron(III) ethylenediaminetetraacetate and ascorbic acid (a model of a peroxidase system) salicylates are oxidised in aqueous solution by hydrogen peroxide (or oxygen) into 2,3- and 2,5-dihydroxybenzoic acids (yield 50–70% on salicylate)[30].

Phenoxyacetic acid and its halogen-substituted analogues are readily oxidised by Fenton's reagent to form $CO_2$, formaldehyde, phenol, and 1,2-diphenoxyethane[31]; the formation of the last compounds is unexpected, and is explained by the reactions:

$$ArOCH_2COOH + \cdot OH \rightarrow ArOCH_2COO^{\cdot} + H_2O \quad (38)$$

$$ArOCH_2COO^{\cdot} \rightarrow ArO\dot{C}H_2 + CO_2, \quad (39)$$

$$2ArO\dot{C}H_2 \rightarrow ArOCH_2CH_2OAr. \quad (40)$$

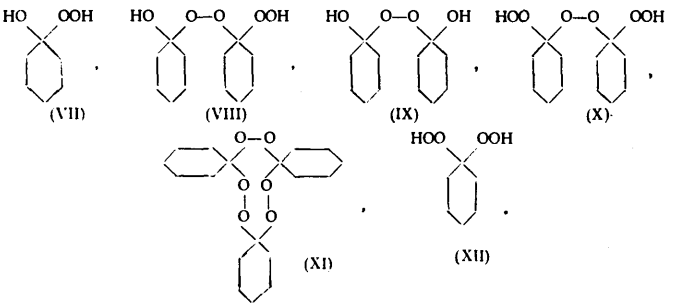
The following is also thought to be a probable mechanism:

$$ArOCH_2COOH + \cdot OH \rightarrow ArO\dot{C}HCOOH \xrightarrow{\text{migration of H}}$$

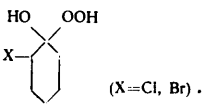
$$\xrightarrow{\text{migration of H}} ArOCH_2COO^{\cdot} \rightarrow ArO\dot{C}H_2 + CO_2. \quad (41)$$

## 2. SYSTEMS COMPRISING ALICYCLIC HYDROPEROXIDES AND METAL SALTS

Cyclohexanone reacts with hydrogen peroxide to give a mixture of the peroxides (VII)–(XII); the structure of these has been much studied[32-36]



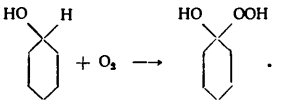

Depending on the method of preparation, one or other of these structures predominates. All the other conversions of the derivative of peroxide cyclohexanone can be considered as reactions of (VII) (1-hydroperoxycyclohexanol); this has not been isolated pure, but Kharasch[36] has prepared the $\alpha$-halogeno-analogues from the $\alpha$-halogenocyclohexanone and hydrogen peroxide:




(XIII)

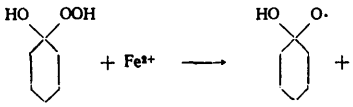
These peroxides (XIII) are individual solid substances and do not form dimeric peroxides of types (VIII)–(XII)[36].

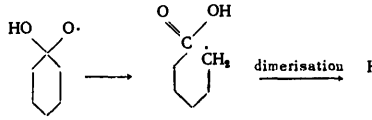
1-Hydroperoxycyclohexanol can be obtained by the autoxidation of cyclohexanol[37]:

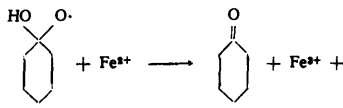


Treatment of the derivatives of peroxide cyclohexanone with an equimolar amount of iron(II) sulphate gives a good yield of decane-1,10-dicarboxylic acid, together with caproic acid, $\omega$-hydroxycaproic acid, polymeric acids, and cyclohexanone[37-41]. Low temperature (-10° to 0°) favours formation of the decanedicarboxylic acid, and the

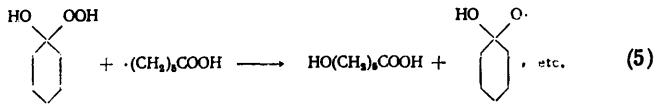
yields of this acid are considerably higher (up to 55%) from "liquid" peroxides of cyclohexanone[41]. These reactions proceed by a free-radical mechanism:


(1)


(2)


(3)

$$HOOC(CH_2)_5\,Fe^{3+} + H_2O \rightarrow HOOC(CH_2)_4CH_2 + Fe^{2+} + OH\,. \quad (4)$$


(5)

Treatment of 2-chloro-1-hydroperoxycyclohexanol with iron(II) sulphate produces a dichlorodecane-1,10-dicarboxylic acid in which the disposition of the halogens has not been established; from subsequent work[14] it may be assumed that this acid is a mixture of isomers with structure (XIV) predominating:

$$HOOC(CH_2)_4CHCl{-}CHCl(CH_2)_4COOH\,.$$
(XIV)

Introduction of butadiene into the peroxide derivative of cyclohexanone $-Fe^{2+}$ system has given[40] $C_{20}$ unsaturated dicarboxylic acids in 65–75% yield:

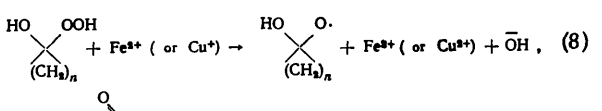
$$HOOC(CH_2)_5^{\cdot} + C_4H_6 \rightarrow \underset{(A)}{HOOC(CH_2)_5CH_2CH{=}CH{-}\dot{C}H_2} + \quad (6)$$

$$+ \underset{(A)}{HOOC(CH_2)_5CH_2\dot{C}HCH{=}CH_2}\,.$$

$$2A \xrightarrow{\text{dimerisation}} C_{20}\text{ unsaturated dicarboxylic acids.} \quad (7)$$

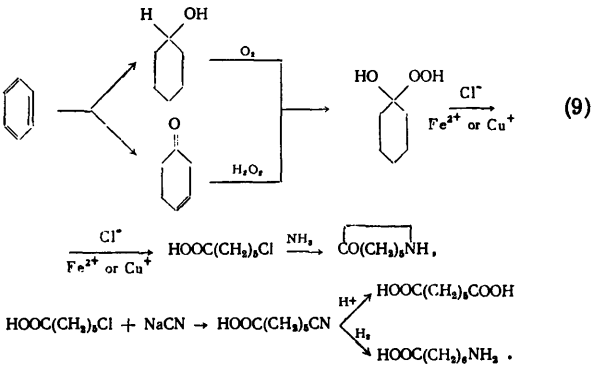
In the presence of an alcohol the corresponding esters are obtained. Similar products are obtained from cyclopentanone, but in lower yield.

Several recent interesting processes are based on the redox reactions of peroxide derivatives of cyclohexanone and other alicyclic peroxides[14,42–49]. Treatment of 1-hydroperoxycycloalkanols with aqueous solutions of equimolar amounts of iron(II) or copper(I) salts in the presence of an excess of hydrogen halides (or their salts), or of alkali metal azides, cyanides, or other salts, at -30° to + 30° gives good yields of the corresponding ω-substituted alkanoic acids[43–48,50,51]:

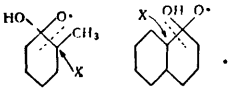

(8)

where X is Cl,[44] Br,[44] I,[44] $N_3$,[48] SCN,[50] CN,[48] $S_2O_3Na$,[50] or $ROCS_2$,[51] and $n$ is 4 or 5. The ω-substituted acids are the only products of this reaction; the cycloalkanone which is also formed is the initial starting material and is recycled. Thus a peroxide derivative of cyclohexanone gives ε-chlorocaproic acid in a yield of more than 90% (based on ketone), and the product is readily isolated in satisfactorily pure form (> 99%).

This reaction is the basis of the proposed method for the production of the main starting materials for polyamide resins from benzene[42]:


(9)

Analogous reactions have also been carried out with alkyl-substituted cyclic ketones and perhydrohydroperoxynaphthol[47]. The main product in the decomposition of 1-hydroperoxy-2-methylcyclohexanol by copper(I) or iron(II) salts in the presence of halide anions is the ε-halogenoheptanoic acid, and perhydro-1-hydroperoxynaphth-1-ol gives mainly the γ-(2-halogenocyclohexyl)butyric acid; thus the rupture of the C–C bond when the oxygen radical isomerises occurs mainly on the side which the substituent occupies:



Treatment with alkali of ε-thiocyanocaproic acid produced by (8) gives εε′-dithiodicaproic acid in high yield[50]:

$$2\,HOOC(CH_2)_5SCN \xrightarrow{NaOH} HOOC(CH_2)_5SS(CH_2)_5COOH\,, \quad (10)$$

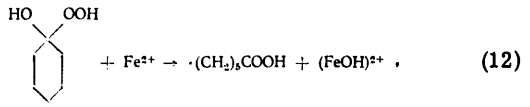
and the same product is obtained from the ε-substituted caproic acids $HOOC(CH_2)_5X$, where X is $-S-C\overset{S}{\underset{OC_2H_5}{<}}$ or $S_2O_3Na$.[50,51] Similarly δδ′-dithiodivaleric acid is obtained from a peroxide derivative of cyclopentanone[50,51].

The oxidation of the free radicals by metal salts — generally iron(III) or copper(II) halides, of type (8) — has been thought to proceed by ligand transfer[14,49], the reduction of the metal salt occurring with direct transfer of a halogeno-ligand to the free radical in the transition state (XV):

$$R^{\cdot} + M^{n+}X_n \longrightarrow \underset{(XV)}{[R{\cdot}X{-}MX_{n-1} \longleftrightarrow R{-}X\ MX_{n-1}]} \rightarrow RX + M^{+n-1}X_{n-1}\,. \quad (11)$$

In the absence of a suitable ligand the free radicals are oxidised, under analogous conditions, by a competing reaction involving electron transfer. For example, decanedicarboxylic acid is not produced when 1-hydroperoxycyclohexanol is reacted with a mixture of $FeSO_4$ and $CuSO_4$, the main reaction product being hex-5-enoic acid

(in 76% yield based on reacted ketone, or 61% based on $H_2O_2$)[14,49], which is formed by the mechanism:



$$+ Fe^{2+} \rightarrow \cdot(CH_2)_5COOH + (FeOH)^{2+}, \quad (12)$$

$$\cdot(CH_2)_5COOH + Cu^{2+} \rightarrow CH_2{=}CH(CH_2)_3COOH + Cu^{+} + H^{+}, \quad (13)$$

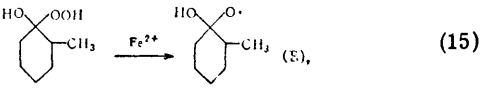
$$Cu^{+} + (FeOH)^{2+} \rightarrow Cu^{2+} + (FeOH)^{+}. \quad (14)$$

It is not thought that a classical carbonium ion is produced as an intermediate in this reaction, since when it is carried out in an aqueous or alcoholic medium only a very small quantity of substituted hexanoic acids is obtained. The optimal yield of hex-5-enoic acid cannot be obtained if catalytic quantities of the metal salts are used. In practice relatively large amounts of $FeSO_4$ (100–200% based on $H_2O_2$) and slightly smaller amounts of $CuSO_4$ (about 50 mole %) are required.

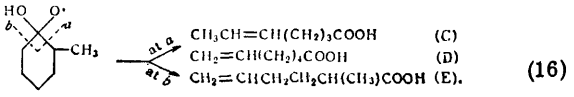
The used solution of $FeSO_4$ and $CuSO_4$ can be recycled, because of the low conversion of $Fe^{2+}$ ions in the reaction.

In acidified aqueous methanol the reaction produces methyl hex-5-enoate, together with caproic acid formed as the result of abstraction of hydrogen from the solvent.

The isomerisation of 2-substituted 1-hydroxycyclohexyloxy-radicals occurring in reactions involving electron or ligand transfer has been investigated; thus a mixture of heptenoic acids is obtained (in 43% yield based on the ketone) in the reaction of 1-hydroperoxy-2-methylcyclohexanol with $FeSO_4$ and $CuSO_4$:



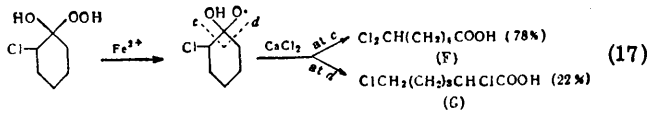
(E), (15)



(C) $CH_3CH{=}CH(CH_2)_3COOH$
(D) $CH_2{=}CH(CH_2)_4COOH$
(E) $CH_2{=}CHCH_2CH_2CH(CH_3)COOH$ (16)

The acid (E) is present in a concentration of 5 mole %, and hence when the radical (B) isomerises the rupture of the C–C bond proceeds almost completely from the side of the methyl group. The acids (C) and (D) are present in the mixture in amounts of about 60% and 40%.

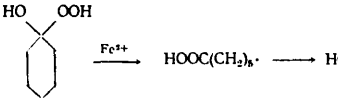
Treatment of 2-chloro-1-hydroperoxycyclohexanol with $FeSO_4$ and $CuSO_4$ gives a low yield of chlorohexenoic acids (~10%). With $FeSO_4$ and $CuCl_2$, dichlorocaprolic acids are produced, in 37% yield based on the ketone:



$Cl_2CH(CH_2)_4COOH$ (78%) (F)
$ClCH_2(CH_2)_3CHClCOOH$ (22%) (G) (17)

The relative amounts of the isomers (F) and (G) show that rupture of the C–C bond occurs about four times as frequently on the side of the chloro-substituent as on the unsubstituted side.

Aliphatic acids and esters are obtained in the decomposition of 1-hydroperoxycyclohexanol with iron(II) salts in the presence of various halogen compounds and thiols[52], and are produced by recombination and transfer of the radicals formed in the system:



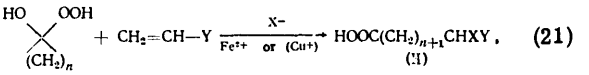
$$\cdot(CH_2)_5COOH + CCl_4 \rightarrow Cl(CH_2)_5COOH + \cdot CCl_3, \quad (18)$$

$$\cdot CCl_3 + \cdot(CH_2)_5COOH \rightarrow CCl_3(CH_2)_5COOH, \quad (19)$$

$$2\cdot CCl_3 \rightarrow C_2Cl_6. \quad (20)$$

In carbon tetrachloride, the reaction produces $\epsilon$-chlorocaprolic, decanedicarboxylic, and $\omega$-trichloroheptanoic acids in yields of 17, 30, and 6% respectively; in methanethiol, the products are caproic acid, decanedicarboxylic acid, and 6-(methylthio)hexanoic acid $CH_3S(CH_2)_5COOH$ in yields of 26, 21, and 12%.

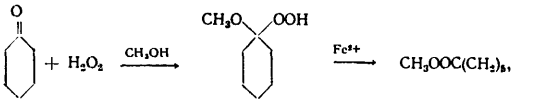
Acrylonitrile (or acrylates) and halogen have been added on to the carboxyalkyl radicals by the reaction[53,54]:



(H) (21)

where $n$ is 4 or 5, Y is CN or COOR, and X is Cl or Br. The $\omega$-halogenoalkanoic acids are also formed. Saponification of hydration of the compounds (H) gives the corresponding dicarboxylic acids in yields of 20–30 mole % (based on the initial ketone).

Kochi and Rust[55] have studied the competing processes occurring in the reaction of 1-hydroperoxycyclohexanol in methanol with butadiene (or chloroprene, styrene, or acrylonitrile) in the presence of $FeSO_4$ and $CuSO_4$. Under these conditions the 5-(methoxycarbonyl)pentyl radical adds on butadiene, and the resulting radical is oxidised by the copper(II) salt to give a good yield of methyl methoxydecenoates. The competing reactions are the oxidation of 5-(methoxycarbonyl)pentyl radicals by the copper(II) salt to give methyl hex-5-enoate and 5-methoxyhexanoate, and dimerisation of the radicals:



$$CH_3OOC(CH_2)_5\cdot + C_4H_6 \rightarrow [CH_3OOC(CH_2)_6CH{=}{=}{=}CH{=}{=}{=}CH]\cdot, \quad (22)$$

$$2\,[CH_3OOC(CH_2)_6CH{=}{=}{=}CH{=}{=}{=}CH_2]\cdot \rightarrow \text{three isomeric dimethyl eicosadienedioates}, \quad (23)$$

$$[CH_3OOC(CH_2)_6CH{=}{=}{=}CH{=}{=}{=}CH_2]\cdot + Cu^{2+} \rightarrow [CH_3OOC(CH_2)_6CH{=}{=}{=}CH{=}{=}{=}CH_2]^{+} + Cu^{+}, \quad (24)$$

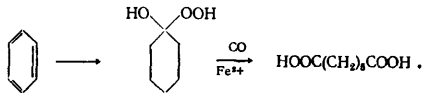
$$[CH_3OOC(CH_2)_6CH{=}{=}{=}CH{=}{=}{=}CH_2]^{+} + CH_3OH \xrightarrow{-H^{+}} \begin{cases} \rightarrow CH_3OOC(CH_2)_6CH{=}CHCH_2OCH_3 \\ \rightarrow CH_3OOC(CH_2)_6CH(OCH_3)CH{=}CH_2, \end{cases} \quad (25)$$

$$CH_3OOC(CH_2)_5\cdot + Cu^{2+} \rightarrow \begin{cases} \rightarrow CH_3OOC(CH_2)_3CH{=}CH_2 \\ \rightarrow CH_3OOC(CH_2)_4CH_2^{+} \xrightarrow[-H^{+}]{CH_3OH} CH_3OOC(CH_2)_6OCH_3. \end{cases} \quad (26)$$

The ability of alkenes to add to the 5-(methoxycarbonyl)-pentyl radical decreases in the series‡: $CH_2{=}CHCH{=}CH_2$, $CH_2{=}C(CH_3)CH{=}CH_2 > CH_2{=}C(CH_3)CH{=}CH_2 > C_6H_5CH{=}CH_2 > > CH_2{=}CHCN > CH_2{=}C(CH_3)CH_2Cl > CH_2{=}CHBr > CH_2{=}CCl_2$.

‡ Presumably one of the isoprenes should be chloroprene (Ed. of Translation).

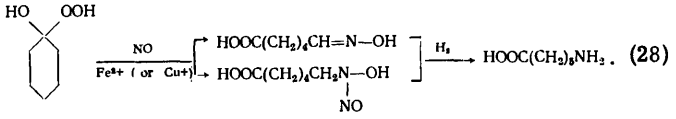
Carbon monoxide has also been added to the carboxyalkyl radicals obtained from 1-hydroperoxycyclohexanol[56,57]. Best results are obtained at pressures above 10 atm. The process may be utilised to prepare $\alpha\omega$-dicarboxylic acids, especially pimelic acid, from benzene:




(27)

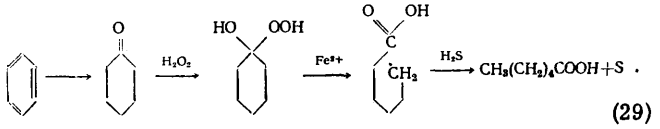
The decomposition of hydroperoxides in the presence of sulphur dioxide proceeds analogously, with the formation of sulphonic acids[57]; however, the greater activity of $SO_2$ as compared with CO enforces the use of dilute solutions, so as to avoid reduction of the peroxide to cyclohexanone.

Addition of nitrogen monoxide to the carboxyalkyl radicals followed by hydrogenation of the resulting nitrogen compounds produces amino-acids[58-60].



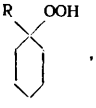

(28)

The decomposition of cyclic hydroperoxy alcohols in the presence of an iron(II) salt and hydrogen sulphide is the basis of a new method for the conversion of cyclic ketones into monocarboxylic acids having the same number of carbon atoms[61]. It may be utilised in the production of hexanoic acid from benzene[42]:




(29)

The autoxidation of alicyclic hydrocarbons or ethers[62,63] produces the hydroperoxides:

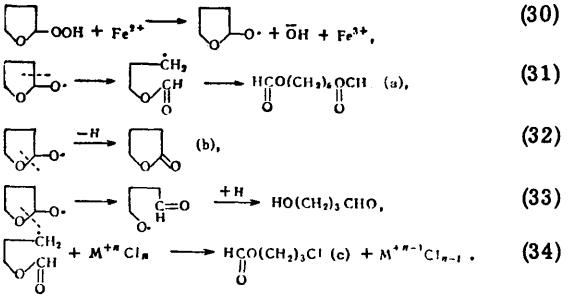



where R is alkyl or alkoxy.

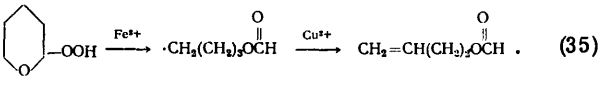
The reaction of methylcyclopentyl and methylcyclohexyl hydroperoxides with $FeSO_4$ has given[64] dodecan-2,11-dione and tetradecan-2,13-dione respectively, in yields of 40–55%. When 1,3-dienes are introduced into such systems, long-chain unsaturated diketones are obtained[65], of the general formula RMMR, where R is a ketoalkyl group and M is a butadiene or isoprene residue; the yield of such unsaturated ketones may reach 70%.

By introducing halide ligands into a system consisting of a cyclic hydroperoxide and $Fe^{2+}$ (or $Cu^{+}$) ions, Minisci and Belvedere[66] have developed efficient methods for the production of $\omega$-halogenated ketones and esters; thus methylcyclopentyl and methylcyclohexyl hydroperoxides give 6-chlorohexan-2-one and 7-chloroheptan-2-one respectively, in yields of ~ 50%. The reaction of methylcyclohexyl hydroperoxide with $FeSO_4$ and $CuSO_4$ produces hept-6-en-2-one in yields of up to 90%.[14] The mechanism of these reactions is identical with that already considered in respect of the hydroperoxyalcohols.

The above reactions have been extended to the hydroperoxides of cyclic ethers, which can be obtained by autoxidation of the ethers. The reaction of a tetrahydrofuryl hydroperoxide with $FeSO_4$ has given[67] hexamethylene diformate, see (a) below, 13.8% yield; $\gamma$-butyrolactone (b), 31.4% yield; and traces of 4-hydroxybutanol. In the presence of metal halides, no dimerisation of the radicals to produce (a) occurs, and 3-chloropropyl formate is obtained (c), 42% yield. The reactions involved are:




The reaction of tetrahydropyran-2-yl hydroperoxide with $FeSO_4$ gives octamethylene diformate in good yield[68]. In the presence of $FeSO_4$ and $CuSO_4$ but-3-enyl formate is obtained in 20% yield[14]:




(35)

If $CuCl_2$ is introduced into this system, 4-chlorobutyl formate is produced in 36% yield[69].

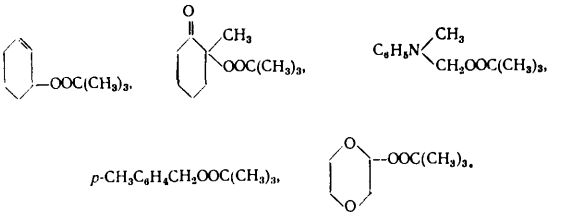
The reductive decomposition of tetrahydro-2,5-dimethylfuranyl hydroperoxide[70,71] gives 1-methylheptamethylene diacetate (46%) and s-butyl acetate (32%); in the presence of $CCl_4$, no s-butyl acetate is obtained, but 4-chlorobut-2-yl acetate (19%) is formed.

## 3. SYSTEMS COMPRISING ACYCLIC PEROXIDES AND METAL SALTS

The addition of catalytic quantities of copper(I) and certain other transition metal salts profoundly affects the course of the reaction between organic peroxides and certain organic compounds in solution[72,73]. In some cases such addition reduces the rate of or inhibits the reactions, and in others the reverse, causing rapid decomposition of the peroxides[75] and catalysing reaction of the peroxides with the solvents to give products which are unusual for normal free-radical reactions[73,74].

These investigations have led to some new and efficient synthetic methods. Thus a new method has been developed[74] for the introduction of peroxide groups into organic molecules by the reaction of t-butyl (or cumyl) hydroperoxide with many types of organic compound in the presence of catalytic amounts of copper, cobalt, or manganese salts at 70–100°. The peroxide group can be introduced in this way, with excellent yields, into compounds such as cyclohexene, 2-methylcyclohexanone,

cyclohexanone, dimethylaniline, xylene, and dioxan, to produce



The peroxide group replaces the most labile hydrogen atom.

A mechanism for the reaction has been proposed which involves the formation of intermediate complexes of the free radicals with molecules of the hydroperoxide:

$$ROOH + M^{+} \rightarrow RO\cdot + M^{2+} + \bar{O}H \quad (M=Cu,\ Mn,\ Co), \tag{1}$$

$$RO\cdot + R'H \rightarrow ROH + R', \tag{2}$$

$$R'\cdot + ROOH \rightarrow R'HOOR \ (complex), \tag{3}$$

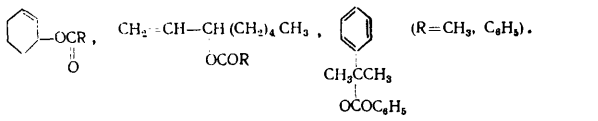
$$ROOH + M^{2+} \rightarrow ROO\cdot + M^{+} + H^{+}, \tag{4}$$

$$ROO\cdot + R'H \rightarrow R'HOOR \ (complex), \tag{5}$$

$$R'HOOR + oxidant \rightarrow R'OOR + (oxidant + e) + H^{+}. \tag{6}$$

The oxidant may be the $M^{2+}$ ion or the hydroperoxide. The formation of free carbonium ions by the reaction $R^{+}$ + oxidant $\rightarrow R'^{+}$ + (oxidant + $e$) is excluded, since practically no acetates are formed when acetic acid is used as reaction medium, but the yield of peroxide is not reduced.

t-Butyl peroxy-esters react smoothly with alkenes in the presence of catalytic amounts of copper or cobalt salts, producing allyl esters in good or moderate yields[73,76]; thus cyclohexene, oct-1-ene, and cumene have given 3-acyloxycyclohexenes, 3-acyloxyoct-1-enes, and $\alpha\alpha$-dimethylbenzyl benzoate respectively:



While in the absence of catalyst such reactions usually lead to a mixture of isomers, in the presence of copper or cobalt salts the reaction is specific: the acyloxy-group substitutes in the $\alpha$-position to the double bond.

The use of gas–liquid chromatography for the separation and identification of the reaction products has shown[77-79] that the reaction between t-butyl peroxy-esters and alk-1-enes under the influence of catalytic amounts of copper salts produces not only the 3-acyloxyalk-1-enes, but also their isomers, the 1-acyloxyalk-2-enes. This gives grounds for assuming that the reaction involves the formation of relatively free carbonium ions which undergo rearrangement in the course of reaction. The reaction mechanism proposed by Kochi[77,78] and Walling[79] comes down to the multistage process represented by:

$$CH_3COOOC(CH_3)_3 + Cu^{+} \rightarrow CH_3COO^{-} + Cu^{2+} + (CH_3)_3CO\cdot, \tag{7}$$

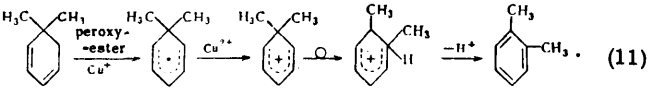
$$(CH_3)_3CO\cdot + RH \rightarrow (CH_3)_3COH + R\cdot, \tag{8}$$

$$R^{\cdot} + Cu^{2+} \rightarrow R^{+} + Cu^{+}, \tag{9}$$

$$R^{+} + CH_3COO^{-} \rightarrow ROCOCH_3. \tag{10}$$

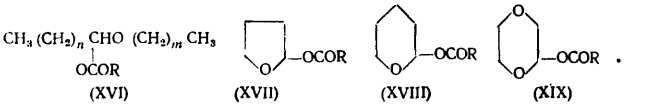
This is a chain reaction maintained by the $Cu^{I}$ and $Cu^{II}$ states of copper.

An interesting rearrangement with 1,2-transition of alkyl groups has been observed by Walling and Lawitsas[79] in the reaction between t-butyl peracetate and 6,6-dimethylcyclohexa-1,3-diene in the presence of copper salts; $o$-xylene was produced in 6% yield, but it is not formed in the absence of the copper or the peroxy-ester. The production of $o$-xylene clearly demonstrates the intermediate formation of a carbonium cation:



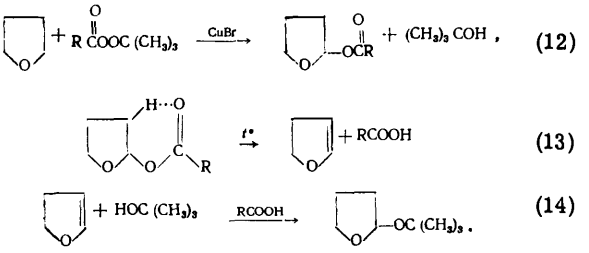
(11)

Aliphatic, aromatic, and cyclic ethers react smoothly with t-butyl peroxy-esters at 67–90° in the presence of CuCl or CuBr[76,80-88]. The primary reaction products are the acyloxy-substituted ethers — for example (XVI)–(XIX) — but these are unstable under the experimental conditions, and partially decompose into the corresponding carboxylic acids and unsaturated ethers[82]:



(XVI) (XVII) (XVIII) (XIX)

2,3-Dihydrofuran (13) is obtained in 66% yield from 2-benzoyloxytetrahydrofuran (XVII). The unsaturated ethers add on the t-butyl alcohol, giving the corresponding acetal (14); this stage is catalysed by the carboxylic acid:



(12)

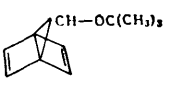
(13)

(14)

The reaction is general for ethers containing two methylene groups adjacent to the ether oxygen. Diethers such as dioxan give more stable acyloxy-derivatives, which on prolonged heating are slowly converted into the corresponding acetals (in low yield).

The analogous sulphur compounds are obtained in good yields by reaction of thioethers with t-butyl peroxy-esters[83,89,90].

A particular type of substitution occurs[91,92] in the reaction of t-butyl peroxy-esters with norbornadiene under the influence of catalytic amounts of CuBr; this produces 7-t-butoxynorbornadiene in 26% yield:



The mechanism of the catalytic action of copper salts on the reactions of organic peroxides has been considered by Kochi[14,77,78,93-95] and by Walling[79].

In the presence of large quantities of copper salts, the products obtained depend to a considerable extent on the nature of the anion; for instance, $CuCl_2$ and $CuBr_2$ oxidise the alkyl radicals to the corresponding alkyl halides, while under analogous conditions $CuSO_4$ gives unsaturated compounds and solvolysis products. Primary alkyl radicals in the presence of $CuSO_4$ give mainly unsaturated compounds, and tertiary alkyl, benzyl, and allyl radicals give solvolysis products. A desired product can therefore be obtained by suitable choice of reaction conditions. The examples given below illustrate these general statements (see also Section 2).

The reaction between t-butyl hydroperoxide and butadiene in the presence of $FeSO_4$ produces t-butoxy radicals, which readily add on to butadiene, and the resulting t-butoxybutenyl radicals dimerise [96]. When carried out in aqueous methanol in the presence of $FeSO_4$ and $CuSO_4$, [14,94] this reaction gives a good yield (55–60%) of the isomeric methyl ethers of t-butoxybutenols of the composition

$$(CH_3)_3COCH_2CH(OCH_3)CH{=}CH_2 \quad (\sim 66\%),$$
$$trans\text{-}(CH_3)_3COCH_2CH{=}CHCH_2OCH_3 \quad (\sim 32\%),$$
$$(CH_3)_3COCH_2CHOH.CH{=}CH_2 \quad (\sim 2\%).$$

The mechanism of such reactions has already been discussed in Section 2.

The reaction of t-butyl hydroperoxide with butadiene in the presence of the $Fe^{3+}/Fe^{2+}$ or $Cu^{2+}/Cu^{+}$ system and $Cl^-$, $Br^-$, $SCN^-$, or $N_3^-$ ions gives good yields of compounds $(CH_3)_3CO(C_4H_6)X$, where X is Cl, Br, SCN, or $N_3$. [19,97] For example, the reaction between t-butyl hydroperoxide (0.63 g-mole), butadiene (0.30 g-mole), $FeCl_3.6H_2O$ (0.55 g-mole), $FeSO_4.7H_2O$ (0.32 g-mole), and LiCl (0.56 × × g-mole) at -10° to -15° produces a mixture of 1-chloro--4-t-butoxybut-2-ene and 3-chloro-4-t-butoxybut-1-ene in a yield of 98% on the diene or 47% on the peroxide [97].

Investigation of the reactions of the t-butoxy-radical, which is fairly strongly electrophilic in the presence of chloride, azide, and thiocyanate anions and alkenes, has shown the direction of reaction to depend on the donor–acceptor properties of the substituents in the alkene molecule [19]. With butadiene the reaction is:

$$(CH_3)_3COOH + Fe^{2+} \rightarrow (CH_3)_3CO\cdot + Fe^{3+} + \bar{O}H, \quad (15)$$
$$(CH_3)_3CO\cdot + C_4H_6 \rightarrow (CH_3)_3COC_4H_6\cdot, \quad (16)$$
$$(CH_3)_3COC_4H_6\cdot + (FeX)^{2+} \rightarrow (CH_3)_3COC_4H_6X + Fe^{2+}. \quad (17)$$

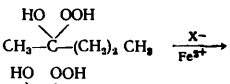
Cyclopentadiene behaves analogously to butadiene. Under the same conditions, styrene forms 1-chloro-1-phenylethyl t-butyl ether in the presence of chloride ions, and a mixture of $C_6H_5CHN_3CH_2OC(CH_3)_3$ and $C_6H_5CHN_3CH_2N_3$ in the presence of sodium azide. Clearly, in the latter case two parallel processes take place:

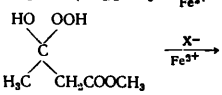
$$(CH_3)_3CO\cdot + C_6H_5CH{=}CH_2 \rightarrow C_6H_5\dot{C}HCH_2OC(CH_3)_3 \xrightarrow{(FeN_3)^{2+}} \xrightarrow{(FeN_3)^{2+}} C_6H_5CHN_3CH_2OC(CH_3)_3, \quad (18)$$
$$(CH_3)_3CO\cdot + (FeN_3)^{2+} \rightarrow N_3\cdot + Fe^{3+} + (CH_3)_3CO^-, \quad (19)$$
$$N_3\cdot + C_6H_5CH{=}CH_2 \rightarrow C_6H_5\dot{C}HCH_2N_3 \xrightarrow{(FeN_3)^{2+}} C_6H_5CHN_3CH_2N_3. \quad (20)$$

A t-butoxy-radical of reduced reactivity is observed in the decomposition of t-butyl hydroperoxide in the presence of the $Fe^{3+}/Fe^{2+}$ system, chloride ions, and acrylonitrile, when $\alpha$-chlorobutyronitrile is obtained as main reaction product. This is because the strongly electrophilic t-butoxy-radical cannot react with the ethylenic bond of the acrylonitrile, which is electron-deficient in nature, and it therefore decomposes to give a methyl radical, which has nucleophilic properties:

$$(CH_3)_3CO\cdot \rightarrow CH_3COCH_3 + CH_3\cdot, \quad (21)$$
$$CH_3\cdot + CH_2{=}CH{-}CN \rightarrow CH_3CH_2\dot{C}HCN \xrightarrow{(FeCl)^{2+}} CH_3CH_2CHClCN + Fe^{3+}. \quad (22)$$

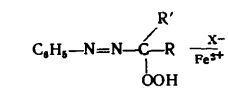
The decomposition of peroxides of acyclic ketones with iron(II) or copper(I) salts in the presence of $Cl^-$, $SCN^-$, or $N_3^-$ ions gives the corresponding substituted alkanes [56]:


$$\xrightarrow[Fe^{3+}]{X^-} CH_3CH_2CH_2X + CH_3COOH, \quad (23)$$

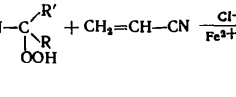

$$\xrightarrow[Fe^{3+}]{X^-} CH_3OCOCH_2X + CH_3COOH. \quad (24)$$

The reaction of peroxides of acyclic diketones or keto--esters with iron(II) sulphate in the presence of butadiene produces diketones and esters of long-chain dicarboxylic acids [98,99].

The reaction of hydroperoxides of ketone phenylhydrazones with iron(II) or copper(I) salts in the presence of $Cl^-$, $Br^-$, $SCN^-$, or $N_3^-$ follows the course of the Sandmeyer reaction, with the formation of the correspondingly substituted aryl compounds [100]:


$$\xrightarrow[Fe^{3+}]{X^-} C_6H_5X + R'COR + N_2. \quad (25)$$

The reaction of these hydroperoxides with acrylonitrile or acrylates under analogous conditions (the Meerwein reaction) [101] gives good yields of the $\alpha$-substituted $\beta$-phenylpropionitriles or $\beta$-phenylpropionate esters respectively:

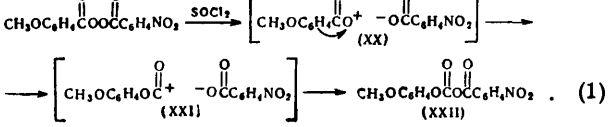

$$+ CH_2{=}CH{-}CN \xrightarrow[Fe^{3+}]{Cl^-} C_6H_5CH_2CHClCN + R'COR + N_2. \quad (26)$$

## 4. IONIC REACTIONS OF PEROXIDES UNDER THE INFLUENCE OF LEWIS ACIDS

Recent years have seen the accumulation of much experimental material which shows that certain peroxides can decompose in solution by an ionic, as well as a radical, mechanism [102–107].

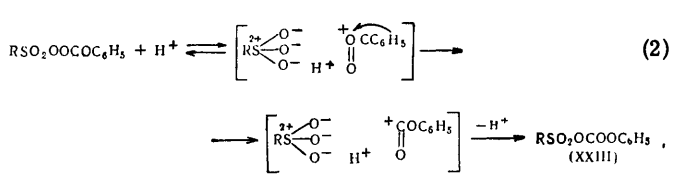
The ionic reactions of peroxides are catalysed by polar solvents [102,103], strong acids [102–107] and Lewis acids ($AlCl_3$, $SbCl_5$, $FeCl_3$, $BF_3$, etc.) [104,106,108–114].

Heterolytic decomposition of peroxides leads most frequently to intramolecular rearrangement [102–105,110,113], and hence to loss of the ability to initiate radical polymerisation [102,103]. For example, *p*-methoxybenzoyl--*p*-nitrobenzoyl peroxide decomposes by a radical mechanism in benzene, but by an ionic mechanism in the strongly polar thionyl chloride, producing a mixed anhydride of *p*-nitrobenzoic acid and mono-(methoxyphenyl) carbonate (XXII) [102]:


$$\xrightarrow{SOCl_2} \left[CH_3OC_6H_4\overset{+}{C}O \quad {}^-OCC_6H_4NO_2\right] \longrightarrow \quad (XX)$$
$$\longrightarrow \left[CH_3OC_6H_4O\overset{+}{C} \quad {}^-OCC_6H_4NO_2\right] \longrightarrow CH_3OC_6H_4OCOCC_6H_4NO_2. \quad (1)$$
(XXI) (XXII)

The *p*-methoxyphenyl radical in the cation (XX) migrates to the peroxidic oxygen to form the carbonium cation (XXI); recombination of the ions then gives the mixed anhydride (XXII).

Alkanesulphonyl peroxides decompose in organic solvents (irrespective of their polarity) by an ionic mechanism[111], with the formation of the mixed anhydrides (XXIII); this reaction is catalysed by the alkanesulphonic acid which is produced by the initial homolytic decomposition of the peroxide[104,105]:

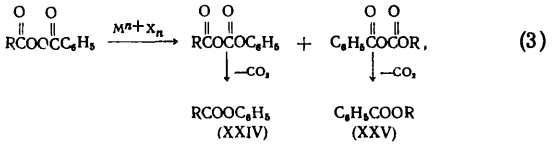


(2)

(XXIII)

where R is $CH_3$, $C_2H_5$, n-$C_3H_7$, or iso-$C_3H_7$. If the sulphonic acid is bound (for example, by means of dry powdered potassium carbonate[104,105]), the peroxides decompose predominantly by a radical mechanism; on the other hand, addition of a sulphonic acid or of aprotonic acids ($AlCl_3$, $SnCl_4$, or $SbCl_5$) directs the reaction towards the heterolytic isomerisation (2), the mixed anhydrides of alkanesulphonic acid and monophenyl carbonate (XXIII) being obtained in more than 85% yield.

Analogous rearrangements are undergone by benzoyl peroxide[102,108,109,115,116] under the influence of $AlCl_3$ or $SbCl_5$, and by unsymmetrically substituted analogues of benzoyl peroxide and other non-symmetric acyl peroxides under the influence of $BF_3$.[113] The acyl phenyl carbonates produced by the heterolytic rearrangement are unstable, and decompose in the presence of aprotonic acids to form the corresponding esters (in 70–95%) and $CO_2$:

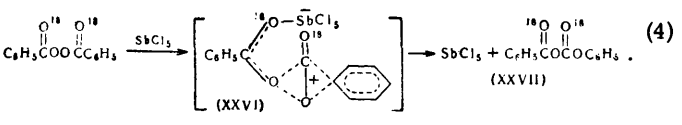


(3)

(XXIV) (XXV)

where $M^{n+}X_n$ is $AlCl_3$, $SbCl_5$, or $BF_3$, and R is $C_6H_5$, *p*-$CH_3OC_6H_4$, *p*-$CH_3C_6H_4$, *p*-$ClC_6H_4$, *p*-$BrC_6H_4$, *p*-$NO_2C_6H_4$, *o*-$CH_3C_6H_4$, *o*-$ClC_6H_4$, $CH_3$, $ClCH_2$, $C_2H_5$, etc. Depending on R, either (XXIV) or (XXV) may predominate; thus the reaction produces 100% (XXIV) when R is *p*-$NO_2C_6H_4$, and 100% (XXV) when R is *p*-$CH_3OC_6H_4$.

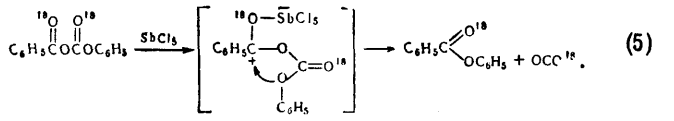
Denney and coworkers have investigated the heterolytic rearrangement, under the influence of $SbCl_5$, of benzoyl peroxide[115,116] and of some other peroxides[117–118], labelled with $^{18}O$ in the carbonyl group; the resulting ester — (XXIV) or (XXV), R = $C_6H_5$ — still contains $^{18}O$ in the carbonyl group, but the phenolic oxygen does not contain the remaining $^{18}O$. It is therefore concluded that the heterolysis of the peroxide does not produce free carbonium cations, but that the rearrangement proceeds in the transitional complex (XXVI):



(4)

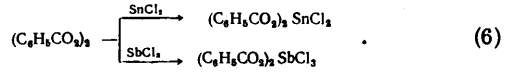
(XXVI) (XXVII)

Under the influence of the $SbCl_5$ the mixed carbonate (XXVII) rapidly decomposes as follows:



(5)

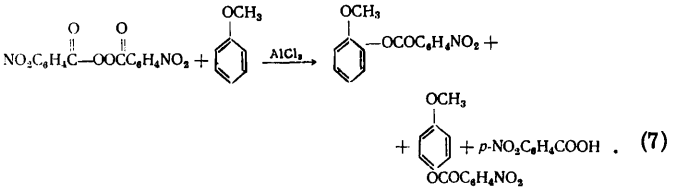
Benzoyl peroxide reacts quantitatively with $SnCl_2$ and $SbCl_3$ at room temperature as follows[119]:



(6)

Apparently, in these reactions the benzoyl peroxide splits homolytically at the O–O bond, and the resulting benzoyloxy-radicals react with the salt present, the $Sn^{2+}$ and $Sb^{3+}$ being converted into $Sn^{4+}$ and $Sb^{5+}$ respectively.

Edward and coworkers have recently shown[114] that under the influence of an equimolar amount of $AlCl_3$ *pp'*-dinitrobenzoyl peroxide can react with strongly nucleophilic solvents (anisole, mesitylene, 1,3-dimethoxybenzene) at 0–25° by a Friedel–Crafts type reaction, giving moderate yields of the corresponding *p*-nitrobenzoates:

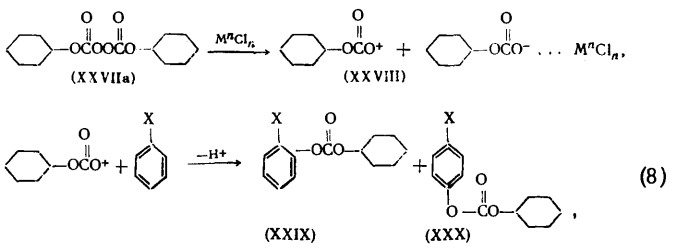


(7)

The peroxide apparently splits heterolytically at the O–O bond, and the resulting *p*-nitrobenzoyloxy-cation attacks the aromatic ring. This electrophilic attack is facilitated by electron-donating substituents, and does not occur with benzene or toluene.

The reaction between dicyclohexyl peroxodicarbonate (XXVIIa) and aromatic compounds under the influence of $FeCl_3$,[112] $SbCl_5$, $SbCl_3$, and $AlCl_3$ has been investigated. In the absence of the aprotonic acids, the peroxodicarbonate decomposes homolytically in toluene at 50–65° to form $CO_2$ and cyclohexyloxy-radicals, which partially disproportionate in a "cage" of solvent, and partially react with the toluene, the resulting benzyl radicals dimerising to produce 1,2-diphenylethane[120].

Catalytic amounts of aprotonic acids ($SbCl_5$, $FeCl_3$) do not affect the decomposition of the peroxodicarbonate, since they are removed from the sphere of reaction as solid complexes[120]. If the aprotonic acids are added in amounts of 10–50 mole %, the homolytic reaction with the solvents is suppressed, and the peroxodicarbonate enters into a Friedel–Crafts reaction with aromatic compounds, forming the corresponding mixed carbonates (XXIX, XXX):



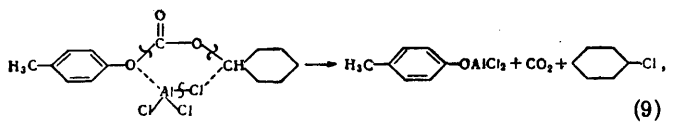
(8)

(XXVIIa) (XXVIII) (XXIX) (XXX)

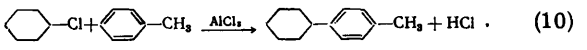
where X is H, $CH_3$, $OCH_3$, or Cl.

The cyclohexyloxycarboxy-cation (XXVIII) is fairly reactive and does not require activation of the aromatic ring by electron-donating substituents; under the influence of $FeCl_3$ it reacts with benzene to give a 17% yield of cyclohexyl phenyl carbonate, and with toluene to give cyclohexyl *o*-tolyl and cyclohexyl *p*-tolyl carbonates in yields of 34% and 7% respectively. Electron-donating substituents favour the electrophilic attack; thus even in the absence of Lewis acids anisole reacts to give cyclohexyl *o*-methoxyphenyl and cyclohexyl *p*-methoxyphenyl carbonates in good yield.

Strong Lewis acids, such as $AlCl_3$, can decompose the mixed carbonates. The main product of the decomposition of the peroxodicarbonate in toluene at 40–60° in the presence of 50 mole % $AlCl_3$ is *p*-tolylcyclohexane (40% yield), which is obtained as the result of decomposition of the initial cyclohexyl tolyl carbonates (XXIX) and (XXX):



(9)



(10)

When carried out in chlorobenzene the reaction produces *p*-chlorophenylcyclohexane. The reaction mechanism is confirmed by the quantitative liberation of hydrogen chloride.

The ionic reactions of peroxides with solvents are almost restricted to the examples given[112,114]. However, the growing interest in such processes suggest that in the near future the ionic reactions of peroxides will form the basis of new methods of synthesis.


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# ADVANCES IN THE CHEMISTRY OF POLYETHYLENEIMINE (POLYAZIRIDINE)†

D. S. Zhuk, P. A. Gembitskii, and V. A. Kargin

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† Since polyethyleneimine is an industrial product, and really a straight-chain compound, it has seemed advisable to retain this name in the translation, while the more systematic *aziridine* is used for the monomer (Ed. of Translation).

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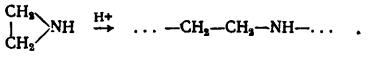
Polyethyleneimine has been produced on the industrial scale since 1938, in Germany by the Badische Anilin- und Soda-Fabrik AG. at Ludwigshafen and in the USA by the Chemirad Corporation. It is used mainly for the water--repellent finishing of paper and textiles[1-4], for conferring dyeability on them[5], in the manufacture of reactive dyes[6], for the production of anion-exchange resins, films, and membranes[7-9], in the foundry industry[10], and as an additive to motor fuels[11].

## 1. METHODS OF SYNTHESISING POLYETHYLENEIMINE

Polyethyleneimine is obtained mainly by the polymerisation of aziridine. Another simple and convenient method for obtaining it is the thermal decomposition of 2-oxooxazolidine. Polyethyleneimine of low molecular weight (in the form of a mixture mainly of triethylenetetramine and tetraethylenepentamine) — the so-called polyethylenepolyamine — is manufactured in large quantities by the condensation of dichloroethane in ammonia or ethylenediamine[12], and is used as a hardening agent for epoxide resins.

## 2. POLYMERISATION OF AZIRIDINE

The polymerisation of strained three-membered rings constitutes a special aspect of the more general question of the conversion of rings into linear polymers. Unlike other methods of synthesising compounds of high molecular weight, the polymerisation of rings generally involves no change in electronic structure (provided that the peculiarities of the type of bond in strained three-membered rings are disregarded) or in the number of chemical bonds in the system: only the way in which the bonds are arranged is changed. Although a C–N bond in the ring is cleaved on the polymerisation of aziridine, a similar bond is formed in the linear polyethyleneimine molecule:



Thermodynamically, the possibility of polymerisation of ring monomers is determined by the accompanying change in free energy. The strain in three-membered rings results in the polymer being more stable thermodynamically than the monomer, and their heat of polymerisation (~23 kcal mole$^{-1}$ for aziridine)[13] provides a measure of this strain. Thus, in their tendency to polymerise, three-membered rings are close to a double bond in olefins (heat of polymerisation ~22.5 kcal mole$^{-1}$).

An aspect, requiring separate consideration, is the kinetic possibility of polymerisation, i.e. the mobility of the relevant bonds under the reaction conditions, since thermodynamically unstable compounds may be quite stable kinetically, and will not polymerise if they contain no labile bond. As example we can cite cycloalkanes, for which, in spite of their fairly considerable thermodynamic instability (e.g. ~25 kcal mole$^{-1}$ for cyclopropane), conditions of polymerisation have not yet been found‡. In this case the complete equivalence of all the bonds in the ring is responsible for the thermodynamic instability of strained alicyclic rings at high temperatures manifesting itself specifically[15] in their homolytic thermal isomerisation into ethylene derivatives.

Three-membered heterocycles (aziridine, oxiran, thiiran) are completely stable kinetically when absolutely pure, owing to the similarity in the energy characteristics of all the cyclic bonds. However, they polymerise in the presence of certain activators (polymerisation catalysts), which act selectively on the carbon–heteroatom bond. In fact it has been shown[16] that absolute dry§ and pure aziridine does not polymerise even at 150°. The most usual polymerising agents are acids[17-24] (including carbon dioxide[25,26], acid salts[18-20], and phenol[27]), alkylating agents[18,28-30], boron trifluoride[18,31-33], anhydrous iron(III) chloride[33], silver nitrate or perchlorate[34], surface-active substances (kieselguhr, activated carbon[20], aluminium oxide, silica gel, etc.[32]), ammonia under pressure[35], and water¶. Any reagent which can convert the ring nitrogen atom into the quadrivalent state (by salt formation, oxidation, or coordination) can act as a polymerisation catalyst for aziridine.

Bases, which are known to catalyse the anionoid polymerisation of oxides, do not cause the polymerisation of aziridine[32]. Peroxides and ultraviolet radiation†, which induce the free-radical polymerisation of vinyl compounds, are also ineffective in this respect[32]. Inhibitors of free--radical polymerisation do not exhibit the polymerisation of aziridine. Sodium, potassium, sodamide, and strontium carbonate exert an inhibiting action[18,32].

### Mechanism

There is no consensus of opinion concerning the mechanism of the polymerisation of aziridine. German authors[24,32,39] regard it as a case of polycondensation, which presupposes intermediate formation of an addition product with the catalyst, involving cleavage of the aziridine ring (in the case of hydrochloric acid, for example, 2-chloroethylamine hydrochloride is formed), and its occurrence in two stages

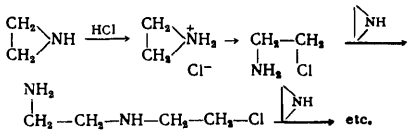
‡ One paper has been published[14], describing the preparation of a polymeric product from phenylcyclopropane under high pressures (up to 2000 atm).

§ A special technique has been worked out[16] for preparing absolutely dry aziridine. The dry product (dried by standing over sodium) is distilled under vacuum and condensed over sodium which has been freshly cut and warmed in a vacuum. On cooling with solid carbon dioxide, the sodium dissolves to form a bright blue solution. The aziridine is distilled off from the resulting solution into a carefully evacuated flask. A solution of sodium is not formed if the aziridine has not undergone preliminary drying.

¶ Water is a peculiar polymerisation catalyst for aziridine. In the presence of water alone[36,37] polymerisation is extraordinarily slow (even at elevated temperatures) and usually ceases at the tetramer stage. Water has been proposed[37] as a specific catalyst for the dimerisation, trimerisation, and tetramerisation of aziridine.

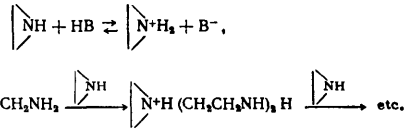
† Results reported by Japanese workers[38], showing the polymerisation of aziridine when irradiated on poly(vinyl chloride), do not contradict the above statement. Careful investigation has established that, in contrast to the radical mechanism of vinyl polymerisation, the polymer is formed in this case by the usual acid polymerisation of aziridine catalyst by OH or COOH groups produced on exposure of the substrate polymer.

– intramolecular version (rate-determining stage) and anionoid fission:



This mechanism is inconsistent with the more thorough and rigorous kinetic investigations of British[16,40] and American[18] workers. No explanation is provided of the fact that the reaction of 2-chloroethylamine hydrochloride with the feebly anionoid aziridine is of the second order, whereas the reaction of this compound with the strongly anionoid caustic potash obeys a different kinetic law. 2-Chloroethylamine hydrochloride was not isolated from reaction mixtures undergoing polymerisation, although it itself was shown to polymerise slowly at room temperature[18].

These workers suggested a mechanism of cationoid additive polymerisation of polar type, involving stepwise reaction of the aziridinium ion with uncharged rings:

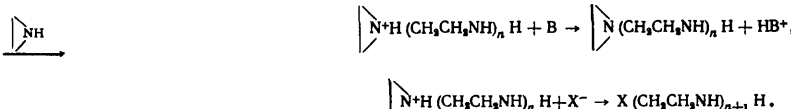


The first of these reactions is reversible, and since the rate of growth of the polymer chain is slower than transfer of a proton, all the protons will be distributed in a definite fashion among the various basic centres in the polymerising mixture. The distribution is a function of the relative concentration and basic strength of these centres. In the early stages most of the protons are combined with monomeric molecules, and the main product of polymerisation is the dimer. When the concentration of the dimer has become considerable relative to that of the monomer, formation of the trimer, tetramer, and higher polymers begins: i.e. as in chain transfer by a radical or by an ion in vinyl (radical or ionic) polymerisation, we have here a protonation transfer equilibrium.

During the progress of the reaction, the degree of polymerisation will increase, and products of low molecular weight will gradually disappear. This is confirmed[16] by the successive chromatography (on paper) of the polymerisation products of aziridine. On the first chromatogram up to seven different spots or bands (up to the octamer) are distinguished, with an unresolvable band due to higher polymers. Two faint spots were also observed, more mobile than the dimeric spots, which were shown to be caused by traces of aminoethanol and 2-2′-aminoethylaminoethanol (a hydrolysis product of the dimer).

It is also possible that two polymeric molecules may combine through their terminal aziridine groups. This is supported by the increase in the degree of polymerisation in mixtures containing no monomeric aziridine[16], and also by the spontaneous polymerisation of the specially synthesised dimer of aziridine[41].

Chain termination (in this case deactivation of the quaternary ion) can occur on abstraction of a proton by a base B (e.g. by a monomer molecule, an amino-group or an aziridinyl group of a polymer, an anion, water, etc.) or when the ring is opened by an anion:

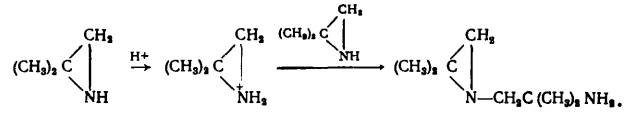


If in the latter reaction $X^-$ represents an aziridinyl group of a polymer, the polymer chain becomes branched.

Thus although aziridine undergoes additive polymerisation, and only a few reactive aziridinium ions are present at any given instant, the general character of the process resembles stepwise polycondensation, in which all molecules contain reactive groups because of the very rapid redistribution of hydrogen ions among the various substances present.

In order to settle the question of the mechanism of this polymerisation, it is of interest to study the behaviour of unsymmetrically substituted derivatives of aziridine, since differences in reaction mechanism, which for unsubstituted aziridine can be revealed only by the kinetic form, lead in this case to structural differences.

It has been shown[42] for the polymerisation of 2,2-dimethylaziridine that the reaction involves fission of the bond between nitrogen and the cyclic methylene group (the dimer was isolated, and its structure established by a separate synthesis):



This direction of ring cleavage corresponds‡ to the bimolecular inversion mechanism $S_N2$ of interaction between charged and uncharged 2,2-dimethylaziridine rings.

The conclusion that other alkylated aziridines polymerise by an $S_N2$ type of mechanism is confirmed indirectly by a rough comparison of their rates of polymerisation§. Alkylated aziridines containing a cyclic primary carbon atom (2-methylaziridine, 2-ethylaziridine, 2,2-dimethylaziridine) are found to polymerise as readily as does aziridine itself. In contast, the polymerisation of the

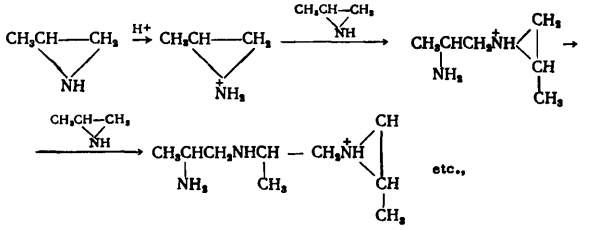
‡ As noted above, preferential rupture of a cyclic bond at a primary rather than a secondary or a tertiary carbon atom indicates an inversion mechanism, whereas preference to a tertiary in relation to a primary atom would indicate an ionisation mechanism [$S_N1$].

It has been shown[43] that change to a more nucleophilic ion or a donor molecule can produce a bimolecular inversion with structures which are subject to an ionisation mechanism in the presence of less powerful nucleophiles. It must be noted in this connection that the aziridinium nitrogen should exert a considerable effect (through carbon attached to the nitrogen) favouring inversion.

§ Kinetic investigation of the polymerisation of alkylated aziridines is complicated by the solubility characteristics of the polymers. Thus the polymer of 2,2-dimethylaziridine, in contrast to polyethyleneimine, is insoluble in water and soluble in ether. This makes it difficult to use viscometric methods in studying the kinetics of polymerisation. To determine reaction rates the authors distilled unchanged monomer from an alkaline solution of the reaction mixture.

alkylated rings containing no primary carbon atom (*trans*--2,3-dimethylaziridine, 2,2-dimethyl-3-propylaziridine) is extraordinarily difficult.

Polymerisation of the optically active (+)- and (-)-2-methylaziridines (with the ether-$BF_3$ complex or with HCl) yields[33] solid polymers which soften at ~60–80° and show strong optical rotation (up to ±100°) opposite in sign to that of the monomer. The high degree of optical activity and the considerable rise in softening point compared with polymeric (±)-2-methylaziridine suggest a high degree of preservation of asymmetry during polymerisation. This is compatible only with an $S_N2$ type of ring cleavage at a primary carbon atom:



since the latter is accompanied neither by the formation nor by the rupture of bonds attached to the asymmetric carbon atom.

## Kinetics

Let us discuss briefly the kinetics of the acid polymerisation of aziridine. If the catalyst concentration is assumed to remain substantially unchanged during the reaction, the polymerisation of aziridine, which according to the above mechanism is a second-order reaction (with respect to the aziridine rings), can be represented by the equation

$$\frac{1}{1-p} - 1 = \frac{p}{1-p} = Kt,$$

where $p$ is the fraction of the monomeric aziridine which has reacted. On the further assumption that the molecular-weight distribution resembles that calculated for polycondensation[44] and is independent of temperature, reaction velocity, etc., we obtain $X^{-0.5} - 1 = Kt$,¶ where $X$ is the fraction of the monomer unchanged.

If the time variation of polymerisation with various acids is plotted as $p/(1-p)$ against $t$ (Fig. 1), the progressively diminishing slope of the curves indicates a gradual decrease in rate during the reaction, which is most clearly shown in the early stages. Two types of explanation are possible for this phenomenon: (1) the aziridine nitrogen atom in monomer or polymer is more strongly basic than an amino--nitrogen atom, and as a result competes more vigorously for possession of a proton; and (2) the catalyst is consumed in the course of the reaction.

Careful dilatometric kinetic investigations have shown[16] that the molecular-weight distribution is independent of the nature or concentration of the catalyst. This implies that the relative distribution of protons among the various basic centres (aziridine nitrogen in monomer and polymer, primary and secondary amino-nitrogen in the polymer) is identical. In this case the reaction velocity at any stage

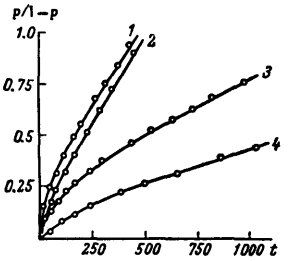



Fig. 1. Polymerisation of aziridine in the presence of various acidic catalysts (dependence of degree of conversion on time): 1) 0.025 M chloroacetic acid; 2) 0.054 M toluene-*p*-sulphonic acid; 3) 1.00 M benzoic acid; 4) 0.88 M dichlorophenol.

in the conversion will be proportional to the concentration of protons, and can be expressed mathematically as

$$-\frac{d[M]}{dt} = \sum^{x,y} K_{xy}[M_x][M_yH^+], \qquad (1)$$

where $M_x$ represents an uncharged terminal aziridine ring in a polymer having a degree of polymerisation of $x - 1$, and $M_yH^+$ is a charged aziridinium ring in a polymer having a degree of polymerisation of $y - 1$, while [M] is the total concentration of aziridine rings.

Thus the hypothesis that the catalyst concentration remains constant during polymerisation is incorrect (at least for the acids investigated), and the slowing down in the early stages of the reaction is caused not by formation of a strongly basic dimer but by diminution in the catalyst concentration†. The consumption of catalyst during polymerisation in the presence of hydrochloric, hydrobromic, and sulphuric acids, whose anions are able to compete with an aziridine molecule in opening a protonated aziridine ring, is not unexpected, since all three acids are capable of reacting with aziridine to form open-chain products.

The polymerisation of aziridine in the presence of perchloric, picric, and other acids having very feebly nucleophilic anions occupies a special position. In this case the original hypothesis, that the catalyst concentration is constant during polymerisation, proves to be correct, and Eqn. (1) remains valid. The only side-reaction in this case can be solvolytic opening of the aziridine rings (by hydrolysis, alcoholysis), which, however, makes no effective difference to the kinetic interpretation.

With the first group of acids considered here, in contrast, the reaction velocity is greatly dependent[16] on the acid used, since the kinetics of the breakdown of catalyst in a side-reaction with the aziridine varies with the different acids. In this case the kinetic interpretation must take into account the differences in the partial consumptions of monomer in the side-reaction. These differences

¶ This equation is of the same form as for a reaction of order 1.5 with respect to the monomer.

† The first hypothesis can also be rejected on the basis of the following simple experiment. Rates of polymerisation in the presence of 10–15% of added strong bases (dimer of aziridine, n-butylamine, piperidine) were compared[16] with the course of reaction in the absence of these additions. The slight retarding effect can be attributed to dilution of the aziridine.

are most definite in form with strong acids (sulphuric, hydrochloric, toluene-*p*-sulphonic) and with weak acids. (acetic and benzoic acids, 2,4-dichlorophenol). Whereas with strong acids the kinetics of catalyst destruction are consistent with their complete ionisation in aziridine solution, the kinetic treatment for weak acids is based on the hypothetical formation of ion-pairs. The kinetic regularities for both cases will be examined in detail below.

Thus, although the polymerisation of aziridine is additive, it differs from vinyl additive polymerisation (radical or ionic) in two main features. Firstly, as a result of the presence of a transfer equilibrium, all monomeric and polymeric molecules are capable of being activated (and deactivated). This produces definite kinetic characteristics resembling those observed in condensation polymerisation. Secondly, the partial consumption of catalyst usually exceeds that of the monomer, whereas the opposite is the case in other types of polymerisation.

## Strong Acids

Changing the initial concentration of the strong toluene-*p*-sulphonic acid has no effect[16] on the course of polymerisation (which in all experiments is represented by a single curve relating extent of conversion with time — Fig. 2). Thus although the catalyst is consumed during the reaction, the rate of polymerisation at any instant is proportional to the catalyst concentration:

$$-\frac{d[M]}{dt} \propto [HA]_0. \qquad (2)$$

The similarity in the catalytic activity of all strong acids (for the polymerisation of aziridine) shows that they are practically completely ionised in aziridine. Consequently $\Sigma[BH^+] = [HA]$ at time $t$. If $[M_yH^+]/[BH^+]$ is independent of the acid concentration, so that $[M_yH^+] \propto [HA]$, substitution of this expression in Eqn. (1) yields

$$-\frac{d[M]}{dt} \propto [HA], \qquad (3)$$

i.e. the rate of polymerisation at time $t$ is proportional to the instantaneous acid concentrations, and consequently the ratio of the fractional decrease in concentration of the monomer to the fractional decrease in concentration of the acid should be constant:

$$\frac{[HA]\,d[M]/dt}{[M]\,d[HA]/dt} = K. \qquad (4)$$

On substituting here the relation (3), we obtain $-d[HA]/dt \propto \propto [HA]^2$ (a relationship of the second order with respect to the acid concentration). It is consistent with the consumption of acid by the reaction

$$\overset{+}{\text{N}}\text{HR} + A^- \rightarrow ACH_2CH_2NHR, \qquad (a)$$

where R = H or a polymer chain of any length.

For this latter reaction, too, we can write

$$-\frac{d[HA]}{dt} = \sum^{y} K_{yA^-}[A^-][M_yH],$$

and if we substitute, in view of the above, $[A^-] = [HA]$ and $[M_yH^+] \propto [HA]$, we obtain the general expression for the rate of polymerisation of aziridine given previously (p. 518). Thus the kinetics of polymerisation catalysed by a strong acid which is able to cause only one side-reaction of type (a) can be regarded as completely elucidated by the case discussed here of toluene-*p*-sulphonic acid. Polymerisation in the presence of hydrochloric and sulphuric acids is also of this type.

## Weak Acids

The above kinetic regularities do not occur with weak acids. In the case of benzoic acid the overall rate is greater than would be expected for the first order with respect to the initial acid concentration. The discrepancy is especially clearly marked (see Fig. 3) in the later stages of the reaction, at which with a low concentration of benzoic acid reaction has practically ceased, although the greater part of the aziridine still remains unchanged.

It has already been noted that the catalytic action of weak acids is far weaker than that of strong acids even in the initial stages of the reaction. Strong acids are assumed to undergo complete dissociation in aziridine solution. In order to explain the low catalytic activity of weak acids, we must either assume that they undergo equilibrium dissociation (with considerable quantities of the undissociated form present) or suppose, by analogy with ionic vinyl polymerisation[45], that they form not free ions but ion-pairs of the type $\overset{+}{\text{N}}\text{H}_2A^-$, whose catalytic activity (their tendency to ring-opening) is presumably less than that of the free aziridinium ion.

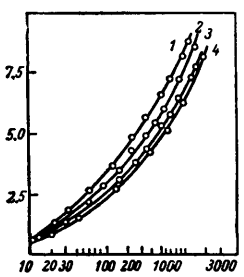



Fig. 2. Dependence of rate of polymerisation of aziridine at 40° on initial concentration (wt.%) of a strong acid (toluene-*p*-sulphonic):
1) 6.1; 2) 3.85; 3) 2.30; 4) 1.30.

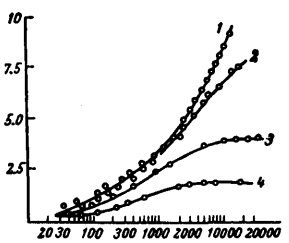
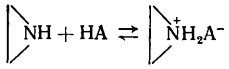



Fig. 3. Dependence of rate of polymerisation of aziridine at 40° on initial concentration (wt.%) of a weak acid (benzoic):
1) 12.25; 2) 5.72; 3) 3.47; 4) 1.53.

If we now accept that the equilibrium in the reaction



is displaced completely to the side of the ion-pair, the kinetic treatment for the case of weak acids will be entirely analogous to that given above for strong acids (with toluene-*p*-sulphonic acid as example) except that the concentration of the free aziridinium ion has been replaced by that of the ion-pairs. The relationship (3) remains valid. However, destruction of the catalyst, which was a second-order reaction with strong acids, becomes a first-order reaction with ion-pairs. Consequently $-d[HA]/dt \propto [HA]$, and Eqn. (4) for strong acids is replaced in the case of weak acids by the equation

$$\frac{[HA]\, d\,[M]/dt}{[M]\, d\,[HA]/dt} = K\,[HA],$$

according to which the fractional decrease in catalyst concentration (and hence the rate of polymerisation), corresponding to the fractional decrease in monomer concentration, will exceed the decrease in the acid concentration. In other words, the initial rates will fall more rapidly for the most dilute solutions of the acids, as actually occurs when benzoic acid is used.

Thus the hypothesis of the existence of ion-pairs provides a good explanation of the difference in kinetic behaviour between strong and weak acids. There may also be intermediate cases.

## 3. THERMAL DECOMPOSITION OF 2-OXOOXAZOLIDINE

Another important method of obtaining polyethyleneimine is provided by thermal decomposition of the cyclic urethane 2-oxooxazolidine. Thermolysis of this compound in a strongly alkaline solvent (trishydroxyethylamine) yields monomeric aziridine[46]; thermolysis which is uncatalysed or is catalysed by weakly basic catalysts results in polyethyleneimine[47,48]. The simplicity of the synthesis of 2-oxooxazolidine and of its pyrolysis, the absence of complicated catalysts, solvents, or special apparatus, and also the avoidance of the use of the highly toxic[49-51] and mutagenic aziridine have led to the appearance of many theoretical and practical papers on this line of research within a short period[46-48,52-55].

The possibility of obtaining polyethyleneimine while avoiding the use of aziridine was first reported in the patent literature[47], without any data on the properties or composition of the pyrolysis products, only the information being given that the maximum nitrogen content reached in the polymer was 23.7%. A more detailed account[48] showed that polyethyleneimine is not the only product of thermal decomposition, for three substances of low molecular weight (one solid and two liquid) were isolated together with the polymer. One of the liquid products was aminoethanol, which was regarded as produced by the hydrolysis of aziridine formed as an intermediate. The other two substances were considered to be substituted ureas. Infrared-spectroscopic investigation of the polymer showed that it also contained carbonyl groups. Japanese workers have recently described in a series of papers[52-54] a careful investigation of the composition of the thermolysis products of various substituted 2-oxooxazolidines (as well as of 2-oxooxazolidine itself), and the kinetics and mechanism of this reaction.

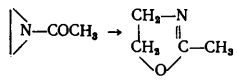
### Thermolysis Products

The pyrolysis of 2-oxooxazolidine at 230° and atmospheric pressure in a stream of dry nitrogen is accompanied by the evolution of only ~61% of the theoretical quantity of carbon dioxide[53], and hence ~39% of the 2-oxooxazolidine is converted into other thermally stable carbonyl compounds. Disappearance of the carbonyl band of 2-oxooxazolidine in the infrared spectrum (at 1760 $cm^{-1}$) of the pyrolysate is accompanied by the appearance of a new carbonyl band (at 1686 $cm^{-1}$).

The pyrolysate was separated into four components (Table 1) by careful fractionation. In agreement with the above observations by Jones and his coworkers[48], the first fraction consists of aminoethanol. The structure of 1-2′-hydroxyethyl-2-oxoimidazolidine (second fraction) and of 1-2′-aziridinylethyl-2-oxoimidazolidine (third fraction) was proved by analysis, infrared examination, and comparison with synthetic preparations. The large quantity of products of low molecular weight (~62%) is probably explained by the solubility of 2-oxooxazolidine at temperatures above 80° in the pyrolysis products, which increases the likelihood of side-reactions.

The infrared spectrum of the fourth, polymeric fraction contains three amide absorption bands, at 1695, 1495, and 1275 $cm^{-1}$, which are analogous to bands in the spectra of the second and third fractions. Thus these results suggest that the polymeric products of the pyrolysis of 2-oxooxazolidine consist of a mixture of polyethyleneimine fractions of low molecule weight‡, some of them containing terminal 2-oxoimidazolin-1-yl rings.

The pyrolytic decarboxylation of 3-acetyl-2-oxooxazolidine gives, together with the corresponding polymer, a considerable quantity of 2-methyl-$\Delta^2$-oxazoline[53], probably formed by a rearrangement of *N*-acetylaziridine



resembling the rearrangement of *N*-benzoylaziridine into 2-phenyl-$\Delta^2$-oxazoline[58].

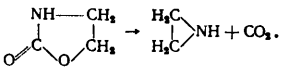
TABLE 1. Composition of pyrolysate of 2-oxooxazolidine.

| Fraction | B.p., °C | M.p., °C | Compound | Content, % |
|---|---|---|---|---|
| 1 | — | — | aminoethanol | 4.76 |
| 2 | 180—185 (3.5 mm) | 51.5 | 1-2′-hydroxyethyl-2-oxoimidazolidine | 52.38 |
| 3 | — | 239 | 1-2′-aziridinoethyl-2-oxoimidazolidine | 4.76 |
| 4 | — | — | polyethyleneimine | 38.1 |

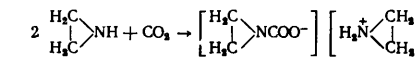
‡ The relatively low molecular weight of polymers obtained by the thermolysis of 2-oxooxazolidine is consistent with investigations of the depolymerisation of polyethyleneimine and its *N*-substituted derivatives. The latter are usually depolymerised at lower temperatures than is polyethyleneimine itself[41]. Thus poly-*N*-phenethylethyleneimine and poly-*N*-n-butylethyleneimine are completely depolymerised to the corresponding piperazines at 150° and 200° respectively. Although polyethyleneimine itself depolymerises to piperazine only at 280°,[56,57] branched-chain polyethyleneimine molecules can be regarded as representing a particular case of *N*-substituted derivatives of polyethyleneimine, so that the temperature of pyrolysis is linked with the structure of the polymer.

## Mechanism

According to Jones[48] the mechanism of the thermal decomposition of 2-oxooxazolidines is best explained by the formation of aziridine in the first stage of the reaction

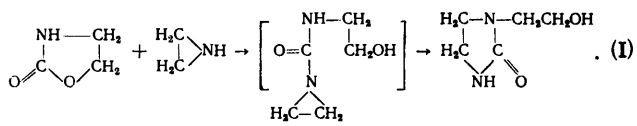


In fact, aziridine, while being extremely stable in strongly alkaline medium, readily polymerises in the presence of acids, forming polyethyleneimine by a stepwise mechanism (p. 517) promoted by aziridinium cations. Initiation of the polymerisation of aziridine by carbon dioxide can be written



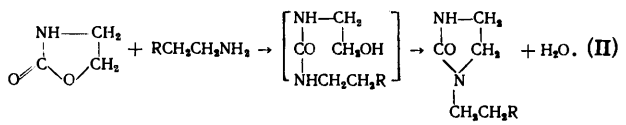
This route and also pyrolytic polymerisation initiated by certain acidic impurities or traces of water probably lead to the formation of polyethyleneimine instead of aziridine in the thermolysis of 2-oxooxazolidine.

The formation of secondary products in pyrolysis can also be explained by the intermediate formation of aziridine. For example, 1-2′-hydroxyethyl-2-oxoimidazolidine results from nucleophilic attack on the 2-oxooxazolidine molecule by aziridine followed by cyclisation of the adduct:



(I)

Similar attack on 2-oxooxazolidine by the terminal group of a polymer with subsequent elimination of water from the adduct leads to the formation of various 1-2′-aminoethyl--substituted derivatives of 2-oxoimidazolidine:



(II)

Actually, the compound in which R =  , i.e. 1-2′-aziridinylethyl-2-oxoimidazolidine, and a polymer having the structure (II) represents two other products of the pyrolysis of 2-oxooxazolidine. The water evolved according to Eqn. (II) is probably used up in opening the aziridine rings (to form aminoethanol) and also end-groups in the polymer.

However, the above mechanism of the formation of 1-substituted 2-oxoimidazolidines of low molecular weight and terminal 2-oxoimidazolidinyl groups on polymer chains necessarily presupposes the absence of substituents in position 3 of 2-oxooxazolidine, and consequently in position 1 of aziridine. Thermal decomposition of 3-substituted cyclic urethanes results[53] in the complete evolution of carbon dioxide, and the infrared spectrum of the pyrolysate contains no frequencies due to carbonyl groups. The pyrolysate of 3-*p*-chlorophenyl-2-oxooxazolidine consists entirely of poly-*N*-*p*-chlorophenylethyleneimine of low molecular weight. Even when decomposition of this oxooxazolidine was stopped after the evolution of half the theoretical quantity of carbon dioxide, the band at 1767 $cm^{-1}$ (due to carbonyl in the original oxooxazolidine) could be detected in the pyrolysate at half the intensity observed with the original compound; no new carbonyl absorption bands were observed.

Thus, in contrast to the usual decarboxylative polymerisation, in which decarboxylation and polymerisation occur simultaneously, in the thermolysis of oxooxazolidines these two processes are completely independent reactions.

## Kinetics

Study of the rate of the uncatalysed decarboxylation of 2-oxooxazolidine has shown[54] that in this case the decomposition is autocatalytic. It is seen from the graph in Fig. 4 that the rate of conversion $dx/dt$ first increases as reaction proceeds, reaches a maximum, and then decreases. Such a dependence of rate on $x$ represents the characteristic rate curve for autocatalytic reactions. Here it is the principal reaction products — aziridine and its polymer — which develop the autocatalytic properties.

A comparative study of the rates of decarboxylation of various 3-substituted 2-oxooxazolidines has established[54] that the ring is cleaved at the C–N bond, not at C–O (Table 2). In fact the reactivity of a 3-aryl-2-oxooxazolidine is greatly dependent on the electronic character of the substituent in the benzene ring: electron-acceptor groups accelerate decarboxylation, whereas electron-donor groups slow it down.

Thus the cleavage of the C–N bond in oxooxazolidine is the rate-determining stage in the process of decarboxylation.

A kinetic study of the catalytic decarboxylation of 2-oxooxazolidines in the presence of aromatic amines has shown that the resulting pyrolysate exerts a stronger catalytic effect than does the aromatic amine added as catalyst, the rate of conversion being represented by a curve having a maximum, which is characteristic of autocatalytic reactions.

In the presence of high-boiling aliphatic amines, however, the reaction velocity has its highest value at the

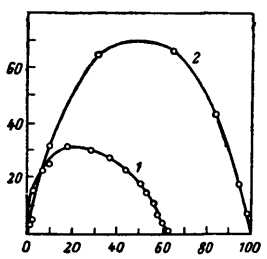



Fig. 4. Variation in rate of uncatalysed decarboxylation of 2-oxooxazolidines during reaction:
1) 2-oxooxazolidine (200°); 2) 3-*o*-nitrophenyl-2-oxooxazolidine (230°).

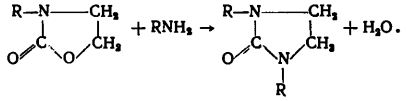
TABLE 2. Relative rates of decarboxylation of 3-substituted 2-oxooxazolidines.

| Oxooxazolidine (R–Ox) | Relative rate |
|---|---|
| $C_6H_5Ox$ | 1 |
| $p$-$CH_3$—$C_6H_4$—Ox | 0.7 |
| $p$-Cl—$C_6H_4$—Ox | 1.9 |
| $p$-$O_2N$—$C_6H_4$—Ox | 130.0 |

beginning. The descending curve in Fig. 5 (in contrast to the expected linear dependence of $dx/dt$ on $X$ for this pseudo-first-order reaction) is explained by consumption of the added amine in the side-reactions of ammonolysis of the intermediate aziridine

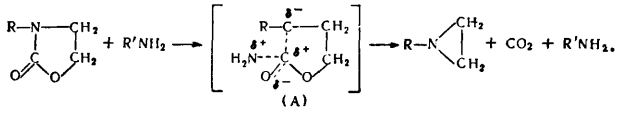


and condensation with the initial 2-oxooxazolidine

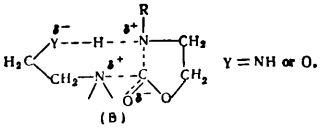


Polyamines and amino-alcohols are still more active decarboxylation catalysts[54]. Since the catalytic effect of the former exceeds the value calculated from the number of amino-groups, while it is generally absent from alcohols, a "push-pull" type of mechanism is suggested. As applied to the decarboxylation of 2-oxooxazolidines, this may consist in simultaneous nucleophilic attack by the amino-group on the positively charged carbonyl carbon atom in the oxooxazolidine and electrophilic attack by hydrogen in another amino-group (or more probably in a hydroxy--group) at the nitrogen in the urethane group of the oxooxazolidine.

Thus whereas the uncatalysed decarboxylation of oxooxazolidines and the reaction in the presence of aromatic amines are autocatalytic, the reactions catalysed by aliphatic amines, polyamines, and amino-alcohols progess in two different ways depending on the structure of the catalyst. If a simple amine is used as catalyst, reaction goes mainly through the transition state (A):



In the reaction catalysed by an amine containing a $\beta$-$NH_2$ or $\beta$-OH group, on the other hand, the active transition complex probably approximates to structure (B)



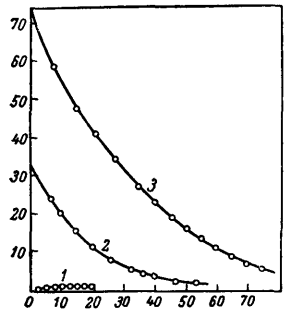


Fig. 5. Type of variation in rate of decarboxylation of 2-oxooxazolidines during reaction at 230° (1 M $p$-nitrophenyl-2-oxooxazolidine catalysed by different concentrations of n-dodecylamine in dibenzyl ether):
1) no catalyst; 2) 0.5 M; 3) 1 M.

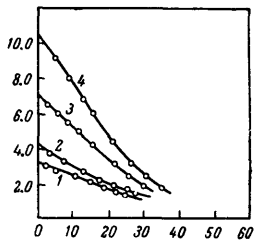
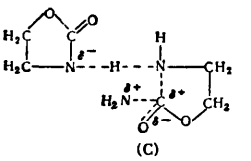


Fig. 6. Nature of variation in rate of decarboxylation at 230° of different concentrations of 2-oxooxazolidine catalysed by different concentrations of n-dodecylamine in dibenzyl ether:
1) 0.5 M + 0.75 M; 2) 0.5 M + 0.5 M;
3) 1 M + 0.75 M; 4) 1 M + 0.5 M.

In the presence of simple aliphatic amines, the decarboxylation of 2-oxooxazolidine follows a peculiar course[54] (see Fig. 6). All curves for rates of conversion with different initial concentrations of 2-oxooxazolidine are seen to converge to a single point (at about 60% conversion). The corresponding kinetic calculations show that in this case the initial rate of decarboxylation is of the second order with respect to the oxooxazolidine and of the first order with respect to the amine. These features can be explained by a peculiar, coordinated mechanism, in which the amine attacks the oxooxazolidine as a nucleophile, while another oxooxazolidine molecule attacks it as an electrophile. The transition state can be represented by the structure (C)



## 4. PROPERTIES OF POLYETHYLENEIMINE

### Molecular Weight

Oligomeric polyethyleneimine, obtained by the acid polymerisation of aziridine, is a viscous, almost colourless resin, which can be freed from fractions of low molecular weight by electrodialysis through cellulose acetate membranes[32]. The molecular weight of polyethyleneimine oligomers has been determined by cryoscopy[18] in diphenylamine, determination of the maximum quantity of dibromoethane necessary for the complete cross-linking of all the aziridine (and amino-) groups in the polymer[59], and viscosity measurements on aqueous solutions[18]. The corresponding Staudinger viscosity constant for a 1% solution of polyethyleneimine in water $K_{\bar{m}} = 2.8 \times 10^{-4}$ was obtained by extrapolation of the relative viscosity curve for purified polyethylenepolyamines. Polyethyleneimine was found to be an oligomer of comparatively low molecular weight.

The degree of polymerisation of polyethyleneimine can be calculated[24] theoretically from the molecular proportions of aziridine and of the catalyst, but the practical values

are always lower owing to the presence in the polymer of fractions of low molecular weight. Polymerisation of aziridine in the presence of the usual acidic catalysts may yield polymers of molecular weight not exceeding[24,32,60] 1000–2200, § the mean-molecular-weight of the polyethyleneimine depending on the conditions of polymerisation[24]: it is increased by increasing the initial concentration of aziridine at constant temperature, and lowered by increasing the catalyst concentration. If polyethyleneimine of as high molecular weight as possible is desired, the initial solutions of aziridine must be as concentrated as possible and a minimum amount of catalyst must be used. In practice this minimum amount is 1 mole % based on the aziridine (because of the consumption of acid in side-reactions[16]).

Theoretically this corresponds[24] to a polymer of molecular weight 4300 (if pure aziridine is used in the absence of solvent). In practice, however, this is impracticable, since increasing the aziridine concentration above 50% greatly increases the rate of polymerisation, which then is often explosive in character[32,63,64]. The explosiveness is due to inadequate removal of the heat of polymerisation at high reaction velocities.

Raising the temperature also increases the rate of polymerisation[24]. The effect of temperature depends substantially on the initial concentration of aziridine: it is considerably greater at high concentrations than with dilute initial solutions.

The comparatively low molecular weight of polyethyleneimine obtained by the acid polymerisation of aziridine in aqueous and alcoholic solutions is probably established when polymerisation ceases owing to the gradual cleavage of the aziridinyl groups at the ends of the growing polymer chains (as a result of solvolysis or side-reaction with the catalyst, see above). Polymerisation of aziridine with catalysts which do not cause ring-opening as a side-reaction (in non-aqueous media), and in the absence of contamination by compounds of low molecular weight, can probably lead to the synthesis of polyethyleneimine of higher molecular weight. Special attentian is being paid to the polymerisation of aziridine in the presence of catalysts of high molecular weight, e.g. surface-active substances or cation-exchange resins.

### Degree of Branching

Polyethyleneimine can contain up to 38% of nitrogen in the form of primary amino-groups[65-67]: i.e. it is a strongly branched polymer. The formation of such polymers is observed mostly when polymerisation is continued until the monomer has been almost completely converted. Infrared examination[67] of polyethyleneimine shows it to contain primary, secondary, and tertiary nitrogen atoms (bands at 2.9, 6.3, 9.0, and 9.6 μm). In the polymerisation of aziridine in the presence of 1 mole % of HCl the degree of branching increased with rise in temperature and increase in the acid concentration[66]. It is interesting that at low temperatures (20°) the degree of branching diminishes with fall in the acid concentration (from 38% to 12%);

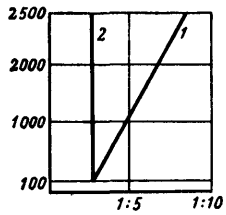



Fig. 7. Dependence of degree of branching of polyethyleneimine on catalyst (HCl) concentration for polymerisation of $C$ = 50% of aziridine at:
1) 20°; 2) 80°. The molar ratio of aziridine to catalyst is plotted as ordinate.

at high temperatures (80°) it is independent of concentration and has the value 38% (see Fig. 7). The complete polymerisation of polyethyleneimine at high temperatures results in the degree of branching again increasing to 38%.

Unbranched polymers can be obtained by the polymerisation of an $N$-substituted aziridine. Thus the preparation has been described[13] of a straight-chain polyethyleneimine (up to a molecular weight of 2000) by the polymerisation of $N$-benzenesulphonylaziridine (by heating or in the presence of traces of boron trifluoride).

## 5. REACTIONS OF POLYETHYLENEIMINE

### Ionisation Equilibrium

Three papers have been published[59,67,68] on the use of potentiometric titration to study the ionisation of polyethyleneimine. Although different specimens of the polymer were employed, the results show quite good agreement. The titration curve for polyethyleneimine in aqueous potassium chloride (Fig. 8) resembles that for monoacid bases, except that the pH values fall more sharply than with amines of low molecular weight. This indicates that the NH groups in the polymer have a far smaller ability to combine with acid than have the simpler amines. The basic strength of the NH groups in polyethyleneimine is increased by the presence of a neutral salt (KCl). Thus a 0.01 M solution of the polymer in 1 $N$ KCl has pH 9.89, while the equivalence point is at pH 4.4. The equivalence point is reached at 66% neutralisation: in other words, only two-thirds of the basic groups in polyethyleneimine can be titrated. A similar phenomenon is observed with proteins[68] and with poly-$N$-vinylimidazole[69].

Similar results have been obtained[67] by the back titration of polyethyleneimine hydrochloride with alkali. Exact neutralisation is achieved after 34% of the hydrochloride HCl has been titrated. The curve representing titration of the hydrochloride with alkali is inverted with respect to the titration curve for the basic polymer.

The acid dissociation constant of polyethyleneimine $K_a \simeq 10^{-9}$ has been calculated[67] by means of the modified Henderson–Hasselbalch equation for polyelectrolytes. This equation is valid only up to a degree of dissociation of $\alpha = 0.5$. Over this range polyethyleneimine conforms to Katchalsky's theory of polyelectrolytes[70]; above $\alpha = 0.5$ it behaves as a monomeric acid.

§ Although the molecular weight of industrial specimens of polyethyleneimine produced by the BASF firm probably lies within or near the above limits, with American specimens[61] $M$ = 30 000–40 000 and even[62] 100 000.

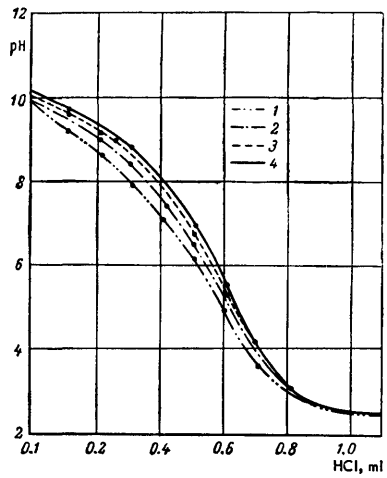



Fig. 8. Curves representing potentiometric titration of a 0.01 M solution of polyethyleneimine with 0.5 *N* HCl in the presence of various concentrations of neutral salt (*N* KCl): 1) 0.1; 2) 0.5; 3) 1.0; 4) 2.0.

British workers succeeded[59] in titrating amino- and aziridinyl groups in the polymer separately, obtaining $pK_a$ values of 9.0 and 10 respectively. Calculation of the constants was based on Katchalsky's equation for chain polyelectrolytes[71].

Very similar results were obtained in a study of the ionisation of polyethyleneimine which had been cross-linked with dibromoethane[72]. Although the titration curves were similar in form to those for the oligomer, a difference was caused by the appearance of new nitrogen atoms which could not be titrated even at pH 1–2, i.e. extremely feebly basic (tertiary) atoms. Their number corresponds exactly with the number of dibromoethane molecules which have reacted. The results of the titration of oligomeric polyethyleneimine become clear when it is remembered that specimens of the polymer usually contain up to 38% of tertiary nitrogen atoms owing to branching.

## Salts of Polyethyleneimine, Complex Formation

Viscosity measurements on partly neutralised aqueous solutions of polyethyleneimine[67] show that maximum viscosity occurs at 80% neutralisation. Further addition of electrolyte merely screens the charges on the long-chain polymer molecule. This weakens the electrostatic repulsion between ionised groups, as a result of which the extended filaments of ionised polyethyleneimine pass more and more into random tangles, as with uncharged fibrous molecules.

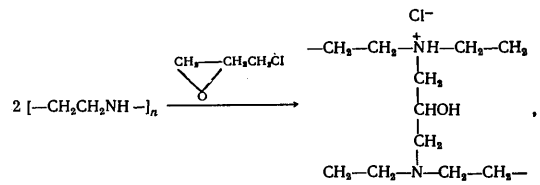
It has also been found that polyethyleneimine salts are strongly hydrolysed in solution (up to 30%). Titration of cross-linked polyethyleneimine with different acids gives the sequence – acetate < chloride < toluene-*p*-sulphonate – for the affinity of the resin for anions. The degree of swelling of the corresponding salts of the cross-linked oligomer in water falls in the same sequence, which indicates increasing association of the ions owing to van der Waals forces of adhesion between the anions and the polymer chains.

Polyethyleneimine has been found[67,72] to absorb copper (and also cobalt and nickel) to form ammines. Complex formation is accompanied by a decrease in the basic strength of the polymer and in the viscosity of aqueous solutions, owing to the weakened hydrophilic character produced by screening of the ionic groups by the complexing copper ions. The ammines of polyethyleneimine with copper and nickel can be completely dried, and the resulting powders, unlike polyethyleneimine itself, are not hygroscopic.

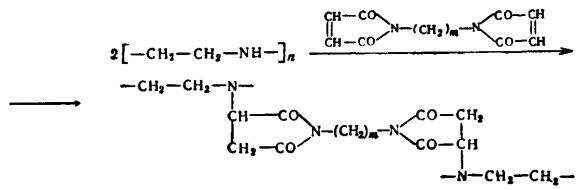
Study of the salts of polyethyleneimine is of interest for the fundamental theory of polyelectrolytes in view of the exceptionally high charge density of the ionic groups.

## Cross-Linking of Polyethyleneimine Chains (Hardening Reactions)

The preparation of purely aliphatic anion-exchange resins of extraordinarily high capacity, based on polyethyleneimine networks, has attracted special attention to the study of the cross-linking of this polymer by various substances. Among cross-linking agents which have been used are 2,3-epoxypropyl chloride[73,75]



dichloroethane and dibromoethane[74], formaldehyde[72], and maleimide[75]



(cross-linking by addition to an activated double bond).

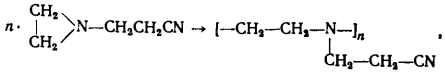
The reaction with dibromoethane has been studied the most thoroughly. The minimum quantity of the latter required to form a gel with polyethyleneimine is[72] 0.028 mole g-equiv.$^{-1}$. To obtain a mechanically stable resin, however, this quantity must be increased fivefold (to 0.16 mole g-equiv.$^{-1}$). Only a small proportion of the dibromoethane was actually found to form cross-links between the polyethyleneimine chains, most of it reacting with nitrogen atoms in the same chain to form small closed loops. Drying the resin at 100° produces further cross-linking (the degree of swelling is diminished). Cross-linked polymers obtained by this method are stable to acids and alkalis for 2–3 months.

## *N*-Substituted Polyethyleneimines

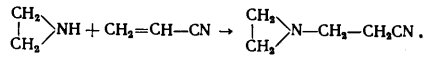
Acetylation of polyethyleneimine with acetic anhydride yields a water-soluble *N*-acetyl derivative, which has been proposed[76] as a blood-plasma substitute. Acylation (acetylation and benzoylation) of polyethyleneimine has been suggested as a method for determining its degree of branching, but the results obtained are not very reliable.

A probably more reliable method is reaction of the terminal amino-groups of polyethyleneimine with nitrous acid by Van Slyke's procedure[65], and also conductimetric titration.

Poly-*N*-cyanoethylethyleneimine has been obtained[77] by the polymerisation of β-aziridinylpropionitrile:



which in turn is readily obtained by the cyanoethylation of aziridine:

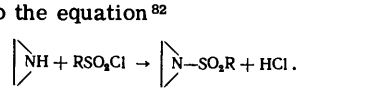


Benzoylation. The Schotten–Baumann benzoylation of polyethyleneimine gives[18] a viscous white product soluble in chloroform, which after reprecipitation in ligroin is obtained as a white powder having a softening point of 110°.

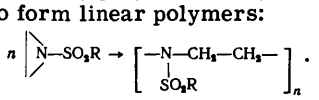
Poly-*N*-nitrosoethyleneimine. This compound has been obtained[18,78] as an insoluble precipitate by the addition of hydrochloric acid to polyethyleneimine in aqueous sodium nitrite solution. The nitrogen content of the resulting polymer differs markedly from the calculated value.

Poly-*N*-sulphonylethyleneimines. These polymers have been obtained both by the reaction of polyethyleneimine with sulphonyl chlorides[79] and by the direct polymerisation[80,81] of *N*-sulphonylaziridines (the methanesulphonyl, benzenesulphonyl, toluene-*p*-sulphonyl, naphthalene-1-sulphonyl, etc. derivatives).

Liquid or low-melting solid *N*-sulphonylaziridines are obtained by the reaction of sulphonyl chlorides with aziridine according to the equation[82]



Polymerisation of the initial aziridine by the hydrogen chloride formed is prevented by carrying out the reaction in the presence of alkali. The monomeric *N*-sulphonylaziridines thus obtained are readily polymerised by heating or by the action of alkali to form linear polymers:



The most effective polymerisation catalysts are organic bases, including aziridine. Polymerisation is inhibited by acids (e.g. arenesulphonic acids and acetic acid).

Poly-*N*-sulphonylethyleneimines are chemically stable solids of high melting point, insoluble in the usual organic solvents and extremely resistant to hydrolysis (by alkalis and acids). Their physical properties can be modified by carrying out polymerisation in the presence of alkaline catalysts. The degree of polymerisation can be controlled to a certain extent by varying the temperature and duration of polymerisation.

*N*-Sulphonylaziridines are readily polymerised on substrates — textiles, paper, etc.

Methylation. The methylation of polyethyleneimine has been accomplished[83] by the action of dimethyl sulphate on an aqueous solution of the polymer, with subsequent neutralisation with sodium carbonate. The product of exhaustive methylation obtained is a readily water-soluble polymer, which is used for pretreating cellulosic fibres before the application of direct dyes.

A large amount of specialised work has been done on the industrial exploitation of the reaction of polyethyleneimine with cellulose[84,85], and this has been reviewed by Machida[86].

## 6. COPOLYMERS OF AZIRIDINE

### Copolymers with Carbon Monoxide and Carbon Disulphide

Rubberlike solid products are obtained by the copolymerisation of aziridine with carbon monoxide[87] and with carbon disulphide[88,89]. Reaction with the former is carried out at high temperatures (150°) and high pressures of carbon monoxide (~2000 atm). Results of elementary analysis on the product of m.p. 211° correspond to the formula $[(C_2H_5N)_2CO]_n$.

### Copolymers with Cyclic Oxides

Depending on the relative proportions of the components, copolymers of aziridine with oxiran and methyloxiran can be obtained as viscous oils of various consistencies[90]. The products have not been investigated in greater detail. They have been used for the processing of textiles. A patent[91] has proposed the use as ion-exchange membranes of copolymers of aziridine with 2,3-epoxypropyl chloride obtained by heating the components (in the proportions 12 : 1) without a catalyst.

A detailed study of the copolymerisation of aziridine with oxides in the presence of various Lewis acids has been made by Overberger and his coworkers[92]. They have shown that even the most active of the catalysts examined (the ether complex of boron trifluoride) gives a product which is not a true copolymer, but consists of a polyamine main chain which has been β-hydroxylalkylated by the epoxides. Actually, the reaction with 1-ethylaziridine, which cannot form side-chains with the oxides, gave a copolymer containing 86 mole % of aziridine residues, while epoxide residues were present only as end-groups (resulting from chain termination). Complex formation between the catalyst and basic polymeric and monomeric aziridine derivatives evidently makes it incapable of catalysing the growth of epoxide chains.

### Copolymers with Diisocyanates and Isothiocyanates

Many synthetic resins, from viscous oils to solids, have been obtained[93-99] by the condensation (effected by heating or by the action of acids, alkalis, etc.) of aziridine with aliphatic or aromatic diisocyanates and isothiocyanates, e.g. with 4-methyl-1,3-phenylene diisocyanate.

### Copolymers with αβ-Unsaturated Acids, Aldehydes, and Ketones and with Acrylonitrile

The products described in the patent literature[77,98,100,101] are probably polymers of *N*-substituted aziridines, obtained by the addition of aziridine to the vinyl components.

Copolymers with *N*-Sulphonylaziridines

The copolymerisation of mixtures of a sulphonylaziridine and aziridine occurs spontaneously[81], the resulting polymer containing both components. The properties of the copolymers obtained differ from those of polyethyleneimine and of polysulphonylethyleneimines. They depend on the relative proportions of the components. With small amounts of aziridine, resins are obtained which are insoluble in water and in acids. Copolymers containing not less than 5 moles of aziridine per mole of *N*-sulphonylaziridine dissolve in acids, alkalis, and organic solvents. Depending on the contents of the components, the state of aggregation of these copolymers varies from viscous oils to solid resins.

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The growing interest in the chemistry of polyethyleneimine is due not only to the developing fields for its industrial application. The intrinsic interest of this branch of the chemistry of macromolecular compounds is connected both with the peculiar character of the reactivity of functional groups in a polymer chain and with the problem of the special features of multifunctional polymers.

The polyethyleneimine system — the simplest heterochain polymer and polybase — is most convenient for investigations on these lines. This system is formed by replacing one-third of the carbon atoms in polyethylene with nitrogen atoms. While preserving several of the properties of polyethylene (including thermal stability), it is nevertheless highly reactive.


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# STEREOCHEMISTRY OF THE HYDROXY-MERCURATION OF ALKENES

N. S. Zefirov

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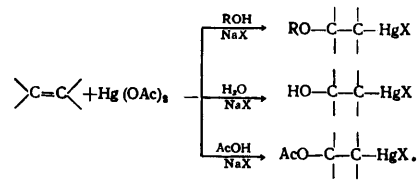
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## I. INTRODUCTION

In 1892 Kucherov discovered that mercury(II) salts are capable of addition to a C–C double bond[1]. Eight years later — in 1900 — Hofman and Sand[2] developed this reaction, and in subsequent investigations it was shown that the reaction of alkenes with mercury(II) salts leads to the formation of hydroxyalkylmercury compounds and their derivatives:




Since then, hydroxymercuration has remained a subject widely studied from various viewpoints. Hydroxyalkylmercury compounds, being readily available, find application as pesticides, antiseptics, diuretics, preservatives, seed dressings, etc.

The alkoxyalkylmercury halide derivatives obtained in this way were used to solve several important theoretical problems. Thus the example of electrophilic substitution

by mercuric chloride on *cis*-2-methoxycyclohexylneophylmercury showed that the configuration is retained during bimolecular electrophilic substitution at a saturated carbon atom[3].

Hydroxymercuration can be applied to alkenes of various structures; it is simple to perform and usually takes place with high yields. Chatt[4] has reviewed the extensive literature on this reaction.

However, despite intensive study, the stereochemistry of hydroxymercuration has not yet been strictly established. On the one hand, the difficulty of determining the configuration of mercurated alcohols was due to the impossibility of using chemical methods, since in chemical reactions the C–Hg bond is affected and the reactions proceed with substitution at the asymmetric carbon atom, whereas the stereochemistry of electrophilic substitution at a saturated carbon atom has become known only in the last few years. On the other hand, the use of physical methods of investigation, for example, X-ray diffraction or the measurement of dipole moments, also did not allow the configuration of mercurated alcohols to be determined unambiguously and conclusively and in some instances led to incorrect conclusions. Thus in 1951 Brook and Wright[5] made an X-ray diffraction analysis of 2-methoxycyclohexylmercury chloride, obtained by the methoxymercuration of cyclohexene, and found that it has the *trans*-configuration. Because of this, in Chatt's review[4] the information on the hydroxymercuration was interpreted from the standpoint of *trans*--addition. However, in later studies[6-8] (see also Kreevoy and Kowitt[9]) Wright assumed error in the X-ray data and even expressed the opinion that this method is generally not very dependable when applied to the products of hydroxymercuration. [Now, however, the X-ray diffraction method is considered reliable (see IV, 2) (Ed. of Translation)].

The present review considers the stereochemistry of the hydroxymercuration of alkenes, which only recently has been established reliably, using various methods. It will be necessary to consider also some earlier work, already reviewed by Chatt[4]. Note that there is also a review by Wright[6] dealing with the hydroxymercuration of alkenes, but all its stereochemical conclusions are wrong.

## II. MECHANISM OF THE REACTIONS OF HYDROXYMERCURATION AND DEHYDROXYMERCURATION

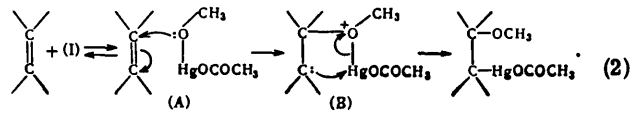
Because of the above-mentioned difficulties in establishing the configuration of mercurated alcohols attempts were made to determine it starting from the stereochemical requirements of the reaction mechanism.

The addition of mercury salts is electrophilic and the presence of electron-acceptor substituents hinders the reaction. Hydroxymercuration proceeds stereospecifically: from the *cis*- and *trans*-isomers of alkenes different diastereomers are obtained free from the second isomer as impurity; the reaction is not accompanied by *cis–trans* isomerisation of the alkene. The hydroxymercuration product of the *cis*-alkene is usually called the $\alpha$-diastereomer; the $\beta$-diastereomer is formed from the *trans*-alkene, and also on isomerisation of the $\alpha$-isomer. The dipole moment of the $\alpha$-diastereomer is usually less than the $\beta$-diastereomer. The rate of hydroxymercuration of the *cis*-alkene is greater than that of the *trans*--alkene, which allows this reaction to be used to determine the configuration of the alkenes. Kinetic investigations showed that the reaction is second-order[6-8].

The mercurated alcohols are readily dehydroxymercurated, and because of this Nesmeyanov[10] called them "quasicomplex compounds". Dehydroxymercuration also proceeds stereospecifically and leads to the alkene of the original configuration, and many examples[11] have shown that the diastereomer with the lesser dipole moment is dehydroxymercurated more readily.

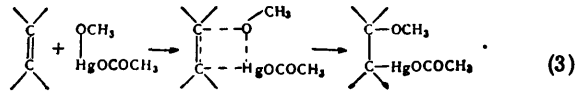
Two alternative mechanisms have been proposed for the hydroxymercuration. Wright[6,12,13] proposed a non-ionic mechanism in which there is first alcoholysis (hydrolysis) of the mercury(II) acetate with formation of a hydroxoacetatomercury(II) or an acetatoalkoxymercury(II) complex, which then reacts with the alkene in the slow stage of the reaction:

$$CH_3OH + Hg(CH_3COO)_2 \rightleftharpoons \underset{(I)}{CH_3OHgOCOCH_3} + CH_3COOH, \qquad (1)$$



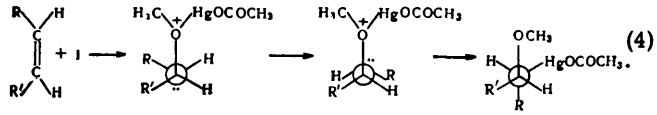
(2)

It is assumed that acetatomethoxymercury(II), (I), is in rapid equilibrium with mercury(II) acetate in methanol solution. Note that in the case when stages A and B are distinct this mechanism is inadmissible, since it presumes nucleophilic attack on the double bond by the methoxy oxygen. This difficulty is easily overcome by assuming that the slow stage of the reaction proceeds through a four-centred transition state:



(3)

In accordance with this reaction mechanism, hydroxymercuration should proceed as a *cis*-addition. Therefore in all of Wright's studies[6,7] the $\alpha$-diastereomer is given the *cis*-configuration. The most substantial argument in support of the molecular mechanism is thought by Wright to be the fact that the rate of hydroxymercuration is greater in methanol than in water[7,14]. To explain possible instances of *trans*-addition, Wright introduced the "coordinative dipole" mechanism[14], according to which during the stage of the A → B change in scheme (2) there is rotation around the C–C bond:



(4)

This mechanism is undoubtedly incorrect, since the hydroxymercuration reaction is considered in essence again as a nucleophilic addition.

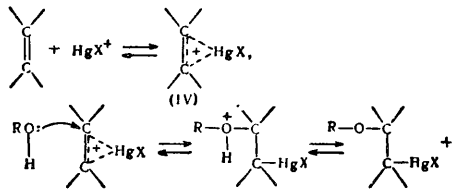
Winstein and coworkers[15] proposed an ionic mechanism on the basis of a study of the distribution of cyclohexene between carbon tetrachloride and water or an aqueous solution of mercury(II) nitrate; it was found that cyclohexene forms two types of complexes with the mercury ions, by schemes (5) and (6):

$$C_6H_{10} + Hg^{2+} \overset{K_1}{\rightleftarrows} \underset{(II)}{C_6H_{10}Hg^{2+}}, \qquad (5)$$

$$C_6H_{10} + Hg^{2+} + H_2O \overset{K_2}{\rightleftarrows} \underset{(III)}{C_6H_{10}\overset{+}{H}gOH} + H^+, \qquad (6)$$

where $K_1 = 2.2 \times 10^4$ and $K_2 = 5.0 \times 10^4$.

The authors formulated the structure of these complexes by analogy with the "bromonium" cation[16] and expressed the opinion that similar complexes, especially singly-charged complexes of type (III), are intermediates in hydroxymercuration, which proceeds in this way by schemes (7)–(8):



(7)

(8)

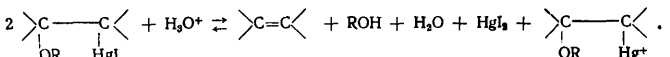
In accordance with this mechanism — by analogy with the discovery of other bridged ions which may be formulated as $\pi$ complexes — hydroxymercuration should take place as a *trans*-addition.

Although subsequently Brook and Wright[17] found that under these conditions cyclohexene is converted into formylcyclopentane, this, however, does not disprove the results of Winstein and coworkers[15], since the rate of such a conversion is far less than the rate of reaching equilibrium in the distribution of cyclohexene between two phases (the measurements were made after 0.5, 1, and 1.5 h and were extrapolated to zero time).

One of the arguments put forward by Wright against an ionic mechanism[14] is the absence from the outer electron cloud of the mercury ion of free electron pairs by which a cyclic "onium" ion could be formed, analogous to that originally proposed, for example, for the bromine cation[16]. However, the cyclic ion proposed by Winstein and coworkers[15] must be considered essentially as a $\pi$ complex[21] The electronic structure of the complex of the mercury ion with an alkene was considered by Dewar[18] (see also Kreevoy and Kowitt[9]), who proposed that in the alkenemercury(II) ion (IV) the $6sp$ hybrid orbital of the mercury atom overlaps with the two $2p$ orbitals of the carbon atoms, forming a pseudoaromatic structure. Here additional stabilisation is also possible with participation of the $5d$ electrons of the mercury and the antibonding $\pi$ orbital of the alkene[9].

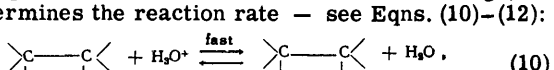
However, not one of the mechanisms of hydroxymercuration presented above explains certain features of this reaction; for example, catalysis by peroxides and by oxygen[11].

It seemed possible to draw reliable stereochemical conclusions only by studying the mechanism of dehydroxymercuration. Kreevoy showed[9,19-22] in 1959 that dehydroxymercuration by perchloric acid proceeds by the following stoichiometric equation:

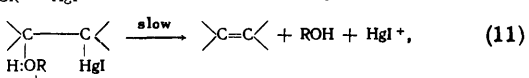


(9)

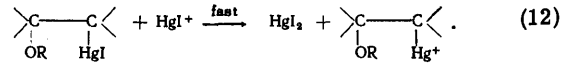
Detailed study of the mechanism of this reaction showed[9,19-22] that in the first stage there is a rapid and reversible addition of a proton to the alkoxy oxygen atom, with subsequent formation of alkene in the second stage, which determines the reaction rate — see Eqns. (10)–(12):



(10)



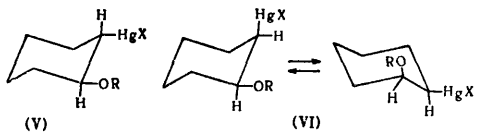
(11)



(12)

The reaction takes place very readily; for example, the rate of dehydroxymercuration of 2-hydroxypropylmercury(II) iodide is $10^{11}$ times as great as the acid-catalysed dehydration of propan-2-ol[9].

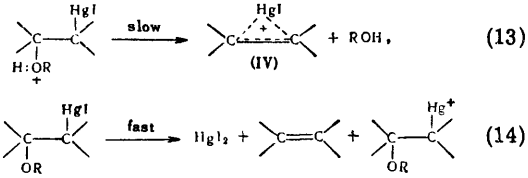
From the results of kinetic studies of the dehydroxymercuration of $\alpha$- and $\beta$-2-methoxycyclohexylmercury(II) chloride, (Va) and (VIa) respectively, Kreevoy[9,21] drew convincing conclusions about the structure of the transition state at the stage which determines the rate of the reaction, Eqn. (11).



(a) R=CH$_3$; (b) R=H.

The $\alpha$-diastereomer (Va) is dehydroxymercurated approximately $10^6$ times faster than the $\beta$-diastereomer (VIa); for the $\alpha$-diastereomer $\Delta H^{+} = 17.75 \pm 0.19$ kcal × × mole$^{-1}$ and $\Delta S^{+} = 4.6 \pm 0.6$ cal mole$^{-1}$ deg$^{-1}$, whereas for the $\beta$-diastereomer $\Delta H^{+} = 26.2 \pm 0.7$ kcal mole$^{-1}$ and $\Delta S^{+} = 4.5 \pm 2.0$ cal mole$^{-1}$ deg$^{-1}$.

Starting from these results for the rate-determining stage a structure was adopted for the mercurinium ion (IV) analogous to that proposed earlier[15]. Reactions (11) and (12) can be more strictly represented by Eqns. (13) and (14):

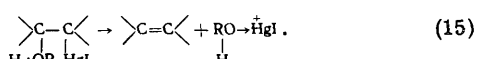


(13)

(14)

If the mercury and oxygen are in the *trans*-position, there will be a synchronous withdrawal of the ROH group and formation of the mercurinium ion, which proceeds without appreciable steric hindrance[9,21]. The required coplanarity of the groups being detached can be attained with little distortion of the bond angles only for the *trans*-isomer (in the diaxial conformation). Hence the dehydroxymercuration of the *trans*-isomer requires a lower activation enthalpy than the *cis*-isomer, and the $\alpha$-diastereomer (Va) can be ascribed the *trans*-configuration. It is noteworthy that the activation entropies for the two diastereomers are similar. This shows that the solvation in the two transitional states is about the same.

The mechanism proposed by Wright can also be considered in its application to dehydroxymercuration where the rate-determining stage for the reaction is represented by the equation:



(15)

When, in accordance with Wright's results, the *cis*-configuration is taken for the $\alpha$-diastereomer, then its higher rate of dehydroxymercuration should be due to the solvation of the mercury ion being detached by the methanol being better than that by water, which is generally improbable. Furthermore, the difference in the rates of dehydroxy-

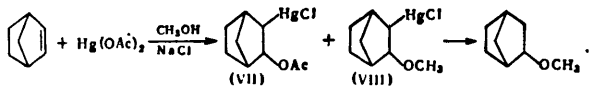
mercuration of two isomers should be due normally to differences in the entropies of activation rather than to the activation enthalpies[9].

Hence the information about dehydroxymercuration allows the *trans*-configuration to be fairly reliably ascribed to the α-diastereomer obtained by the hydroxymercuration of cyclohexene.

## III. HYDROXYMERCURATION OF BICYCLOALKENES (IN THE ABSENCE OF PRELIMINARY COORDINATION OF THE MERCURY ION WITH THE SUBSTITUENTS)

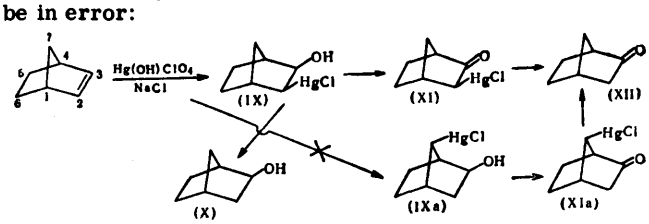
Of great interest in establishing the stereochemistry of hydroxymercuration is the study of this reaction in the case of bicyclo-bridged systems of the norbornene type. The geometry of these alkenes predetermines *exo*-attack of the reagent being added on, as was confirmed by an extremely large number of varied reactions[23-25]. On this basis the HgX group can be ascribed *exo*-configuration and then the problem of determining the stereochemistry of hydroxymercuration leads to the determination of the configuration of the hydroxy- or alkoxy-groups respectively.

In 1959 there appeared work by Wright and coworkers[7] and a brief communication by Traylor and Baker[26] devoted to the hydroxymercuration of norbornene. However, the stereochemistry of hydroxymercuration was interpreted differently in these papers. Wright and coworkers[7] found that under the action of mercury(II) acetate norbornene forms 3-acetoxynorborn-2-ylmercury(II) chloride (VII) or 3-methoxynorborn-2-ylmercury(II) chloride (VIII):



Unexpectedly, this reaction is essentially different in its stereochemical result from the hydroxymercuration of ordinary alkenes and undoubtedly takes place heterolytically, since it is catalysed by acids. The α-diastereomer formed is relatively stable to the action of acids whereas the β-diastereomer very easily undergoes dehydroxymercuration in acid; the dipole moment of the α-diastereomer is greater than that of the β-diastereomer. In the reduction of the α-diastereomer (VIII) methyl *endo*-norbornyl ether was obtained, and from this it was concluded that the α-diastereomer is the *trans*-isomer, additional confirmation of which was given by consideration of dipole moments. Since the stereochemistry of this reaction is the antithesis of what is observed for alkenes of the cyclohexene type, Wright considers that the hydroxymercuration of the latter should proceed as a *cis*-addition, that is, in accordance with the non-ionic mechanism.

Traylor and Baker[26] also concluded that the stereochemistry of the hydroxymercuration of norbornene is different from that observed for ordinary alkenes, but on reducing the α-diastereomer (IX) they obtained *exo*-norborneol (X) and therefore the alleged preparation of methyl *endo*-norbornyl ether in the above work[7] is considered to be in error:

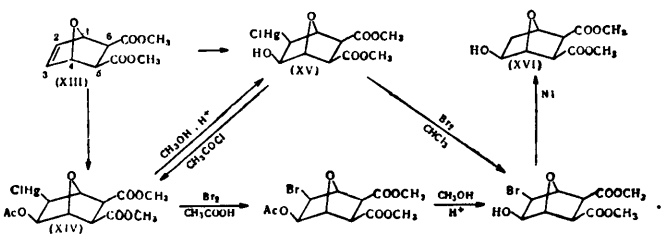


Hence the hydroxymercuration of norbornene proceeds as a *cis-exo*-addition, while the hydroxymercuration of ordinary alkenes takes place as a *trans*-addition through the intermediate mercurinium ion.

As is well known, ionic addition to norbornene can be accompanied by a Wagner–Meerwein rearrangement. This possibility was not considered by Wright and coworkers[7], whereas Traylor and Baker specially confirmed the absence of the rearrangement by oxidising the α-diastereomer (IX) to the ketone (XI) and reducing the latter with sodium stannite to norcamphor (XII), which is characteristic for the α-ketomercury chloride derivatives. However, this series of reactions is not a strict demonstration of the absence of rearrangement. The double bond of norbornene can participate in the stabilisation of the carbonium formed during the solvolysis of the 7-substituted derivatives[27,28]. Therefore the preparation of norcamphor can be explained starting from the structure of the *syn*-3-hydroxynorborn-*exo*-7-ylmercury(II) chloride for the α-diastereomer (IXa), assuming the interaction of the 2-keto- and 7-chloromercury-groups in the ketone (XIa) on reduction.

The stereochemical data on the hydroxymercuration of norbornene were supplemented by Yur'ev and coworkers[29-31] in a study of the hydroxymercuration of a similarly constructed bicyclo-system — 7-oxanorbornane, having an oxygen bridge atom, for which the correctness of the *exo*-addition rule had been shown earlier[32]. In order to avoid the Wagner–Meerwein rearrangement, the model selected for studying the stereochemistry of hydroxymercuration was the dimethyl ester of *exo-cis*-7-oxanorborn-2-en-5,6-dicarboxylic acid (XIII). The presence of electron-acceptor groups in this type of bicyclo-compound greatly reduces the rate of solvolysis of halides[33], stabilises the α-oxide ring[34] and results in most of the additions at the double bond proceeding without the Wagner–Meerwein rearrangement[35,36], although in principle all courses of the reaction with rearrangement are possible also in the presence of electron-acceptor groups[35,36].

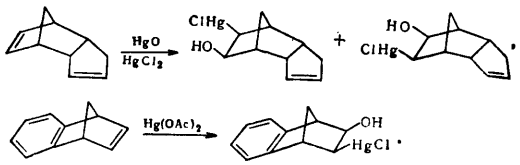
Hydroxymercuration of the diester (XIII) leads to the acetoxy- (XIV) or hydroxy-derivative (XV), depending on the conditions[31]:



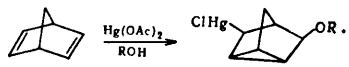
The compounds obtained, like *exo-cis*-3-hydroxynorborn-2-ylmercury chloride (IX), seemed relatively stable in acid. The *exo*-hydroxydiester (XVI) was obtained by a series of successive conversions from (XIV) and (XV), the configuration of which had been established earlier[31,32]. Hence the hydroxymercuration of the diester (XIII) proceeds by an *exo-cis*-addition (additional proofs are given below).

In 1963 Traylor and Baker showed that the hydroxymercuration of bicyclopentadiene and benznorbornene takes

place as an *exo-cis*-addition without the Wagner–Meerwein rearrangement[37]:



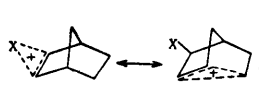
It is interesting that norbornadiene reacts with mercury(II) salts as a homoallyl system with participation of the two double bonds and formation of a 6-acetoxy- or 6-alkoxy-tricyclo[2,2,1,$0^{3,5}$]hept-2-ylmercury(II) chloride[38,39]:



From the above information on the study of hydroxymercuration there is no doubt that stereochemically the course of this reaction depends on the type of alkene taking part: in unsaturated bicyclo-systems having sterically hindered *endo*-attack, hydroxymercuration proceeds as a *cis*-addition, whereas the hydroxymercuration of ordinary alkenes of the stilbene or cyclohexene type takes place as *trans*-addition.

It must be emphasised, however, that the problem of the reason for *cis*-addition in hydroxymercuration is not completely clear. The opinion has already been expressed in the literature that strongly solvated bridged onium ions or $\pi$ complexes can, in the case of hindrance to *trans*-attack by a nucleophilic agent, undergo *cis*-opening of the ring as revealed by the products[26,31,37]. This finds confirmation in the stereochemistry of additions or rearrangements taking place through an intermediate $\pi$ complex of a proton with the alkene, or a bridged "protonium" ion. The disclosure of such an undoubtedly strongly solvated ion proceeds anomalously stereochemically in comparison with the usual *trans*-opening of intermediate cyclic onium ions (or $\pi$ complexes), as has been shown by several examples[40,41]. Similar behaviour can occur during hydroxymercuration. Confirmation of this is obviously provided by the fact that the action of mercury(II) acetate in methanol on norbornene gives a mixture of 3-acetoxynorborn-2-ylmercury chloride (VII) and 2-methoxynorborn-2-ylmercury chloride (VIII).[7] In the case of *trans*-addition the methanol concentration is immeasurably greater than that of the acetate anion, and the reaction leads almost solely to the formation of the methoxy-derivative. In the case of *cis*-addition, the anion which attacks the intermediate mercurinium ion is taken from the solvate sheath of the mercury ion.

However, the hindrance to *trans*-opening of the mercurinium ion obviously cannot be explained solely by the steric shielding of the double bond from the *endo*-side. It was noted[37] that in bicyclo-systems it is difficult to attain a planar transition state for *trans*-addition. However, examples of *trans*-opening of an $\alpha$-oxide ring[32,32] or of *trans*-addition at the double bond[36] nevertheless show the possibility in principle of such a transition state. Yet another factor is probably required in explaining the cases of *cis*-hydroxymercuration in bicyclo-systems, namely, the contribution in the transition state of a structure with partial delocalisation of the electrons of the 1,6- and 4,5-bonds:



An analogous explanation was postulated for instances of radical *cis*-bromination[43], but it can probably be applied also to heterolytic processes. The contribution of this type of structure was also introduced to explain some instances of *endo-exo*-isomerisation[44].

It has also been suggested that *cis*-hydroxymercuration is due to the directional effect of the double bond in the bicyclo-systems studied[37]. If this is really so, then the hydroxymercuration of strained monocyclic alkenes of the cyclobutene and cyclooctene type should also proceed as a *cis*-addition.

## IV. METHODS OF FINDING THE CONFIGURATION OF 2-MERCURATED ALCOHOLS

### 1. Nuclear Magnetic Resonance

In 1961 Anderson and Henry[45] used nuclear magnetic resonance to find the configuration of the $\alpha$-diastereomers obtained by hydroxymercuration of norbornene (IX) and cyclohexene (Vb). In the nuclear magnetic resonance spectrum for (IX) the coupling constant between protons 2 and 3, $J_{23}$, is 6.8 Hz, which agrees closely with the constant found for the *endo-cis*-hydrogen atoms (7.7 Hz) and is greatly different from that found for *trans*-hydrogen atoms (2.2 Hz). Hence (IX) has an *exo-cis*-configuration.

It was found for (Vb) that the hydrogen atom at the carbon attached to the mercury has two coupling constants, equal to 10 Hz and characteristic for axial–axial coupling, and also one constant, equal to 3.5 Hz, characteristic for axial–equatorial coupling. Hence the mercury atom and the hydroxyl group should be in the equatorial position and (Vb) should have *trans*-configuration.

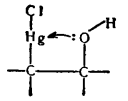
### 2. X-Ray Diffraction

As mentioned above, Brook and Wright ascribed the *trans*-configuration to $\alpha$-2-methoxycyclohexylmercury(II) chloride (Va) and the *cis*-configuration to the $\beta$-isomer (VIa) on the basis of X-ray diffraction studies. Later, Wright suggested that these results are questionable and unreliable[6–8] (see also Kreevoy and Kowitt[9]). However, as has now been established, the configurations deduced from the X-ray diffraction studies are correct. Obviously doubt about the possibilities of applying this method to organomercury compounds are greatly exaggerated and Brook and Wright's original data[5] are reliable.

### 3. Infrared Spectroscopy

Traylor and Baker[37] developed a method of determining configuration by comparison of the infrared spectra of hydroxymercuration products and the corresponding hydroxy-compounds in the region of the stretching vibrations of the hydroxyl group. In this region in the infrared spectrum of 2-mercurated alcohols there is only one absorption band, which shows the absence of a hydrogen bond between the hydroxyl group and the mercury atom. In the *cis*-compounds there is a single additional interaction,

absent from *trans*-compounds, namely the interaction of the oxygen of the hydroxyl group with the mercury atom:



Owing to this, displacement of the absorption band of the hydroxyl group into the long-wave region should be greater in the case of *cis*-compounds. Experimental investigation showed that the displacement of the hydroxyl group band in *trans*-hydroxymercury(II) chloride derivatives, as compared with the corresponding hydroxy-derivatives is 6–10 $cm^{-1}$, whereas that for the *cis*-hydroxymercury(II) chloride derivatives is 18–22 $cm^{-1}$. However, this method should obviously be used with caution for compounds exhibiting free rotation of a C–C bond or conformational mobility of the ring.

## 4. Dipole Moments

Dipole moments were measured for several pairs of diastereomeric 2-mercurated alcohols[7,11]. Although the measurement of dipole moments is one of the principal methods for establishing the configuration, this method has led to incorrect conclusions in a series of hydroxymercurated alcohols[7]. Only a qualitative correlation has been noted between the rate of dehydroxymercuration and the magnitude of the dipole moment: the diastereomer with the lower dipole moment is more readily dehydroxymercurated in acid[11].

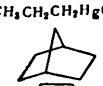
The main difficulty in using dipole moments is, according to Wright[7], the uncertainty in the C–Hg–X angle. On considering the vector scheme of the moments of the C–Hg–Cl group, Wright found that the angle between the moments of the C–Hg and Hg–Cl bonds is acute and amounts to 80°. Hence assuming free rotation, it turns out that the resultant vector moment of the C–Hg–Cl group (3.66 D) precesses 59° relative to the C–Hg bond and in the opposite direction. In this context, the calculations are very difficult, since there are two non-regular functional groups in the molecules of the 2-mercurated alcohols. Therefore, depending on the conformation, the dipole moment can change strongly and the choice of preferential conformations for the given compounds is arbitrary.

We have calculated the dipole moments of some 2-mercurated alcohols and found that dipole moments can be used to determine configuration but the angle C–Hg–X should be taken as 180°. Actually, investigation of the vibrational spectra and electron diffraction studies showed[46] that $HgCl_2$, $HgBr_2$, $HgI_2$, HgBrCl, HgICl, and HgIBr molecules are linear, while in the X-ray diffraction studies[5] mentioned above it was found that the angle C–Hg–X is 180° and 178° for (Va) and (VIa) respectively. Hence the C–Hg–X group can be considered linear, which greatly facilitates the calculation, since it is not necessary to consider the moment of the Hg–X bond separately and the whole moment of the HgX group can be considered directed along the C–Hg bond. The value of the moment along the C–HgCl bond can be taken as approximately equal to the dipole moment of propylmercury(II) chloride (3.70 D in dioxan).

The moment of the methoxy-group was taken as 1.30 D, with 55° as the angle of precession relative to the bond direction[47]. We made the calculation on the assumption that there is free rotation of the methoxy-group; the total moment was calculated as the mean of four moments: from the maximal and minimal values of coordinate $z$ and two extreme values with coordinate $z = \frac{1}{2}(z_{max} + z_{min})$ for the vector of the methoxy-group. The vectorial scheme of the norbornane molecule was taken from Wilcox[48]. The Table gives the dipole moments which we have calculated on this basis and shows that the agreement between the experimental and calculated values is good (except for compound 7) despite several assumptions having been made in the calculation: the interaction between the oxygen atom and the mercury atom in *cis*-compounds has been neglected, and the mean moment of the C–Hg–Cl bonds is unknown and can only approximately be taken as equal to the moment of propylmercury(II) chloride. An unfavourable circumstance is that the dipole moments were measured in dioxan, which can be coordinated differently with the mercury atoms in different isomers. The discrepancy between the found and calculated dipole moments for compound 7 is to be expected, since in the *endo*-derivatives of norbornane there is considerable steric interaction, leading to distorted geometry of the molecule.

Qualitatively, the similarity between the experimental and calculated values is completely adequate for unambiguously establishing the configuration. In rigid cyclic systems in the absence of other groups which exhibit their own substantial dipole moment and in the presence of rotation of the methoxy-group the moment of the *cis*-isomer will be greater than that of the *trans*-isomer, since the moments of the methoxy and chloromercury(II) groups in the *cis*-compound are directed to one side, and in the *trans*-compound the moments of these groups are directed at an obtuse angle. Hence it is also understandable that if in accordance with Wright's results it is assumed that the moment of the –HgCl group is directed to the opposite side with respect to the C–Hg bond at an angle of 59°, then we obtain on calculating in the reverse order of the calculated quantities the value of the dipole moments for the *cis*- and *trans*-isomers.

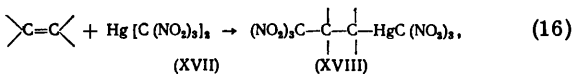
TABLE. Dipole moments of the derivatives of 2-mercurated alcohols.

| Compound No. | Formula | Dipole moment, D | | Δμ | Reference |
|---|---|---|---|---|---|
| | | found | calculated | | |
| 1 | $CH_3CH_2CH_2HgCl$ | 3.70 | | | 7 |
| 2 |  | 0.45 | | | 7 |
| 3 |  | 4.1 | 4.38 | −0.28 | 11 |
| 4 |  | 2.9 | 3.38 | −0.48 | 11 |
| 5 |  | 4.22 | 4.24 | −0.02 | 7 |
| 6 |  | | 3.22 | | |
| 7 |  | 2.77 | 3.80 | −1.03 | 7 |

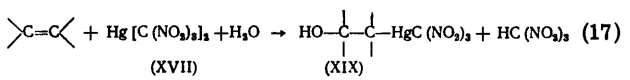
5. Methods Based on Difference in Dehydroxymercuration Rates

As already indicated above, the rate of dehydroxymercuration for the *trans*-isomer is much greater than that for the *cis*-isomer. Therefore on the basis of the measurement of the kinetics of dehydroxymercuration, configurations can be ascribed to pairs of diastereomeric 2-mercurated alcohols and this has been done [9,20,21]. Manolopoulos and coworkers [49] developed a relatively simple semiquantitative method for comparing dehydroxymercuration rates. The inconvenience of this method is that for a strict proof it is necessary to have the $\beta$-diastereomer, which is not always available.

A method of determining the stereochemistry of the addition of mercury salts with the aid of bis(trinitromethyl)mercury(II) (XVII), based essentially on the same principle, was developed by Zefirov and coworkers [50]. This compound is able to add on to alkenes to form derivatives of trinitromethyl-3,3,3-trinitropropylmercury(II) (XVIII) [51-53]:



(16)

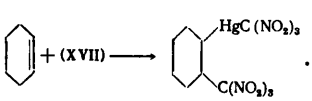


(17)

On carrying out the reactions in water it could be expected that Eqn. (17) would hold, with the formation of derivatives of 2-hydroxyethyltrinitromethylmercury(II) (XIX). However, the formation under such conditions of compounds of type (XIX) is possible only in the case of their stability in acid, since the trinitromethane liberated is itself a relatively strong acid ($K = 6.8 \times 10^{-1}$) [54]. Derivatives of type (XVIII) obtained by Eqn. (16), are extremely stable in acid [53], since their demercuration must be accompanied by rupture of a C–C bond. The stereochemical course of the reaction of hydroxymercuration according to Eqn. (17) should be the same for any mercury salts, especially if the possibility of the intermediate formation of a doubly-charged mercuronium ion of type (II) is taken into account — Eqn. (5).

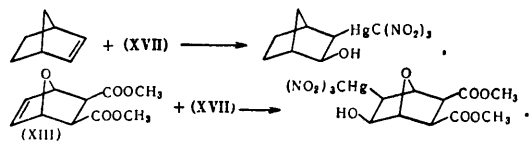
Hence, to determine the stereochemistry of the addition of mercury salts to an alkene the reaction must be carried out with an aqueous solution of bis(trinitromethyl)mercury(II), so that the formation of an addition product of type (XVIII) will show that the hydroxymercuration of this alkene proceeds as a *trans*-addition, whereas the formation of a product of type (XIX) will show *cis*-addition. Compounds of types (XVIII) and (XIX) are easily distinguished in the product analyses.

Actually, the addition of (XVII) to cyclohexene always proceeds with formation of trinitromethyl-2-trinitromethylcyclohexylmercury(II), whatever the solvent [52]:



The configuration of derivatives of type (XVIII) which are obtained has not been established experimentally, but probably *trans*-addition takes place here.

However, norbornene and the dimethyl ester (XIII) react with an aqueous solution of bis(trinitromethyl)mercury(II) according to Eqn. (17), [50] that is, *cis*-addition occurs here:



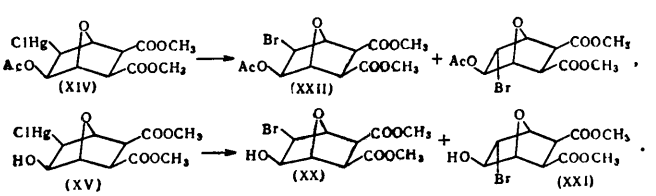
These methods are inapplicable when the stability of the 2-mercurated alcohol is due to some other structural factor. One of such factors is intramolecular closing of lactone rings, and also of tetrahydrofuran or tetrahydropyran rings [52-53].

6. Method of Replacement of HgX Groups

In connection with progress in investigations of the mechanism and stereochemistry of electrophilic substitution at a saturated carbon atom [55,56] it became possible to use chemical methods to determine the configuration of 2-mercurated alcohols. The replacement of halogenomercury-groups by halogen is the most convenient for this purpose, since the configuration of the halogenoalcohols obtained is usually known already or is relatively easily established by the usual methods. The stereochemistry of electrophilic replacement of chloromercury-groups by bromine was first studied by Jensen and Gale [57] who found that in non-polar solvents bromination takes place by a homolytic mechanism with racemisation or partial retention of configuration; bromination in polar solvents, for example, acetic acid, proceeds mainly with retention of the configuration. During bromination in pyridine there is complete retention of the configuration ($S_E2$ reaction), but the yield of the corresponding halogeno-derivative is only 50–65%, due to resinification taking place. Later, these conclusions were refined and supplemented (see Uglova [58]).

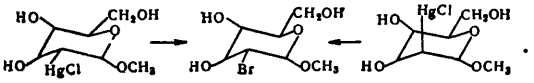
It must be emphasised that there has been no systematic study of the stereochemistry of electrophilic replacement of the HgCl group by halogen in the presence of neighbouring substituents.

Yur'ev and coworkers [31] used the halogenation of 2-mercurated alcohols with replacement of the HgX group as a method of finding configuration; they took as examples *exo*-3-acetoxy-5,6-dimethoxycarbonyl-*endo*-7-oxanorborn-2-ylmercury chloride (XIV) and *exo*-3-hydroxy-5,6-dimethoxycarbonyl-*endo*-7-oxanorborn-2-ylmercury chloride (XV).



It was found that bromination of the hydroxyester (XV) in chloroform leads to the *cis*-bromo-alcohol (XX) mixed with a little of the *trans*-bromo-alcohol (XXI), whereas bromination in pyridine leads only to the *cis*-bromo-alcohol (XX). The bromination of the acetoxyester (XIV) is analogous.

However, Jensen's rule about the retention of the configuration during bromination of organomercury compounds in polar solvents must be applied with caution to 2-mercurated alcohols, since it is possible that the presence of neighbouring substituents can alter the stereochemical result of the reaction. Inversion of the configuration during halogenation in several 2-mercurated alcohols was shown by the example of the bromination of the hydroxymercurated product of D-glucal[49], where both diastereomers gave identical bromomethoxy-derivatives:



Unfortunately, in this work the stereochemistry of bromination was investigated only in methanol and in carbon tetrachloride. Apparently, in the latter solvent reactions can also proceed by a radical, instead of $S_E2$ mechanism and in view of the considerable importance of the question, a study of the stereochemistry of bromination of these compounds in acetic acid and especially in pyridine would be welcome. Furthermore, a paper by Inglis and Schwarz appeared simultaneously[59] in which the hydroxymercuration of D-glucal and its triacetate is considered as *trans*-addition, and hence the results of these two studies are incompatible.

It should also be noted that in finding the configuration of 2-mercurated alcohols by other methods they can act as a convenient model for studying the stereochemistry of electrophilic replacement at a saturated carbon atom.

### 7. Method of Calculating the Angle of Rotation of Optically Active 2-Mercurated Alcohols

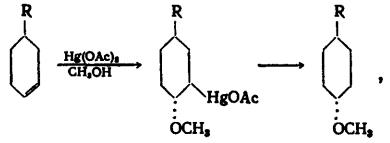
In 1963 Sokolov and Reutov[60] calculated the molecular rotation for certain optically acitive organomercury compounds by Brewster's method and showed that this type of calculation can be used to show the stereochemistry of the addition of mercury salts to alkenes. In 1947 Romeyn and Wright[61] obtained optically active $\alpha$- and $\beta$-2-methoxycyclohexylmercury chloride (Va) and (VIa), with $[M]_D$ = = -139° and +45° respectively, by an asymmetric synthesis. The molecular rotation calculated[60] for the *trans*-isomer (Va) is -130° and hence the $\alpha$-diastereomer should have the *trans*-configuration.

The use of this method is restricted by the difficulty of obtaining optically 2-mercurated alcohols of high purity. Naturally, calculation of the molecular rotation of organomercury compounds is restricted to those models for which Brewster's method is generally applicable[62].

## V. HYDROXYMERCURATION OF ALKENES WHEN THERE IS PRELIMINARY COORDINATION OF A MERCURY ION WITH FUNCTIONAL GROUPS

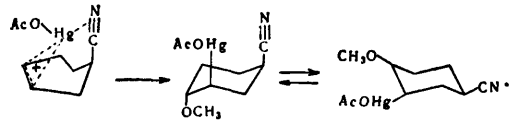
Due to the strong tendency of mercury to form coordination bonds, its preliminary reaction with functional groups attached to the alkene is possible in principle. Depending on the position of the functional group in relation to the reaction centre, such coordination can determine the direction of the initial attack of the mercury ion on the double bond, and consequently can lead to stereochemically anomalous reaction products.

In 1959 Henbest and Nicholls[63] hydroxymercurated 4-substituted cyclohexenes and in subsequent reduction obtained the corresponding *trans*-derivatives:

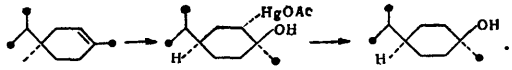


where R = OH, $OCH_3$, $CH_2OCH_3$, $COOCH_3$, CN.

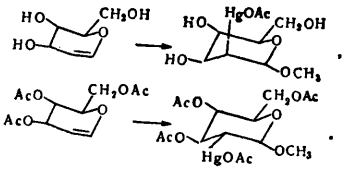
Hence assuming that the hydroxymercuration takes place as a *trans*-addition it follows that the atom of mercury atom is initially coordinated with the substituent and this determines the stereochemical course of the addition in a given case:



In the absence of preliminary coordination the *cis*-derivative is obtained after reduction, as the example of carvomenthene showed[64]:

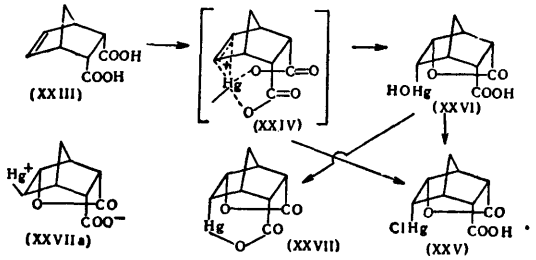


Manolopoulos and coworkers[49] found further that hydroxymercuration of D-glucal takes place as a *cis*-addition, whereas its triacetate is hydroxymercurate with formation of a *trans*-addition product:



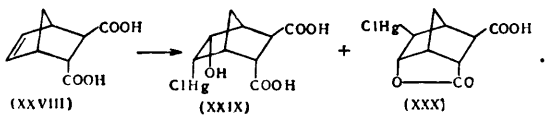
Such a difference in the stereochemical course of hydroxymercuration was explained by the preliminary coordination of the mercury ion with the hydroxyl groups in D-glucal. We must remember, however, that according to the results of Inglis and Schwarz[59] hydroxymercuration of glucal is a *trans*-addition[59], and therefore these studies need experimental verification.

The problems of the stereochemistry of hydroxymercuration when there is preliminary coordination were studied in considerable detail by Wright and coworkers[7,65], using norbornene derivatives with *endo*-functional groups. Thus the hydroxymercuration of the *endo*-norbornene-dicarboxylic acid (XXIII) proceeds as an *endo-cis*-addition to form the lactone (XXV)[7,65]:



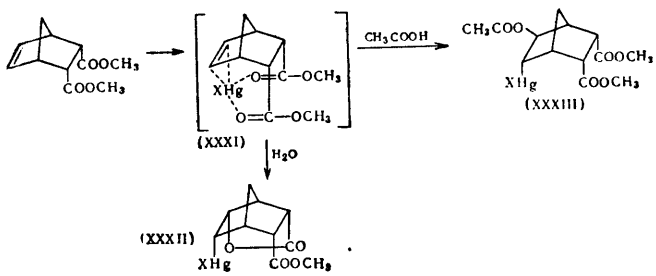
This stereochemical course of the reaction is thought by the authors to be brought about by the preliminary formation of the complex (XXIV). The *endo*-configuration of the HgCl group was demonstrated by obtaining the anhydrolactone (XXVII) by the action of acetic anhydride on the lactonemercury hydroxide (XXVI).

Hydroxymercuration of the *trans*-acid (XXVIII) proceeds less stereospecifically and leads to a mixture of the products of *endo-cis*- (XXIX) and *trans*-addition (XXX)[7]:



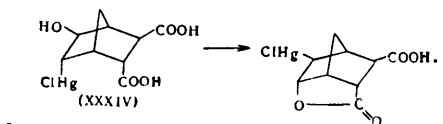
(XXVIII) (XXIX) (XXX)

Preliminary coordination of the mercury ion can also be effected with the methoxycarbonyl groups. Hydroxymercuration of dimethyl *endo-cis*-norbornenedicarboxylate proceeds in different directions with different solvents[7]. The coordination complex formed in the first stage (XXXI) gives the *endo*-lactonemercury chloride (XXXII) in water. In acetic acid, there is *trans*-opening with formation of the diestermercury chloride (XXXIII):



(XXXI) (XXXII) (XXXIII)

However, this paper[7] describes a series of conversions which raise doubts about the correctness of the allotted configurations. Thus, the thermal conversion of the *exo*-hydroxy-acid (XXXIV) into the lactone (XXX) remains uncertain:



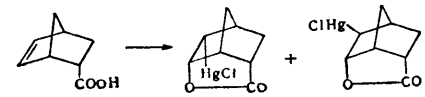
(XXXIV) (XXX)

[Carried out in sodium amalgan (Ed. of Translation)].

The dipole moments measured for many of these substances[7] are not reliable criteria for finding the configurations of such polyfunctional compounds. Essentially *endo-cis*-addition was only shown by the formation of the anhydrolactone (XXVII). The reliability of such a method is subject to doubt[9] and it was suggested that this compound exists in the form of a "zwitter-ion" (XXVIIa) with the mercury atom in the *exo*-position. Compounds existing in the form of "zwitter-ions" were obtained earlier in the hydroxymercuration of certain unsaturated acids[66]. Unfortunately Abercrombie and coworkers[7] did not measure the dipole moment of the anhydrolactone (XXVII).

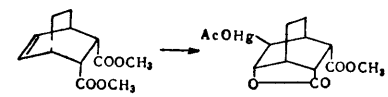
If the anhydro-compounds actually exist as "zwitter-ions" then all the data on the stereochemistry of the hydroxymercuration of norbornene derivatives having *endo*-functional groups, and for which initial *endo*-attack of the double bond by the mercury ion is assumed, due to preliminary coordination of the latter with the *endo*-substituent, must be reconsidered, and the question of the possibility of an anomalous stereochemical course of reaction remains open.

Malaiyandi and Wright[67], in studying the hydroxymercuration of *endo*-norbornenecarboxylic acid, separated two compounds which were given the following configurations:

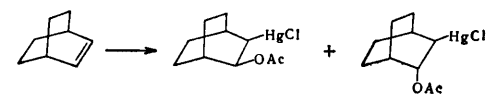


However, in this work the proof of the configuration is not strict — it is based on the analogy between the dipole moments with those of the already available products of the hydroxymercuration of norbornenedicarboxylic acids.

An ester of a bicyclooctenedicarboxylic acid was also first assumed to undergo *endo-cis*-addition[65] but it was found subsequently that *trans*-addition takes place[68]:

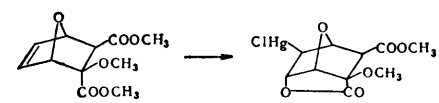


However, according to Traylor's later results[69] hydroxymercuration of bicyclooctene proceeds with formation of a mixture of the products of *cis*- and *trans*-addition:



It is therefore possible that the products of *cis*-addition to the dimethyl bicyclooctenedicarboxylate could not be separated because of experimental difficulties.

Yur'ev and coworkers[70] have shown that the hydroxymercuration of dimethyl 5-methoxy-7-oxanorborn-2-en-*trans*-5,6-dicarboxylate also proceeds by *trans*-addition:



---o0o---

The most general features of the principal stereochemical rules for the addition of mercury(II) salts to alkenes have now been explained. It has been found that unlike other reactions of electrophilic addition at multiple bonds the stereochemical course of this reaction depends strongly on the alkene: the hydroxymercuration of ordinary acyclic and monocyclic alkenes is a *trans*-addition, whereas the hydroxymercuration of unsaturated, strained bridge bicyclo-compounds, having spatial hindrance against *trans*-attack, is a *cis*-addition.

However, there are many problems still awaiting solution. Thus the details of the mechanism of this reaction are still not clear, and the question of the possibility of anomalous stereochemical course of reaction due to preliminary coordination with functional groups has still not been decided unambiguously.

Undoubtedly, further investigation will lead to progress in understanding the fine stereochemical aspects of this reaction and may allow the rules found to be applied to a wider range of other additions.


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# THE REACTIONS OF ANTI-TUMOUR ALKYLATING COMPOUNDS

A. Ya. Berlin and L. S. Yaguzhinskii

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## I. INTRODUCTION

Of the tremendous number of substances that have been tested for anti-tumour activity, a large group of compounds with alkylating properties is outstanding; these compounds attack tumour cells to a somewhat greater degree than normal cells.

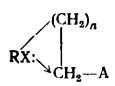
At present these preparations are widely used in the chemotherapy of some types of malignant tumours[1]. There are a number of reviews and monographs dealing with the biological properties of alkylating agents and also with the dependence of biological activity on chemical structure[2-7].

Since the selectivity of anti-tumour activity in these compounds is closely connected with the chemical properties of their electrophilic centres, it is of interest to examine in one review the most important features of the reactivity of those types of alkylating agent which have shown anti-tumour activity clinically or in animal experiments.

## II. REACTIVITY OF ALKYLATING COMPOUNDS

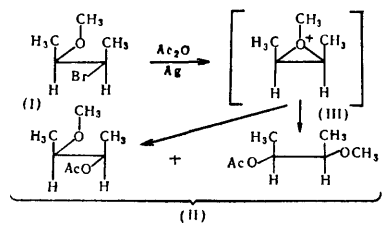
Table 1 gives a list of various types of compounds that have yielded preparations with anti-tumour activity.

In about half the compounds in Table 1 (the first ten) a heteroatom with a free pair of electrons is situated in position 2 or 4 to the electrophilic centre. This structure makes possible interaction between the electron pair and the electrophilic centre of the molecule, which facilitates the intramolecular removal of the substituent A on the carbon atom:

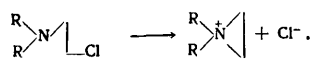


where X is N, O, or S and $n$ = 1 or 3.

When the substituent A is eliminated by an intramolecular reaction, a cyclic cation is usually formed[24,25]. For example, in acetolysis of *D*-2-bromo-3-methoxybutane (I) with acetic anhydride in the presence of silver ions, the racemate of 2-acetoxy-3-methoxybutane (II) is formed; this can only be explained by the formation of an intermediate oxonium cation (III):



There are also direct proofs of the formation of cyclic products in the reactions of some alkyl halides. Thus when aliphatic 2- or 4-chloroalkylamines are dissolved in water, at first rapid separation of chloride ions without material change in the pH of the solution is observed[8,26,27]:



Moreover, stable salts of aziridinium have been separated from 2-chloroethylamines[28]. The rate of formation of the aziridinium ion is directly related to the basicity of the nitrogen atom[29-31] (see Table 2).

The question of the cyclisation of the 2-chloroethylamines is considered in detail in reviews[2,5,33]. According to polarographic results[34], a cyclic cation is also first formed in the hydrolysis of 2-mesylethylamines. Opening

TABLE 1.

| Type of compounds | Formula | References |
|---|---|---|
| 2-Halogenoalkylamines* | $R_2NCH_2CH_2X$ | 1, 5, 8, 9 |
| 2-Aminoethyl methanesulphonates* | $R_2NCH_2CH_2OSO_2CH_3$ | 10, 11 |
| 2-Aminoethyl toluene-*p*-sulphonates | $R_2NCH_2CH_2OSO_2C_6H_4CH_3$-*p* | 12 |
| Polyalcohol derivatives | | |
| a. halogeno-derivatives* | $R(CHOH)_nCH_2X$ | 13 |
| b. esters of methanesulphonic acids | $R(CHOH)_nCH_2OSO_2CH_3$ | 13 |
| c. alkyl sulphates | $R(CHOH)_nCH_2OSO_2OR$ | 11 |
| 2-Halogeno-thioethers* | $RSCH_2CH_2X$ | 14 |
| 4-Halogenoethers | $RO(CH_2)_4X$ | 15, 16 |
| $\alpha$-Halogenocarbonyl compounds* | $RCOCHXR'$ | 17 |
| *N*-Alkylaziridines* | $RN(CH_2)_2$ | 5 |
| 1,2-Epoxides* | $RCHCH_2O$ | 18, 19 |
| Esters of methanesulphonic acid* | $ROSO_2CH_3$ | 1 |
| Esters of *N*-arylsulphamic acids | $ArNRSO_2OR'$ | 20, 21 |
| Diazo-compounds(aliphatic)* | $RN_2$ | 22 |
| *N*-Nitrosoalkylurea derivatives | $RN(NO)CONR'_2$ | 23 |
| Allyl alcohol derivatives* | $CH_2=CHCHROH$ | 24 |

* The anti-tumour activity of representatives of this type has been clinically studied.

TABLE 2. Basicity constants and rate of cyclisation of 2-chloroethylamines[5,32].

| Amine | $pK_a$ | $K$, min$^{-1}$ at 15° |
|---|---|---|
| $(C_2H_5)_2NCH_2CH_2Cl$ | 8.82 | 0.145 |
| $C_2H_5N(CH_2CH_2Cl)_2$ | 6.57 | 0.128 |
| $N(CH_2CH_2Cl)_3$ | 4.39 | 0.073 |
| $C_6H_5N(CH_2CH_2Cl)_2$ | 2.2 | 0 |

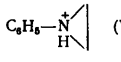
of the aziridinium cation proceeds comparatively slowly in the main by a bimolecular mechanism ($S_N2$),[35] and in agreement with this, stronger nucleophilic agents react more rapidly with the aliphatic chloroethylamines[26,36].

Aromatic 2-chloroethylamines differ somewhat from their aliphatic analogues. Hydrolysis of these compounds proceeds by an $S_N1$-mechanism[37-40]. An intramolecular mechanism is also indicated by the fact that the hydrolysis of nuclear-substituted 2-chloroethylamines of type (IV):

$$p\text{-}RC_6H_4N(CH_2CH_2Cl)_2 \qquad (R = OCH_3,\ CH_3,\ H,\ Cl,\ COOC_2H_5)$$
(IV)

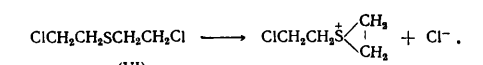
increases with increasing electron-donor properties of R [5] and falls sharply when the chloride ion is added to the solution[41].

The formation of the aziridinium ring in reactions of these compounds has not been proved[2,5,10], since the stability of rings of type (V)


(V)

must be greatly reduced because of the electron-attracting properties of the phenyl nucleus. Aromatic 2-chloroethylamines react faster with acid anions the greater the nucleophilic properties of the anion[37,42]. In this case, in contrast to hydrolysis, the reaction apparently proceeds by an $S_N2$-mechanism.

2-Halogeno-thioethers are very similar in properties to chloroethylamines. A study of the kinetics of hydrolysis of Yperite [mustard gas, bis-(2-chloroethyl) sulphide (Ed. of Translation)] (VI) showed that the intramolecular elimination of chlorine is also the rate-determining step[43,44]:


(VI)

As in the case of the aromatic chloroethylamines, the relative rate of reaction of bis-(2-chloroethyl) sulphide with acid anions increases with the nucleophilic properties of the anion; this probably also explains the change in substitution mechanism[45-47].

The dependence of the reaction mechanism on the nucleophilic properties of the attacking agent is particularly clearly shown in aromatic 2-chloroethyl sulphides[48]. Thus, in the hydrolysis of type (VII) compounds:

$$p\text{-}RC_6H_4SCH_2CH_2Cl \qquad (R = CH_3O,\ CH_3,\ H,\ I,\ Br,\ Cl,\ NO_2),$$
(VII)

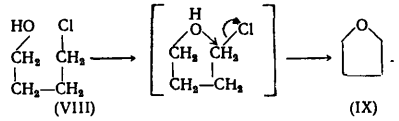
the rate of reaction increases with increasing electron-donor properties of R ($S_N1$-mechanism), but in the reaction with the iodide anion, which is a stronger nucleophilic agent than water, the reaction rate decreases with increasing electron-donor properties of nuclear substituents ($S_N2$-mechanism).

2-Halogenoalcohols, $HOCH_2CH_2X$, behave differently from most of the foregoing compounds in neutral and acid aqueous solutions.

The rate of hydrolysis of these compounds is ten or a hundred times less than the rate of hydrolysis of alkyl halides, which are similar in structure[49]. Reduction in the mobility of the chlorine by the introduction of a hydroxy-group in position 2 is observed both for the primary alkyl halides[50,51], reacting with water mainly by an $S_N2$-mechanism, and for the tertiary alkyl halides[52,53], decomposing under these conditions by an $S_N1$-mechanism.

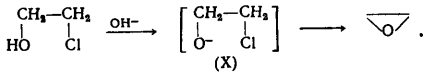
At present it is difficult to give an acceptable explanation of this effect. In any case, the reduction in the rate of the intramolecular reaction under the influence of an atom of oxygen in the $\beta$-position indicates the absence of interaction of the latter with the electrophilic centre of the molecule.

However, in 4-halogenoalcohols such an interaction exists between the oxygen and the $\delta$-carbon atom. Streitwieser[33] explains this by the fact that a five-membered ring is formed more easily than a three-membered one. Hydrolysis of 4-chlorobutanol (VIII) gives tetrahydrofuran(IX):


(VIII) (IX)

In this reaction the rate of elimination of the halide ion is 1000 times greater than in the hydrolysis of 2-chloroethanol[59].

Kinetic data indicate[60,61], that in strongly alkaline solutions of 2-halogenoalcohols the alkoxide ion (X) is formed, and as a result, rapid intramolecular cyclisation takes place:

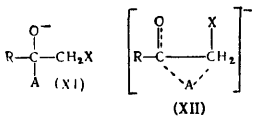

(X)

The rate of elimination of halide from the halogenoalcohols is substantially higher than the rate of elimination from the alkyl halides[62,63].

4-Halogenoethers, $RO(CH_2)_4X$,[15,16] appear to be similar to the corresponding alcohols in their behaviour on acid hydrolysis.

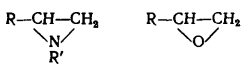
$\alpha$-Halogenoketones, $O{=}C(R)CH_2X$, are close in structure to the types of compounds described above (Table 1), but steric considerations make the interaction of the lone pair of oxygen electrons with the $\alpha$-carbon atom ($\beta$-position to the oxygen) impossible.

$\alpha$-Halogenoketones react with nucleophilic agents by a bimolecular mechanism[64-66]. At first it was assumed that replacement of the halogen proceeds through a polar transition complex (XI).[67] However, such a scheme does not explain the significant difference

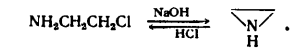

(XI) (XII)

in the rates of reaction of $\alpha$-bromo- and $\alpha$-chloro-ketones with the same reagent[68]. It was therefore postulated that the slow stage of the reaction is the formation of the intermediate (XII).[70,71]

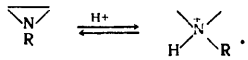
Derivatives of aziridine and ethylene oxide [oxiran]:



are closely related genetically to 2-halogenoalkylamines and 2-halogenoalcohols and are formed by treating the latter two compounds with alkalis[60,72,73]. On the other hand, 2-halogenoalkylamines and 2-halogenoalcohols may be prepared by treating the corresponding cyclic compounds with hydrohalogen acids[42,74,75]:



Aziridine itself is a weak alkylating agent, but it readily adds on a proton to give the reactive aziridinium ion (XIII):



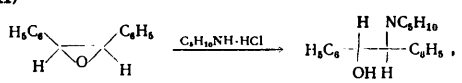
(XIV) (XIII)

The nitrogen atom of the aziridine ring (XIV) having a substituent with electron-acceptor properties should be considered separately. The equilibrium of the protonation reaction will here be strongly displaced to the left in contrast to aziridines not substituted on the nitrogen; however, the cation formed (XIII) must be more reactive because of the greater positive charge on the nitrogen atom.

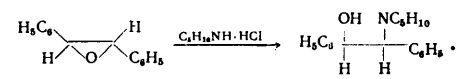
According to Ross[2], these compounds can react by a bimolecular mechanism without the participation of protons as catalyst.

The reactions of oxiran and the reactions of aziridine are catalysed by acids, but oxiran, in contrast to aziridine readily reacts with nucleophilic agents also in neutral and alkaline solutions. The mechanisms of these reactions change according to the conditions. Data on the rate of hydrolysis of substituted 1,2-epoxides in neutral and acid media (Table 3) show that replacement of an electron-donor substituent ($CH_3$–) by an electron acceptor ($ClCH_2$–) in neutral medium leads to an increased rate of reaction, but in an acid medium the opposite effect is observed[5,76]. This shows that in a neutral medium the reaction proceeds by an $S_N2$-mechanism and in acid medium by an $S_N1$-mechanism. This view is supported by a large number of papers[77,83].

A deeper study of some reactions of 1,2-epoxides catalysed by acids showed that the reactions are stereospecific. For example, when *cis*-$\alpha\alpha'$-epoxybibenzyl (XV) is opened by hydrogen halides[84], or by piperidine in the presence of piperidinium chloride[85], the *threo*-isomer is formed (XVI), but *trans*-$\alpha\alpha'$-epoxybibenzyl (XVII) gives the *erythro*-isomer (XVIII)



(XV) (XVI)



(XVII) (XVIII)

TABLE 3. Rate constants for the hydrolysis of 1,2-epoxides in neutral and acid solutions.

| 1,2-Epoxides | $k_{H_2O}$, $s^{-1}$ ($S_N2$) | $k_{H^+}$, $s^{-1}$ ($S_N1$) |
|---|---|---|
| $CH_3$– | $2.2\cdot10^{-6}$ | $123\cdot10^{-3}$ |
| $ClCH_2$– | $5.1\cdot10^{-6}$ | $1.9\cdot10^{-3}$ |

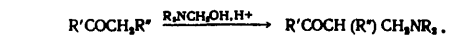
These facts contradict interpretations according to which a free carbonium ion is formed in these reactions ($S_N1$-mechanism).

An explanation of these contradictions has been given on the basis of the "push–pull" mechanism proposed by Swain[86]. According to this scheme, the reaction is regarded as a synchronous approach of the new substituent and removal of the old one; the rate of reaction is determined, on the one hand, by the strength of the interaction of the attacking substituent with the electrophilic centre of the molecular ("push component" of the reaction) and, on the other hand, by the ease of elimination of the old substituent ("pull component"). This mechanism explains[64,87,88] both the stereospecificity of the 1,2-epoxide (a consequence of the synchronism of the substitution), and the characteristics of a unimolecular mechanism shown by these reactions; these are particularly marked in acid solutions since protonation favours the rupture of the C–O bond of the oxide ring.

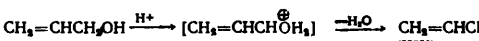
Aminomethanols, $R_2NCH_2OH$, form a characteristic type of alkylating agent. In the presence of acids they form the so-called carbimmonium cation[89]



which is the real alkylating agent[90–92]. Thanks to high activity, this cation can enter into an electrophilic substitution reaction at the carbon atom, for example, in the Mannich reaction[93]:

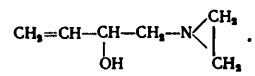


Derivatives of allyl alcohol, $CH_2$=CHCHROH, apparently cannot be regarded as typical alkylating compounds; however, in the presence of acids these compounds can sometimes form a carbonium ion (XIX)[94] which may behave as an alkylating agent:



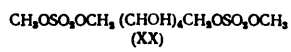
(XIX)

The allyl alcohol residue forms part of the molecule of the anti-tumour compound "Etoksen" ("Tetramin")[95]



Derivatives of esters of methanesulphonic acid, $ROSO_2CH_3$, not containing atoms with a lone pair of electrons are typical alkylating compounds. They react with nucleophilic reagents by a bimolecular mechanism[96–98].

Esters of sulphuric acid, $ROSO_2OR'$, are well known as compounds with pronounced alkylating properties[99]. It has been shown by experiments with labelled water ($^{18}O$) that the hydrolysis of these compounds proceeds simultaneously by $S_N1$- and $S_N2$-mechanisms[100]. There are indications that the mannitol derivative (XX) has anti-tumour activity[11,101]:

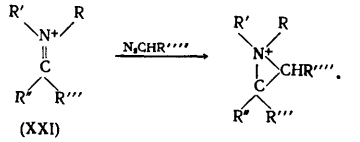


(XX)

Esters of *N*-arylsulphamic acids, $ArNRSO_2$.$OR'$, are hydrolysed in alkaline medium at the same rate as 2-chloroethylamines[102]. The mechanism of this reaction has not been studied.

Diazo-compounds (aliphatic), $RN_2$, as alkylating agents have the important characteristic that they alkylate by a radical mechanism[103].

Reactions of diazo-compounds with the carbimmonium cation (XXI) leading to the formation of aziridine derivatives are interesting[104]:



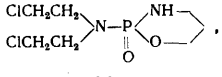
(XXI)

As can be seen from the scheme shown, this reaction *in vivo* might lead to the formation of new alkylating compounds[89,92].

Derivatives of nitrosoalkylurea, $R_2NCON.(NO)R'$, serve as starting materials for the preparation of diazo-compounds[105]. It has been shown in direct experiments that, under biological conditions in the organism, they behave as alkylating agents[23,106], reacting with purine basis of nucleic acids[107].

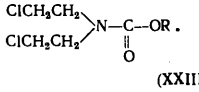
An important property of anti-tumour alkylating agents, which should be pointed out, is their ability to react with nucleophilic centres under relatively mild conditions. The high reactivity of a number of alkylating agents is shown by data on the hydrolysis of chloroethylamines[6,108-110], aziridines[76,111,112] and esters of methanesulphonic acid[2,98]; by data on the reaction of chloroethylamines[8,26] and 1,2-epoxides with the thiosulphate ion[76]; and also by the relative rates of reaction of bis-(2-chloroethyl sulphide and chloroethylamines with different anions[36,42,45,46].

In addition to these, there is a large group of anti-tumour compounds with very low alkylating activity[113]. However, partial decomposition of the molecule of such compounds, which may occur in the body, gives products with relatively high alkylating power. Because of this property, these compounds have been called alkylating compounds with latent activity[114,115]. They include such an effective preparation as the cyclophosphamide "Tsikolfosfan" ("Endoxan")(XXII)[114]:



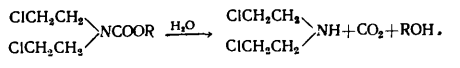
(XXII)

and also a large number of derivatives of carbamic acid of type (XXIII)[115-120]:

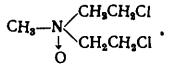


(XXIII)

In compounds of type (XXII) or (XXIII) the electron-acceptor substituent sharply reduces the basicity of the nitrogen, and, as a result, participation of the nitrogen in activating the substitution reaction at the β-carbon atom becomes impossible (see above). Hydrolytic or enzymic decomposition of these compounds under conditions in the body gives bis-(2-chloroethyl)amine[119]:



Bis-(2-chloroethyl)methylamine *N*-oxide ("Nitromin") obviously belongs to the type mentioned above[121]:



The relatively low alkylating properties of this compound should increase when it is reduced under biological conditions in the body to give bis-(2-chloroethyl)methylamine ("Embichin"†).

## III. BIFUNCTIONALITY

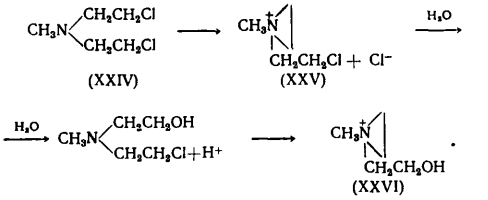
Highly effective anti-tumour alkylating compounds have an important structural feature: as a rule, their molecules contain two electrophilic groups. Compounds with one electrophilic centre have only one-tenth of the anti-tumour activity or they are entirely inactive‡.

This principle was first observed in aromatic[122] and aliphatic[123] chloroethylamines. Later the bifunctional rule was also noted in 1,2-epoxides[124,125], aziridines[124], and methanesulphonic acid esters[126]. Table 4 shows that not one unifunctional compound among the many classes of alkylating compounds has found practical application as a pharmaceutical preparation.

### 1. Mutual Effect of Electrophilic Centres in Bifunctional Alkylating Groupings

The cause of the higher biological activity of multifunctional compounds may lie, in principle, in the change in reactivity of the electrophilic centres as a result of the mutual influence of alkylating residues. It is therefore of interest to examine special features in the behaviour of this type of compound in comparison with the corresponding unifunctional compounds.

Aliphatic bis-(2-chloroethyl)amines, for example (XXIV) when dissolved in water form an aziridinium cation (XXV) at a slower rate then monochloroethylamines[32] (see Table 2)



(XXIV) (XXV) (XXVI)

It is also significant that the second electrophilic centre in such compounds can only enter into reaction after opening of the aziridinium ion (XXV).

The aziridinium ion

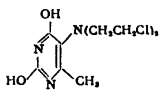
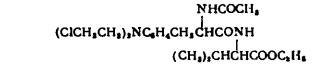
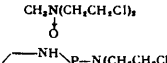
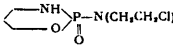
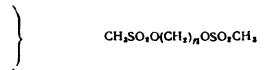
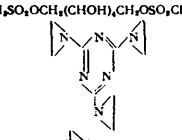
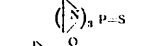
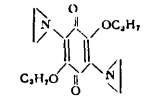
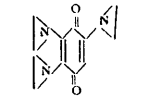
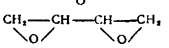
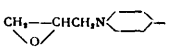


may be regarded as a symmetrical structure with four alkyl substituents on the nitrogen atom; it may therefore

† This is the hydrochloride, also known as Mechlorethamine hydrochloride, etc. (Ed. of Translation).

‡ This rule has a number of exceptions[5]. The main exceptions are compounds which contain, in addition to one alkylating centre, one residue without alkylating properties but nevertheless capable of interacting with some cell components (see p.542).

TABLE 4. Anti-tumour preparations used in practice* (from the Report of Committee of Experts on the Chemotherapy of Cancer [1]).

| Compound | Structural formula |
|---|---|
| Bis-(2-chloroethyl)methylamine | $CH_3N(CH_2CH_2Cl)_2$ |
| Bis-(2-chloroethyl)-2-chloropropylamine | $CH_3CHClCH_2N(CH_2CH_2Cl)_2$ |
| γ-*p*-Bis-(2-chloroethyl)aminophenyl-butyric acid | $HOOC(CH_2)_3C_6H_4N(CH_2CH_2Cl)_2$ |
| β-*p*-Bis-(2-chloroethyl)aminophenyl-α--alanine | $HOOCCH(NH_2)CH_2C_6H_4N(CH_2CH_2Cl)_2$ |
| 4-Methyl-5-[bis-(2-chloroethyl)amino]-uracil |  |
| Ethyl ester of *N*-acetyl-β-*p*-[bis-(2--chloroethyl)amino]phenyl-α--alanylvaline |  |
| 1,6-Bis-(2-chloroethylamino)-1,6-dideoxy-*D*-mannitol | $ClCH_2CH_2NHCH_2(CHOH)_4CH_2NHCH_2CH_2Cl$ |
| Bis-(2-chloroethyl)methylamine *N*-oxide |  |
| 2-[Bis-(2-chloroethyl)amino]perhydro--2-oxo-1,3,2-oxazaphosphorine |  |
| Tetramethylene bismethanesulphonate ($n = 4$) |  |
| Nonamethylene bismethanesulphonate ($n = 9$) | |
| Mannitol 1,6-bismethanesulphonate | $CH_3SO_2OCH_2(CHOH)_4CH_2OSO_2CH_3$ |
| 2,4,6-Triaziridinyl-*sym*-triazine |  |
| Triaziridinylphosphine sulphide |  |
| 3,6-Diaziridinyl-2,5-di-propoxy-*p*--benzoquinone |  |
| 2,3,5-Triaziridinyl-*p*-benzoquinone |  |
| 1,2 : 3,4-Diepoxybutane |  |
| 1,1′-Bis-(2,3-epoxypropyl)-4,4′--bipiperidyl |  |

* The table contains only the preparations that have been most studied clinically.

be supposed that in reactions of this compound there will be rupture not only of the three-membered ring, but in some measure also rupture of one of the bonds of the nitrogen atom with the substituent R or R′.

When two β-chloroethyl residues are present on the nitrogen atom, as for example in compound (XXIV), the probability of elimination of a $CH_3$ group must greatly increase because an aziridinium cation (XXV), (XXVI) is formed twice in the course of the reaction.

Thus, the amine (XXIV) when introduced into the animal body is almost completely destroyed with elimination of a methyl group[127]. According to Warwick, under the same conditions aromatic bis-(2-chloroethyl)amines do not eliminate a phenyl nucleus[128,129].

Bifunctional aromatic 2-chloroethylamines also show some special features connected with the presence of two 2-chloroethyl residues on one nitrogen atom. Because of the lower basicity of the nitrogen atom (Table 2), the rate of hydrolysis of chlorine in these compounds is appreciably less than in the corresponding monochloroethylamines. According to Ross, *N*-2-chloroethyl-*N*-ethylaniline ($pK_a = 3.5$) is hydrolysed under standard conditions to the extent of 58%, but *NN*-di-(2-chloroethyl)-aniline ($pK_a = 2.2$) is hydrolysed only to the extent of 20%.[5] The basicity of some 2,2′-iminodiethanols is nearly 1000 times greater than the basicity of the corresponding bis-(2-chloroethyl)amines[108]. It follows from these facts that after the first chlorine atom in dichlorodiethylamine is replaced by a hydroxyl group, the basicity of the nitrogen atom increases sharply, and this, in turn, should lead to hydrolysis of the second chlorine atom at a faster rate. In fact, with some examples[109] an inflection is observed on the curves of the concentration of chloride ion (Figure); this unambiguously indicates that the hydrolysis is accelerated at a definite stage.

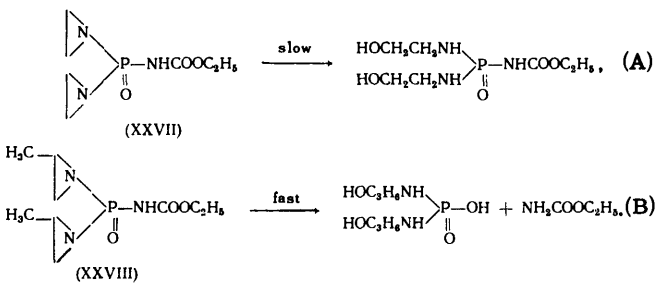
A similar effect should occur in the reactions of bis--(2-chloroethyl)amines with primary and secondary amines. Thus, the bifunctional aromatic chloroethylamines, in contrast to the unifunctional compounds, have a latent reactivity in some reactions; after the first alkylating residue enters into reaction the reactivity of the second increases.

When di-(2-chloroethyl)amines react with tertiary amines the quaternary ammonium salts,

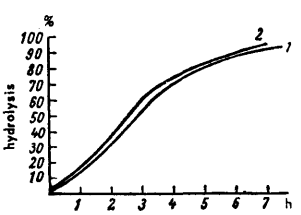
$$ClCH_2CH_2NRCH_2CH_2\overset{+}{N}R'R''R'''$$

are formed; the central nitrogen atom hardly changes its basicity and therefore in such reactions there should be no increase in the reactivity of the second electrophilic centre.

The mutual influence of aziridine residues in different di- and tri-aziridines has not been specially studied. However, it is interesting to note the work of Bardos, in which it was shown that (XXVII) is hydrolysed by Scheme (A), but (XXVIII) is hydrolysed by Scheme (B).[130]

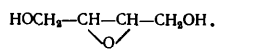


The mutual influence of two oxide rings in bifunctional compounds has also been little studied. Their mutual arrangement in the molecule is of great importance.

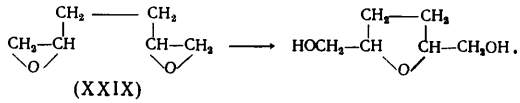



Curves showing the concentration of chloride ion in the hydrolysis of aromatic bis-(2-chloroethyl)amines:
1) *p*-bis-(2-chloroethyl)aminophenylalanine;
2) bis-(2-chloroethyl)aniline.

Ross has noted the fall in the rate of hydrolysis constant of diepoxybutane with time[76]. This may be connected with the formation of a less active intermediate product:



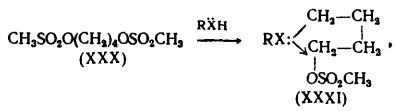
If the oxide rings are separated by two methylene groups (XXIX) a stable tetrahydrofuran ring is formed[131,132]:



(XXIX)

Compound (XXIX) reacts with only one molecule of water; it behaves as a unifunctional compound.

Esters of methanesulphonic acids, for example "Mialosan" ("Mileran") (XXX), containing two alkylating centres, react with strong nucleophilic reagents to form compounds of type (XXXI) in the first stage:

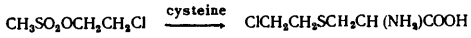


(XXX) (XXXI)

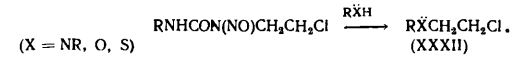
X = NR, O, S)

in which the character of the reactivity of the alkylating residue is materially changed by interaction of the electrophilic centre with the lone pair of electrons of the atom X.

There is indirect information to show that the 2-chloroethyl ester of methanesulphonic acid reacts *in vivo* with cysteine with the formation of 2-chloroethylcysteine, which has high alkylating power[2]:



Among derivatives of nitrosoalkylureas the most active are derivatives of 2-chloroethylurea[106]. When such compounds react *in vivo*, biologically active compounds of type (XXXII) may also be formed:



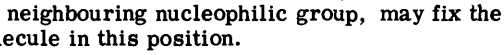
(X = NR, O, S) (XXXII)

Anti-tumour compounds with unsymmetrical bifunctional groupings, in particular the halogenoalkylamines have the interesting property that one of their alkylating centres is very weakly reactive[8,133]. Table 5 shows that the replacement of an alkylating residue with weak reactivity by a residue having no alkylating properties at all leads to disappearances of activity. Compounds in which both electrophilic centres are slightly reactive are devoid of anti-tumour activity.

TABLE 5. Unsymmetrical dihalogenoalkylamines.

| Preparations having anti-tumour activity | Preparations having no anti-tumour activity |
|---|---|
| $CH_3N(CH_2CH_2Cl)(CH_2CH_2CH_2Cl)$ | $CH_3N(CH_2CH_3)(CH_2CH_2CH_2Cl)$ |
| $CH_3N(CH_2CH_2Cl)(CH_2CH_2CH_2CH_2CH_2CH_2Cl)$ | $CH_3N(CH_2CH_2OH)(CH_2CH_2Cl)$ |
| $C_6H_5N(CH_2CH_2Cl)(CH_2CH_2CH_2Cl)$ | $C_6H_5N(CH_2CH_2CH_2Cl)(CH_2CH_2CH_2Cl)$ |

Alkylating compounds containing one alkylating centre and a metabolite residue, for example, serine diazoacetate or diazooxonorleucine,



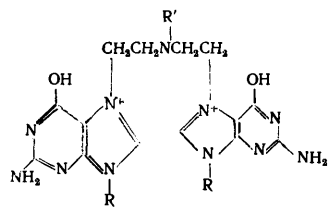
may also be regarded as unsymmetrical bifunctional compounds.

According to Baker[134-137], the natural parts of such molecules are capable of being adsorbed on the active centre of an enzyme, while the alkylating residue, reacting with a neighbouring nucleophilic group, may fix the whole molecule in this position.

## 2. A Special Feature in the Structure of Bifunctional Alkylating Compounds

The overwhelming majority of bifunctional alkylating compounds with pronounced anti-tumour activity are characterised by an important structural feature; the electrophilic centres of the bifunctional compounds are connected together by a chain of atoms which is preserved in the alkylating reaction. Because of this property, such compounds are capable of "stitching" DNA molecules, or cell nucleoproteins, forming so-called cross-linked bonds (cross-linking effect), which, in the opinion of some workers should lead to a sharp dislocation of the mitotic process[138-140].

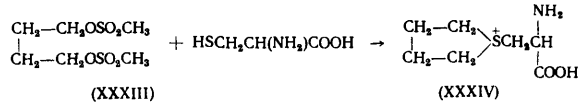
Several experimental results confirming this view have been obtained. Price and coworkers[141] proved indirectly that cross-linked bonds are formed between the DNA chains when DNA is treated with a derivative of bis-(2-chloroethyl)amine; cross-linked bonds are formed between the DNA chains because of the formation of $N_7$ derivatives of guanine:



Lowley and Brookes hydrolysed DNA that had been treated with bis-(2-chloroethyl) sulphide or Embichin, and they separated and identified cross-linked pairs of the bases guanine–guanine and guanine–cytosine[142]. Similar products are formed by the action of bis-(2-chloroethyl) sulphide on nucleic acids *in vivo*.[143]

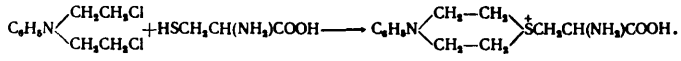
Earlier work of Alexander[144] indicates the possibility of cross-linking chains of DNA by the reaction of bifunctional compounds with phosphate residues.

The property of non-interaction between the two electrophilic centres in bifunctional compounds also favours the reaction of both centres with the same atom to form specific cyclic products. At present it may be considered proved that when "Mileran" (XXXIII) is introduced into the blood of animals, it reacts with cysteine to form a cyclic compound (XXXIV)[4,151-153]

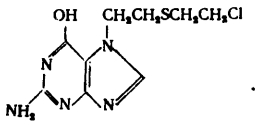


(XXXIII) (XXXIV)

There are also indications that, under biological conditions, the chloroethylamines are capable of forming unstable cyclic products of the thiazan type [128]:

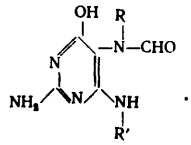


When only one of the two alkylating centres reacts with a molecule of metabolite, compounds termed alkylating metabolites are formed. Timmis showed that an alkylating derivative of guanine is formed in tissue treated with bis-(2-chloroethyl) sulphide [154,155]:



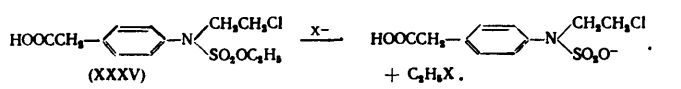
The formation under biological conditions in the body of (2-chloroethyl)cysteine [2] with alkylating properties has been mentioned above.

However, some workers cast doubt on the biological significance of the effect of cross-linking DNA chains [145,146]. Alkylation of DNA is accompanied by degradation of the molecule. Thus alkylation of guanine on the $N_7$-position may lead to the depurinisation of DNA, [141,147] or it is accompanied by the oxidative cleavage of the imidazole ring with the formation of the formyl derivative of an aminopyrimidine [148]:



In the reactions mentioned above, the system of hydrogen bonds in the doubly stranded DNA molecule is destroyed and this facilitates rupture of the DNA; the viscosity of the DNA gradually falls [149]. Brookes and Lowley consider that the high biological activity of bifunctional alkylating agents is due to their ability to destroy simultaneously the structure of both strands of DNA. [150]

Recently, in animal experiments, the anti-tumour activity of a compound containing a new unsymmetrical bifunctional alkylating group has been observed; this is the ester of an *N*-(2-chloroethyl)arylsulphamic acid (XXXV): [20,21]



(XXXV)

The electrophilic centres of compound (XXXV) are separated in the alkylation reaction. The result of this work is a direct proof that non-interaction of the electrophilic centres of bifunctional alkylating agents is not a necessary condition for anti-tumour activity.

---o0o---

The property of alkylating compounds of attacking tumerous tissues cannot be connected with any definite alkylation mechanism. Different types of alkylating compounds with anti-tumour activity differ materially in reactivity. They include compounds capable of reacting with nucleophilic agents by both $S_N1$- and $S_N2$-mechanisms and also compounds that react by a mixed mechanism. Diazo-compounds and derivatives of nitrosoalkylurea react with nucleophilic centres through a stage in which free radicals are formed.

It is interesting to note that the reaction of acylation products does not lead to selective attack on tumour cells (there is not a single anti-tumour "acylating" agent), although acylating compounds (for example, anhydrides, acid chlorides, etc.), like alkylating compounds, contain strong electrophilic centres and are capable of reacting with nucleophilic centres in the living cell.

Examination of the structure and chemical properties of intermediate products of the conversion of alkylating agents under living conditions in the body shows that many of these may be active biologically. This shows that the anti-tumour activity of alkylating compounds is not necessarily the result of their direct action on the cell, but may be connected, at least in some instances [156], with subsequent reactions of the primary interaction products of these compounds with metabolites of the living organism.

It is important to note that the anti-tumour activity of alkylating compounds is connected with their ability to act selectively precisely on those cell processes which determine the difference between tumour cells and healthy cells, and this property must be directly related to the specific chemical behaviour of alkylating agents. The elucidation of this specificity will open the way to further progress in the development of anti-tumour preparations.


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# COMPLEX COMPOUNDS OF GERMANIUM AND ITS STATE IN SOLUTION

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In connection with the increasing interest taken in germanium in the last two decades, many of its complex compounds have been described, particularly in the literature on analytical chemistry, but the available information is extremely limited. In many cases, only the fact of complex formation has been established, and even the composition of the complexes has not been determined. There are very few quantitative data on the stability and other properties of germanium complexes. The incomplete nature of the experimental material makes it difficult to use for the solution of various theoretical and practical problems in technology, analytical chemistry, geochemistry, etc.

No reviews have been published on the chemistry of germanium complexes. Grinberg's monograph [1] characterises the ability of germanium to form complexes, in relation to its position in the Periodic System. Reviews of the chemistry of germanium [2,3] and textbooks of general chemistry give only fragmentary information.

In the present review we have tried to summarise data on the present state of the chemistry of germanium complexes. Since complex formation is closely related to the state of an element in solution and since this question has been insufficiently studied for the case of germanium, we shall examine this problem at the same time.

The chemistry of germanium complexes has certain characteristic features. In accordance with its position in the Periodic System, germanium, which is an analogue of silicon and tin, shows in its complex compounds the dual nature characteristic of an element intermediate between metal and non-metal. As in the case of silicon, complexes with oxygen-containing ligands are more characteristic of germanium, but in the formation of these complexes in aqueous medium, germanium in many cases behaves as a cation, like tin. Like silicon, germanium readily forms heteropoly-acids with molybdenum and tungsten. On the other hand, germanium, like tin, belongs to the hydrogen sulphide analytical group, and forms thio-complexes, although these are less stable than those of tin. Complexes with nitrogen-containing ligands, in the form of addition compounds of the tetrahalides, are known both for germanium and for silicon and tin, but only germanium and tin, unlike silicon, form complexonates.

The characteristic coordination number of quadrivalent germanium is 6, and that of bivalent germanium 4.

## State of Germanium in Aqueous Solution

Bivalent germanium is formed by the reduction of $GeO_2$ with hypophosphorus acid in hydrochloric-acid solution [4,5]. According to Pugh [6], the acidic properties of bivalent germanium hydroxide are similar to those of tervalent arsenic hydroxide. According to the data of Everest and Terrey [7], however, bivalent germanium hydroxide exhibits no acidic properties. These authors concluded that the acidic properties attributed to $Ge(OH)_2$ were due to the presence of quadrivalent germanium. The suggestion of Hantzsch and Carlsohn [8] that equilibrium exists between bivalent germanium hydroxide and germanic acid is not now taken into consideration.

As a result of the ease of hydrolysis and the tendency to form complexes, $Ge^{2+}$ cations do not exist in aqueous solution, although they have been found in crystalline germanium diiodide [9].

Aqueous solutions of $GeO_2$ contain the ions of metagermanic acid $H_2GeO_3$ and pentagermanic acid $H_2Ge_5O_{11}$. The ratio between them is determined by the pH of the solution and the total germanium concentration [10,11]. At a $GeO_2$

concentration less than 0.01 M, only the ions of metagermanic acid are present; the ions of pentagermanic acid are present in more concentrated solutions [12,13] at definite pH values. Everest and Salmon [14,15] showed by the ion-exchange method that in the pH range 6.9–9.4 the only germanium ion is the singly charged ion of pentagermanic acid $HGe_5O_{11}^-$. Above and below these pH values, depolymerisation of the pentagermanate ions takes place with the formation of metagermanic acid. It has been suggested [16,17] that germanium forms not pentagermanate ions but complex heptagermanate ions $HGe_7O_{16}^{3-}$ and $H_2Ge_7O_{16}^{2-}$. Brintzinger [18] showed that in strongly alkaline solutions (2.5 M KOH) quadrivalent germanium is present in the form of $[Ge(OH)_6]^{2-}$ ions. On the basis of all these data, Dhar [19] established the following ranges of existence of various ions of germanic acids in solution —

$$HGeO_3^- \rightleftarrows HGe_5O_{11}^- \rightleftarrows HGeO_3^- \rightleftarrows [Ge(OH)_6]^{2-},$$
$$pH\ 6 \leftrightarrow pH\ 9.4 \leftrightarrow pH\ 11 \leftrightarrow pH > 13.$$

It has not been possible to isolate germanic acids in the solid state from solution. The isolation of pentagermanic acid, reported by Carpeni and Tchakirian [10,20], was not confirmed by later work [21].

The following values are accepted [22] for the ionisation constants of metagermanic acid: $K_1 = 2.6 \times 10^{-9}$ and $K_2 = 1.9 \times 10^{-13}$ at 20°, in accordance with Pugh's measurements [23]. Later, other workers obtained for the first ionisation constant of metagermanic acid values close to that given above: Gulezian and Müller [24] between $1.0 \times 10^{-9}$ and $3.0 \times 10^{-9}$ at 25°, Carpeni [25] $0.79 \times 10^{-9}$ at 12°, and Lourijsen-Teyssèdre [12] $0.89 \times 10^{-9}$. The thermodynamic value of the first ionisation constant of $H_2GeO_3$ according to Antikainen [26] is $1.86 \times 10^{-9}$ at 25°. The values of $K_1$ for metagermanic acid, obtained by Roth and Schwarz [27] ($1.2 \times 10^{-7}$ at 18°) and by Schwarz and Huf [28] ($0.5 \times 10^{-7}$ at 20°) are too high, owing to the inadequate purity of the germanium dioxide used. The value obtained by Carpeni [25] for the second ionisation constant of metagermanic acid ($2 \times 10^{-13}$ at 12°) agrees with the value given by Pugh.

Antikainen [26] established that temperature has an unexpectedly marked influence on the ionisation of metagermanic acid. Thus with increase in temperature from 10° to 45°, the first ionisation constant of $H_2GeO_3$ increases by a factor of almost 20. This marked effect of temperature is not observed with weak acids [29]. Increase in temperature apparently leads to the polymerisation of metagermanic acid and the formation of a certain quantity of the stronger polygermanic acids.

Antikainen [30] also observed the formation of polygermanic acids in the preparation of concentrated (0.23 M) solutions of germanium dioxide by means of a cation-exchange resin. According to him, these solutions contain singly charged di- and tri-nuclear oxoanions of germanium. The polynuclear peroxo-complex of germanium $[Ge_n(H_2O_2)_4]^-$, where $n = 2–3$, is formed by the action of hydrogen peroxide on 0.01–0.02 M solutions of metagermanic acid [31]. The equilibrium constant for the formation of the mononuclear peroxo-complex is $K = [Ge(H_2O_2)_2^-]/[HGeO_3^-][H_2O_2]^2 = 48$. The stability of certain polyoxoanions has been examined by Yatsimirskii [32].

Tchakirian suggested that metagermanic acid, like boric, phosphoric, and arsenious acids, reacts under certain conditions with the sulphates, chlorides, or nitrates of alkali and alkaline earth metals to form complex acids [33].

Hardly any work has been done on quadrivalent germanium cations. De Carvalho and Lederer [34] merely point out the possibility that cationic forms of germanium may exist in acidic solutions. On the basis of a comparison of the solubilities of germanium dioxide and arsenic sesquioxide, Pugh [35] suggested that the basic dissociation constant of $GeO_2$ should be less than that of $As_2O_3$, which is close to $10^{-14}$. Everest and Salmon [14], on the basis of experiments with cation-exchange resins, concluded that no germanium cations are present in solution in the pH range 7–1. The statement [36] that the $Ge^{4+}$ cation is formed at pH 3.36–3.31, according to the equilibrium $GeO_3^{2-} + 6H^+ \rightleftharpoons Ge^{4+} + 3H_2O$, is without foundation and has been criticised [37,38]. $Ge^{4+}$ cations probably appear as one of the equilibrium forms only in strongly acid solutions.

The existence of germanium cations in weakly acidic solutions is confirmed by observation and by everyday analytical practice. Germanium lies in the same group of the Periodic System as tin, titanium, zirconium, and hafnium, for which $MO^{2+}$, $M(OH)_2^{2+}$, and $M^{4+}$ ions are known. Like tin and zirconium, germanium reacts with phenylarsonic acid and its derivatives [39]. In its reactions with sulphides and *o*-hydroxyquinones, the behaviour of germanium is analogous to that of tin. The existence of the germanyl ion $Ge(OH)_2^{2+}$ or $GeO^{2+}$ is confirmed by the formation of germanyl cyanoferrate(II) $[Ge(OH)_2]_2[Fe(CN)_6]$ or $(GeO)_2[Fe(CN)_6].2H_2O$ when potassium cyanoferrate(II) is added to an acidic solution of sodium germanate [40].

Migration experiments have made it possible to detect germanium cations in weakly acidic solutions and to establish the approximate ranges of their existence [41]. The germanium dioxide concentration chosen for these experiments excluded the possibility of formation of colloidal particles of $GeO_2$. The results show that germanium cations are produced at pH ~ 7 and exist together with anions of germanic acids. The relative quantity of germanium cations increases with decrease in pH. These data have been subsequently confirmed by experiments on the sorption of germanium by cation-exchange resins (KU-1, KU-2, and Wofatit No. 4) and anion-exchange resins (AV-16, AV-17, AV-27) on columns [42] and under static conditions [43].

## State of Germanium in Inorganic Acid Solutions

Everest [44] suggests that bivalent germanium exists in acidic solutions only in the form of complex compounds. Hydrohalic acids contain acido-complexes $HGeX_3$, whose salts $MGeX_3$ (where M is an alkali metal and X chlorine, bromine, or iodine) have been isolated [45,46]. The complex phosphate $Ge_3(PO_4)_2.2GeHPO_4$ [44] and complex halogenohypophosphites of germanium $Ge(H_2PO_2)_2.GeCl_2$, $Ge(H_2PO_2)_2.GeBr_2$, and $3Ge(H_2PO_2)_2.GeI_2$ [44,46] have been prepared.

The state of quadrivalent germanium in solutions of inorganic acids has been studied considerably more fully. In hydrofluoric acid, quadrivalent germanium readily forms six-coordinated complexes. Tananaev and Avduevskaya [47] established in the $GeO_2$–HF–$H_2O$ system the existence of complex acids having the compositions $H_2[GeOF_4].2H_2O$ and $H_2[GeF_6].2H_2O$, which were isolated in the solid state. These acids are stronger than hydrofluoric acid; hydrogen hexafluorogermanate $H_2GeF_6$, which is formed at higher HF concentrations, is the strongest acid. No complexes of higher fluorine content are formed. Fluorogermanate complexes are more stable than fluorosilicate complexes. Thus alkali-metal hexafluorogermanates dissolve in

100% HF without decomposition[48], unlike the hexafluorosilicates, which decompose under these conditions with the liberation of silicon tetrafluoride[49]. Comparison of the relationship between the stability of the fluoro-complexes and the position of the element in the Periodic System[50] shows that the stability in general increases with decrease in the radius of the central ion, but this relationship is complicated by the competing influence of the bond between the complex-forming ion and oxygen. The competing influence of the bond with oxygen is clearly shown for the fluoro-complexes of the Ge–Si pair.

Cryoscopic studies[52] in 0.01–0.2 M solutions of K, Rb, and Cs hexafluorogermanates show that a molecule of the salt forms three ions. The solubilities of $K_2GeF_6$, $Rb_2GeF_6$, and $Cs_2GeF_6$ in water at 25° are 0.0221 M, 0.0167 M, and 0.0471 M respectively.

Hexafluorogermanates are decomposed completely by alkalis. The hydrolysis of hexafluorogermanates in water is autocatalytic and takes place by a solvolytic dissociation mechanism[51]:

$$GeF_6^{2-} + H_2O \rightleftarrows Ge(OH)F_5^{2-} + HF.$$

This reaction is followed by rapid hydrolysis of the $Ge(OH)F_5^{2-}$ ion to $GeO_2$.

According to the data of Benoit and Place[53], the hexafluorogermanate complex is not formed in acid solutions. Depending on the HF concentration, mononuclear hydroxofluorogermanate complexes $Ge(OH)_jF_i$ are formed, where the maximum value of $i$ is 5. The overall stability constants of the complexes $Ge(OH)_jF_5^{(j+1)-}$ and $Ge(OH)_jF_4^{j-}$, determined in 0.5 M $HClO_4$, are $\beta_5' = (8.8 \pm 0.2) \times 10^8$ and $\beta_4' = (2.0 \pm 0.3) \times 10^7$ respectively. The fluoro-complexes of germanium, like the tin complexes, are not decomposed by hydrogen sulphide, and this is used in analysis to separate germanium from arsenic[54]. The sorption of hydrogen fluorogermanate on an anion-exchange resin is also used for this separation[55].

The fluorination of metallic germanium by the action of $ClF_3$ in liquid hydrogen fluoride leads to the formation of hydrogen hexafluorogermanate, which can then be isolated as the silver salt[56]. As in the case of aqueous solution, the fluorogermanate complex in liquid hydrogen fluoride is more stable than the fluorosilicate complex, and is readily formed.

The ease of formation of the fluoro-complexes also extends to the fluoro-organometallic compounds of germanium and the fluorogermanes. Thus the addition of KF to trifluoromethyltrifluorogermane $CF_3GeF_3$ in aqueous solution gives a sparingly soluble precipitate of $K_2[CF_3GeF_5]$. Clark and Willis[57] studied this reaction and suggest that in aqueous solution $CF_3GeF_3$ forms ionised molecules of the type $CF_3Ge(OH)_2F_3^{2-}$ and $CF_3Ge(OH)_3F_2^{2-}$ as a result of hydrolysis. The hydrolysis is readily reversible, and the addition of KF to the solutions precipitates $K_2[CF_3GeF_5]$. Monofluorogermane $GeH_3F$ reacts with ammonia at -78° to give[58] the addition product $GeH_3F.2NH_3$, which decomposes at 25° to $NH_3$ and $[GeH_3.NH_3]F$. The latter compound decomposes only at 180°.

The hexachlorogermanate complex is formed much less readily than the hexafluorogermanate complex. The hexachlorogermanates of caesium[59–61] and rubidium[60,61] are formed under special conditions. After unsuccessful attempts[62] tetramethylammonium hexachlorogermanate $[N(CH_3)_4]_2GeCl_6$ was also prepared[60]. Attempts to isolate free hydrogen hexachlorogermanate $H_2GeCl_6$ were unsuccessful[59,61,63]. Nevertheless, the maximum on the solubility curve for germanium dioxide in hydrochloric acid[64] and the mechanism of the extraction of germanium from hydrochloric-acid solutions[65,66] are attributed to the existence of this acid as one of the equilibrium forms. It is claimed that the decrease in the solubility of $GeO_2$ after the maximum[64], and the decrease in the partition coefficient for germanium[65,66], are due to the decomposition of $H_2GeCl_6$ and the separation of $GeCl_4$ as a separate phase with increase in the concentration of hydrochloric acid.

A study of solutions of germanium dioxide and tetrachloride in hydrochloric acid using ion exchange led Everest and Harrison[61] to the conclusion that in 6–9 M HCl an equilibrium exists between metagermanic acid or germanium dioxide and the chlorogermanate anions $GeCl_5^-$ or $GeCl_6^{2-}$. Intermediate acido-complexes of the type $[Ge(OH)_xCl_{5-x}]^-$ and $[Ge(OH)_xCl_{6-x}]^{2-}$, where $x$ = 3 or 4, take part in the equilibrium. It is suggested that the singly charged acido-complex is more likely to be formed. The intermediate acido-complex is the chief form of germanium compound in 6.5–9 M HCl. At HCl concentrations lower than 6.5 M, hydrolysis of the intermediate complex takes place with the precipitation of germanium dioxide. Increase in the hydrochloric acid concentration above 9 M leads to chlorination of the intermediate acido-complex with the separation of germanium tetrachloride as a separate phase. The quantity of $GeCl_6^{2-}$ ions taking part in the equilibrium could not be determined by the ion-exchange method. By measuring the ultraviolet absorption of hydrochloric-acid solutions of germanium tetrachloride, Angerstein and Davidson[67] found that photometrically measurable quantities of $GeCl_6^{2-}$ ions appear in 6–7 M HCl and reach a concentration of 80% in 12 M HCl; with increase in the HCl concentration above 12 M, the concentration of hexachlorogermanate ions increases, but does not reach 100%. This last fact agrees with the data of Benoit and Clerc[68], who consider, moreover, that formation of the $GeCl_6^{2-}$ ion in anhydrous HCl is unlikely. In this, germanium differs from tin, since the $SnCl_6^{2-}$ ion is formed under these conditions[62].

Using the ion-exchange method, Nelson and Kraus[69] obtained results which indicated that the formation of anionic complexes of germanium is negligible at HCl concentrations in the range 0.1–4 M. This was confirmed by later work in the same laboratory[70]. With increase in the HCl concentration, the degree of complex formation increases, giving no maximum up to the highest HCl concentrations and passing through the range of formation of the uncharged $GeCl_4$ species without the separation of germanium tetrachloride as a separate phase. The lack of agreement in this respect with other data[61,64–66,67–69] is most probably due to differences in the germanium concentrations in the solutions. Thus in the experiments of Nelson and Kraus[69] at low germanium concentrations, $GeCl_4$ could not separate as an individual phase because of its dissolution, so that all the germanium remained in solution; increase in the HCl concentration produced hexachlorogermanate ions, which were more strongly absorbed by the resin. The solubility of $GeCl_4$ in hydrochloric acid has been discussed by Knyazev[71].

Brauer and Müller[64] assume that hydrobromic acid solutions contain uncharged complex species of the type $Ge(OH)_{4-x}Br_x$, where $x$ may have values of 1–3, depending on the acid concentration. The existence of a small quantity of species of this type in hydriodic acid is also possible.

The solubility curve for germanium dioxide in sulphuric acid shows a slight maximum at an $H_2SO_4$ concentration of 15 $N$, but this is not explained by Brauer and Müller. The formation of a more soluble sulphato-complex of germanium may be assumed in this case. In general, however, the tendency of germanium to form complexes with sulphate ions is slight. This can be seen from the fact that the solubility curve for $GeO_2$ in sulphuric acid differs little from the corresponding curves for perchloric and nitric acids, in which germanium is thought to form no anionic complexes. Other workers also observed no formation of complexes by germanium in nitric-acid solutions [72,73].

On the basis of the results of a study of ion exchange in germanium dioxide solutions containing sulphate and phosphate ions, Everest and Salmon [15] suggest the existence of complex ions $[GeO_2(SO_4)]^{2-}$ and $[HGeO_2(PO_4)]^{2-}$ in the pH range 7–9. In a study of the reaction of soluble germanium dioxide with orthophosphoric acid, Everest [44] established that in 35–50% $H_3PO_4$ a compound is formed corresponding to the formula $Ge(HPO_4)_2$; this compound is readily hydrolysed and dissolves in concentrated $H_3PO_4$. Avduevskaya and Tananaev [74] consider that the dissolution of germanium dioxide in concentrated orthophosphoric acid is due chiefly to complex formation. They therefore regard the new phase with composition $GeO_2.P_2O_5.2H_2O$, which they isolated, as hydrogen diphosphatogermanate, having the formula $H[Ge(OH)(HPO_4)_2]$ or $H_2[GeO(HPO_4)_2]$.

## Germanium Heteropoly-Acids

On the basis of the work of Pfeiffer [77], who supplemented the theories of Miolati and Rosenheim, the first workers to study germanium heteropoly-acids [68,75,76] ascribed to these compounds the formulae $H_8[Ge(Mo_2O_7)_6]$ and $H_8[Ge(W_2O_7)_6]$. Subsequent work on the preparation, structure, and properties [80,83–92] of germanium heteropoly-acids was related to their extensive use in analysis [93]. The compounds prepared included molybdovanadogermanic [78–83] and tungstovanadogermanic [83–92] heteropoly-acids, in which isomorphous replacement of molybdenum or tungsten in the heteropoly-anion by vanadium takes place. This is confirmed by electron-diffraction studies of molybdovanadogermanic heteropoly-acids [88].

Heteropoly-acids of germanium, like those of other elements, are formed in acid medium. The optimum acidity for molybdogermanic acid is 0.2–0.5 $N$ $H_2SO_4$. Once formed, the germanium complexes are stable in more acidic solution; thus molybdogermanic acid does not decompose [94] even in 3.3 $N$ $H_2SO_4$. The ternary heteropoly-complexes of germanium are less stable than the binary complexes. The acidity of stable solutions of molybdovanadogermanic acid [95] corresponds to 0.20–0.28 $N$.

Germanium heteropoly-acids also decompose with increase in the pH of the solution.

Tchakirian and Souchay [86] found that at pH 3.2 dodecatungstogermanates begin to undergo conversion to undecatungstogermanates. The conversion is almost complete at pH 4.2. At pH > 7.3, undecatungstogermanates decompose completely to germanates and tungstates. The molybdenum heteropoly-complexes are less stable than the corresponding tungsten compounds. The undecamolybdogermanate anion exists in the pH range 3.5–4.2; at pH > 4.2, this compound begins to decompose to germanate and molybdate [96], the reaction being complete at pH 5.4. Unlike molybdosilicic acid, molybdogermanic acid [97] resembles molybdophosphoric acid [98] in its ready decomposition by hydroxy-carboxylic acids, e.g. citric acid.

Spectrophotometric and electron-diffraction study of the blue products of the reduction of germanium heteropoly-acids showed that the heteropolyanions and the blue compounds formed from them have the same structure [87,88]. In the blue anion, part (approximately one-quarter) of the molybdenum or tungsten is present in the quinquevalent state but occupies the same position in the complex as in the original heteropoly-acid. The blue colour is produced as a result of the intensification of the polarisation effect, due to the presence, in the molecule of the compound, of ions of the element with different valencies. In contrast to the previously accepted view [99,100] that the molybdenum or tungsten coordinated in heteropoly-acids exhibits an increased oxidising power, it was shown [87,88] that the redox potentials of the $Mo^{VI}/Mo^{V}$ and $W^{VI}/W^{V}$ systems in heteropoly-compounds are not higher but lower than the potentials of uncomplexed molybdenum and tungsten, and that the increased redox potential is shown by the whole complex heteropolyanion. The introduction of vanadium into the heteropolyanion considerably raises the redox potential of the latter [87].

A large amount of practical information, which has been obtained and used chiefly in analytical chemistry [76,78,85,90,101,112], shows that the germanic heteropoly-acids form no more than tetra-substituted salts with simple and complex inorganic and organic bases. This contradicts the views of Miolati, Rosenheim, and Pfeiffer, according to whom germanium heteropoly-acids should be octabasic. The low basicity of molybdenum and tungsten heteropoly-acids was explained successfully by Keggin and his followers [85,113–115] on the basis of X-ray structural measurements. Physicochemical studies established that dodecatungstophosphoric acid is tribasic [116] and that dodecatungstogermanic [91] and dodecatungstosilicic [117] heteropoly-acids are tetrabasic. On the other hand, there are experimental data confirming the high basicity of certain other heteropoly-acids and these data cannot be explained by Keggin's treatment. Thus it has been shown that dodecamolybdoceric [118–120], dodecamolybdothoric [121], and dodecamolybdostannic [122] heteropoly-acids are octabasic.

Babko and Shkaravskii [123] explain the contradiction between the views of Miolati, Rosenheim, and Pfeiffer on the one hand and Keggin on the other in terms of the ratios of the radii of oxygen and the central ions in the heteropoly-complex. With small central ions (radius 0.30–0.56 Å) — $Bi^{III}$, $Si^{IV}$, $Ge^{IV}$, $P^{V}$, and $As^{V}$ — the compounds should show a coordination number of 4 with tetrahedral configuration of the oxygen environment and a corresponding basicity for the heteropoly-acids of 8 - $n$, where $n$ is the valency of the central ion. With large central ions having a radius of 0.56–0.99 Å — $Sn^{IV}$, $Ce^{IV}$, and $Th^{IV}$ — the octahedron is the more stable, and the basicity of the corresponding heteropoly-acids should be 12 - $n$. Not all of the facts, however, fit into this scheme: dodecamolybdozirconic [124,126] and dodecamolybdotitanic [125,126] heteropoly-acids are tetrabasic, although the radii of the $Ti^{4+}$ and $Zr^{4+}$ ions are greater than 0.56 Å (0.64 Å and 0.87 Å respectively).

The experimental data and theoretical considerations indicate nevertheless that germanium heteropoly-acids are tetrabasic.

## Addition Compounds Formed by Germanium Tetrahalides

The complex-forming properties of germanium tetrahalides are due to the ability of the central atom to fill the *d* level of its outer electronic shell by using the free electron pairs of attached ligands. In the addition products formed by germanium tetrahalides, these ligands are chiefly ammonia [127] and nitrogen-containing bases — hydrazine, piperidine, pyrrolidine [127], ethylenediamine [127,128], 2,2′-bipyridyl [129], 1,10-phenanthroline [130], pyridine [128-130], trimethylamine, *NNN′N′*-tetramethylethylenediamine [131], triethylamine [132,133], and *o*-hydroxyquinoline [128,134]. These addition products are usually readily hydrolysed by water. On the other hand, amines of high molecular weight, e.g. an *N*-dodecyltrialkylmethylamine [135], form stable addition complexes with germanium tetrachloride, and these can be extracted from hydrochloric-acid solutions with non-aqueous solvents.

Addition products are particularly numerous with germanium tetrafluoride, which forms complexes $GeF_4.2L$ and $GeF_4.L$ (here and subsequently L represents a ligand) with compounds containing nitrogen, phosphorus, oxygen, or sulphur [127]. Besides the complexes with the nitrogen-containing compounds listed above, complexes have been prepared with phosphine and trimethylphosphine, with acetone, ethylene oxide, methanol, tetrahydrofuran, and dioxan, with hydrogen sulphide, dimethyl sulphide, methanethiol, and tetrahydrothiophen. These complexes are relatively unstable. It is suggested that the 1:2 complexes have an octahedral structure with *cis*- and *trans*-arrangement of the ligands, and that the 1:1 complexes are polymeric fluorine-bridged structures [127].

Udovenko and Fialkov measured the viscosity [136] and dielectric constant [137] of systems formed by germanium tetrachloride with ethers and esters, and established that in these systems $GeCl_4$, unlike the tetrachlorides of titanium and tin, does not form addition compounds. The lower complex-forming power of germanium tetrachloride compared with $SnCl_4$ and $TiCl_4$ was attributed [136] to the smaller ionic radius of germanium compared with the ionic radii of tin and titanium, and the consequent greater screening of the germanium ion by chloride ions. The greater screening of the germanium ion by chloride ions, compared with the screening by fluoride ions, may also explain the fact that the complex-forming power of $GeCl_4$ is less than that of $GeF_4$.

## Complex Compounds of Germanium with Polyhydroxy-Compounds.

The addition of a polyhydric alcohol or a monosaccharide to a neutral aqueous solution of germanium dioxide leads to a decrease in the pH of the solution as a result of the formation of complex acids which are stronger than simple germanic acids. Tchakirian [33,138], who was the first to describe this phenomenon, assumed that in the case of mannitol a dinuclear complex with a germanium:ligand ratio of 1:1 and the properties of a dibasic acid is formed. Saito [139] found by high-frequency titration and pH and polarographic measurements that in the complex fructosatogermanic acid the germanium:ligand ratio is 1:4, but this was not confirmed by other authors. In addition, a 1:1 complex which is reduced at a mercury electrode is also formed. Contradictory data on the composition of the complexes of germanium with ethylene glycol, glycerol, and mannitol were obtained by Everest and Harrison [140,141] by an ion-exchange method. Antikainen [142,143] established by a differential potentiometric method that germanium forms 1:2 complexes with mannitol, glucose, galactose, mannose, and fructose, and also 1:1 complexes with glycerol and glycols. Antikainen's data were confirmed by pH measurements [144]. It was established that in the presence of excess of glycerol, mannitol, glucose, galactose, and fructose, complex monobasic acids with a germanium:ligand ratio of 1:2 are formed; the thermodynamic ionisation constants of these acids at 25° are $5.05 \times 10^{-6}$, $1.21 \times 10^{-5}$, $8.35 \times 10^{-6}$, $2.39 \times 10^{-5}$, and $1.04 \times 10^{-4}$ respectively. Mannitol [33,138,145-148], fructose [149], and invert sugar [150], consisting of fructose and glucose, are used in analytical chemistry for the alkalimetric determination of germanium.

According to Antikainen [143,151], the ability of polyhydroxy-compounds to form complexes increases in the sequence — ethylene glycol, propylene glycol, butylene glycol, 3-methoxypropane-1,2-diol, glycerol, D-galactose, D-glucose, D-mannose, D-mannitol, and D-fructose. This agrees with the results obtained by other authors [140,152,153]. Antikainen and his coworkers [142,143,151,154,155] determined the formation consists of a large number of complexes of germanium with polyhydroxy-compounds, in order to characterise their relative stability. In the calculations these workers used the apparent ionisation constants of metagermanic acid in the presence of the polyhydroxy-compound and neglected the changes in the activity coefficients of the ions present in the solution with change in the concentration of the polyol, assuming that the latter concentration and the ionic strength of the solution had no influence on the formation constants of the complexes. In fact, however, it has been shown [153] that both the concentration of polyhydroxy-compound and the ionic strength have a marked influence on the formation of polyol complexes of germanium. The thermodynamic constants for dissociation of the diglycerolato-, diglucosato-, digalactosato-, dimannitolato-, and difructosato-germanate complexes, according to the equation $GeL_2^- + m H_2O \rightleftharpoons HGeO_3^- + 2L$, determined with allowance for this influence, have the values $7.85 \times 10^{-2}$, $3.54 \times 10^{-2}$, $7.64 \times 10^{-3}$, $4.04 \times 10^{-4}$, and $4.24 \times 10^{-5}$ respectively at 25°.

Some of the factors influencing the formation of complexes by germanium with polyhydroxy-compounds have been studied [139,151,154,155]. Increase in the number of carbon atoms and hydroxy-groups in the ligand leads to the formation of more stable complexes. Ketoses give more stable complexes than do aldoses. Complexes having the ratio 1:2 are characteristic of polyhydroxy-compounds containing a large number of hydroxy-groups, and the spatial arrangement of the latter is also important. The formation of lactol forms in solution by saccharides decreases their tendency to form complexes. Mutarotation, which changes the spatial arrangement of the hydroxy-groups and depends on the pH of the solution, also influences the formation of complexes. When the saccharide ligand is present in the lactol form, the influence of the number of carbon atoms and hydroxy-groups in less marked than that for an open chain.

## Complexes of Germanium with Carboxylic Acids.

Complexes of germanium with tartaric [156-161], tartronic [159], quinic, 1-hydroxycyclopentanecarboxylic [160], malic [157,158,160], mucic [160,161], phenyllactic, bromomandelic, benzilic, 2-hydroxyoctanoic [162], lactic [161,162], gluconic [160,161,163], mandelic [158-160,162,164,165], and oxalic [33,166-168] acids have been described. Acids such as tropic, diglycollic, glyceric,

ascorbic, and γ-hydroxybutyric acids do not form complexes with germanium [160].

Data on the composition of the complexes of germanium with carboxylic acids are often contradictory. Thus the values of the germanium : ligand ratio given by different authors are 1 : 1 and 1 : 2 for tartaric acid, 1 : 1, 1 : 2, and 1 : 3 for lactic acid, 1 : 1 and 1 : 2 for mucic acid, and 1 : 2 and 1 : 3 for mandelic acid. These discrepancies are due to the fact that the compounds formed and the ranges of their existence in solution have been inadequately studied. The tartrato- and oxalato-complexes of germanium have been studied in more detail, because of their use in analysis [169-172].

Everest and Harrison [161] established by an ion-exchange method that a 1 : 1 tartrato-complex of germanium is formed in the pH range 0.78–9; the complex is decomposed completely at pH > 11. With increase in the germanium concentration in a large excess of tartaric acid, a complex having a germanium : ligand ratio of 2 : 3 is formed; an excess of germanium leads to the formation of a 5 : 4 polynuclear complex. Everest and Harrison did not establish the existence of the 1 : 2 tartrato-complex, but the isolation [169] of barium tartratogermanate $Ba_2GeC_8H_8O_{14}.2H_2O$ indicates its existence.

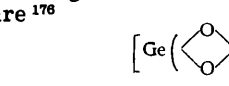
The oxalato-complex of germanium is a dibasic acid; salts of this acid with the organic bases quinine, strychnine, and benzoquinoline have been isolated [33,172-174]. The hexahydrate $H_2[Ge(C_2O_4)_3].6H_2O$ has been obtained in crystalline form [168]. Study of the infrared spectra of solutions of germanium dioxide in oxalic acid confirms that the compound formed is complex [175]. It was found by an ion-exchange method [167] that oxalato-complexes of germanium are not formed in alkaline medium; at pH < 3, complex ions $[Ge(C_2O_4)_3]^{2-}$ are sorbed, together with a small quantity of $[HGe(C_2O_4)_3]^-$ and $[HGeO(C_2O_4)_2]^-$ ions; in the pH range 3–6, and also when the solution contains insufficient oxalate ions, the complexes $[GeO(C_2O_4)_2]^{2-}$ and $[GeO_2(C_2O_4)]^{2-}$ are formed. Solubility studies and measurement of the pH and electrical conductivity [168] in the $GeO_2$–$H_2C_2O_4$–$H_2O$ system also established the existence, in addition to hydrogen trioxalatogermanate, of an intermediate complex acid having a Ge : ligand ratio of 1 : 2; the ammonium and potassium salts of this acid were isolated.

The stability of the complexes of germanium with carboxylic acid has been little studied. According to Vartapetian [158] the stability increases in the order — lactic, malic, mandelic, and tartaric acids.

## Complexes of Germanium with Dihydric Phenols

Germanium dioxide reacts in aqueous solution with simple o-dihydroxy-derivatives (catechol, pyrogallol, benzene-1,2,4-triol, naphthalene-2,3-diol, etc.) to form two types of compound — sparingly soluble neutral complexes $GeL_2.2H_2O$, the so-called germanium–diphenols [176], and the soluble complexes $H_2GeL_3$, termed phenolgermanic acids [177-179] or hydrogen trisdiphenolatogermanates.

Bisarenediolatogermanium complexes are formed in concentrated solutions of germanium dioxide and the dihydric phenol, and are insoluble in organic solvents. The dicatecholatogermanium complex has been assigned the structure [176]



and this has been confirmed by chemical and thermogravimetric analysis [176], by determination of the infrared spectra [180], and by X-ray diffraction studies [181]. The composition $GeL_2.2.5H_2O$ ascribed to this complex [180] does not agree with the above structure.

Bisarenediolatogermanium complexes do not exist in solution but dissociate according to the scheme [176]

$$3\,GeL_2 \cdot 2\,H_2O \rightleftarrows 2\,GeL_3^{2-} + 4\,H^+ + GeO_2.$$

Polarographic, spectrophotometric, and pH measurements have in fact established [182-186] that the only complexes present in germanium dioxide solutions containing dihydric phenols are the corresponding hydrogen trisarenediolatogermanates, which are very strong acids. The thermodynamic second ionisation constants [186] for hydrogen tricatecholatogermanate and tripyrogallolatogermanate at 25° are $(1.85 \pm 0.06) \times 10^{-2}$ and $(2.21 \pm 0.07) \times 10^{-2}$ respectively.

Hydrogen trisarenediolatogermanates are more stable than bisarenediolatogermanium complexes. The formal constants for the formation of the tricatecholato- [185,187], tripyrogallolato- [187], and trithyroninato-complexes [187] were determined without allowance for the ionisation of germanic acid and the corresponding complex acids, and the values do not characterise their true stability. The thermodynamic constants for dissociation of the tricatecholato- and tripyrogallolato-complexes at 25° according to the scheme [188]

$$HGeL_3^- + 3H_2O \rightleftarrows HGeO_3^- + 3H_2L$$

are $(2.16 \pm 0.12) \times 10^{-9}$ and $(0.88 \pm 0.09) \times 10^{-9}$ respectively.

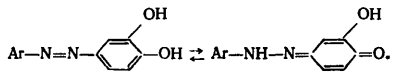
Numerous disubstituted salts of hydrogen trisarenediolatogermanates have been prepared with ammonia, organic bases (pyridine, quinoline, and triphenylmethane dyes), and the complex phenanthrolineiron(II) cation [179]. The formation of phenanthrolinecadmium tricatecholatogermanate $[Cd\,phen_2][Ge(O_2C_6H_4)_3]$ is used for the gravimetric determination of germanium [189], and that of 2,3′-bipyridylium tricatecholatogermanate for the extraction-photometric determination of germanium [190]. The formation of hydrogen tricatecholatogermanate itself is also used in analysis for the volumetric [176,191-193], polarographic [194,195], and amperometric [196] determination of germanium.

Noteworthy complexes are formed by germanium with tannin and humic acids, whose structures are characterised by the presence of one or more aromatic nuclei with two or more phenolic hydroxy-groups. Tannin is of importance in the technology [197] and the analytical chemistry [93,103,198,199] of germanium. In the geochemistry of germanium, the accumulation of the element in coals has been attributed to humic acids. It is suggested that the accumulation is due to the sorption of germanium by humic acids from circulating solutions at the stage when the coal is formed [200-202]. Only preliminary data [203,204] have been given on complex formation by germanium with humic acids, and there are no published data on its complex formation with tannin. This is due to the fact that the individual chemical compounds covered by the general names "tannin" and "humic acids" have been insufficiently studied.

## Complexes of Germanium with Hydroxy-Carbonyl Compounds

Coloured or fluorescent complexes with aromatic hydroxyl-containing ligands play an important part in the analytical chemistry of germanium [93] by providing a basis

for photometric methods for its determination. A characteristic feature of these ligands is the presence of a phenolic hydroxyl in the *ortho*- or, less frequently, the *peri*-position relative to a carbonyl (quinonoid) group, or of two phenolic hydroxy-groups *ortho* to one another, together with a group, *para* or *ortho* to one of these, permitting tautomeric conversion of the compound into an *o*-hydroxyquinone, e.g. for derivatives of 3,4-dihydroxyazobenzene:



All compounds of this class can be divided into two types.

A. Compounds already containing an *ortho*- or a *peri*-hydroxy-carbonyl grouping in the molecule.

(1) Triphenylmethane dyes — pyrogallolaurin, pyrogallolsuccinein, catecholphthalein [205-208], Catechol Violet [209], etc.

(2) Xanthen dyes — gallein [205], coerulein [208], and derivatives of 2,3,7-trihydroxy-6-oxoxanthen with aromatic or aliphatic radicals as substituents on the $C_{(9)}$ carbon atom [210-214], including the familiar photometric reagent for germanium 2,3,7-trihydroxy-6-oxo-9-phenylxanthen or phenylfluorone [215-217].

(3) Flavone dyes — 3-hydroxyflavone [3-hydroxy-4-oxo-2-phenylchromen] [218] and its hydroxy-derivatives: 2',3,4',5,7-pentahydroxyflavone (morin) [218,219], 3,3',4',5,7-pentahydroxyflavone (quercetin), and 3,3',4',5,7-pentahydroxyflavone-6-sulphonic acid (quercetinsulphonic acid) [220,221].

(4) Derivatives of 4*H*-pyran, quinoid dyes of vegetable origin (brazilein [205,207] and haematein [205,207,222]).

(5) The tropolone dye purpurogallin [205-208], and also tropolone itself, 3-hydroxytropolone, and 3-aminotropolone [223]. The latter form colourless complexes with germanium.

(6) Hydroxyanthraquinones, containing a hydroxy-group in the *peri*-position to a carbonyl group and reacting with germanium in concentrated sulphuric acid, e.g. quinalizarin, purpurin, 1,2,4,5,6,8-hexahydroxyanthraquinone [39,224,225], the structurally similar monohydroxynaphthacenequinonesulphonic acid [226], and also acetylquinalizarin [227], which, unlike quinalizarin, reacts with germanium in weakly acidic medium.

(7) Colourless compounds reacting with germanium to form complexes which are luminescent under ultraviolet radiation. These compounds contain a hydroxy-group *ortho* to a nuclear carbon atom attached to a side-chain containing a carbonyl group — 2,4-dihydroxyacetophenone [228], 2,4,6-trihydroxyacetophenone, 2,4-dihydroxy-ω-methoxyacetophenone, 2-hydroxy-4-methoxybenzaldehyde, 2,4-dihydroxybenzaldehyde, and salicylaldehyde [229]. A fluorescent compound with germanium is formed also by benzoin [229], which contains a keto–enol group between two phenyl radicals.

(8) Dihydroxy-derivatives of naphthaquinone [230] — spinazarin, spinochromes B1 and M1, etc.

B. Compounds with an arene-*o*-diol structure, capable of tautomeric conversion into *o*-hydroxyquinones.

(1) *o*-Dihydroxyazo-compounds [205-208] — azobenzene-3,4-diol, 3',4'-dihydroxyazobenzene-4-sulphonic acid, 1-phenylazonaphthalene-2,3-diol, etc.

(2) *o*-Dihydroxy-derivatives of triarylmethanols [205-208] — 3,4-dihydroxytriphenylmethanol, 3,4-dihydroxynaphthyldiphenylmethanol, 4,4'-bisdimethylamino-3",4"-dihydroxytriphenylmethanol, etc.

(3) Schiff bases from dihydroxy-aldehydes and oximes and phenylhydrazones of the latter [205,207] — 3',4'-dihydroxybenzylideneaniline, the phenylhydrazone and oxime of protocatechualdehyde, etc.

(4) 3,5-Dinitrocatechol [205,207].

(5) Anthocyanidins containing hydroxy-groups on the $C_{(3')}$ and $C_{(4')}$ atoms — delphinidin and cyanidin [208] — and also the *o*-dihydroxychromenols with similar structures [231].

(6) Dihydroxy-derivatives of 2-oxochromen — 6,7-dihydroxy-4-methyl-2-oxochromen (methylaesculetin) [230] and 7,8-dihydroxy-4-methyl-2-oxochromen [232].

(7) Dihydroxy-derivatives of benzofuran [208] — 6,7-dihydroxy-3-oxobenzofuran, gallorubin, and 3-*p*-dimethylaminobenzylidene-6,7-dihydroxybenzofuran.

(8) Oxazine dyes — gallocyanine and Modern Violet [205-208].

All these compounds react with germanium in acid medium, forming soluble or insoluble coloured or, less frequently, colourless or fluorescent complexes. These complexes have been insufficiently studied and for many of them even the composition has not been determined. Tchakirian and Bévillard [205-207,233,234] suggested that the reaction of *o*-hydroxyquinone compounds of type A with germanium is due to the presence of the *o*-hydroxyquinone group in the molecule, whereas the reactivity of arene-*o*-diol compounds of type B results from preliminary tautomeric conversion to the *o*-hydroxyquinone form. Later, Bévillard [208,235] abandoned this viewpoint and concluded that these compounds react with germanium in the arene-*o*-diol form to give complexes of the hydrogen phenolatogermanate type [179] having the composition $H_2GeL_3$, and that the quinonoid structures, even if present in the ligand molecule, do not take part in the interaction with germanium.

Kimura et al. [230], who could not establish that reaction takes place between germanium and partly and completely methylated phenylfluorone and 2-hydroxy-1,4-naphthaquinone, came to the same conclusion. Kimura's proof, however, is not convincing, since methylated phenylfluorone in general is unable to form cyclic complexes with metal ions, and for the hydroxynaphthaquinone an equivalent structure is that of 4-hydroxy-1,2-naphthaquinone in which this compound is also unable to form cyclic complexes.

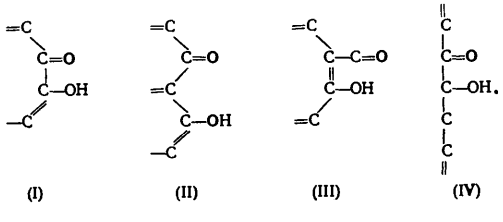
Subsequent studies have established that the complexes of germanium with compounds of type A have a composition different from that of hydrogen phenolatogermanates. Thus for trihydroxyxanthones a Ge : L ratio of 1 : 2 was found [214,236,237]. It was shown that the trihydroxyxanthones containing both groups — *o*-diol and *o*-hydroxyquinonoid — react with germanium [238] and also with zirconium [238], antimony [238], scandium [238], and molybdenum [239] as *o*-hydroxy-carbonyl compounds. Similar proof was obtained for the complexes of germanium with Catechol Violet [240] and purpurogallin [241]. Chloranilic acid, 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone, which is capable of undergoing tautomeric conversion into 3,6-dichloro-4,5-dihydroxy-1,2-benzoquinone, reacts with germanium in the *o*-hydroxy-

quinonoid form [242], forming three coloured complexes with Ge : L ratios of 1 : 1, 1 : 2, and 1 : 3. Kanno [218,243] established that only those hydroxyflavones which have an unsubstituted hydroxy-group on the $C_{(3)}$ carbon atom are capable of reacting with germanium in acid medium: i.e. the reactive group is the $C_{(3)}-C_{(4)}$ *o*-hydroxy-carbonyl group. Analogous results had been previously obtained in a study of the reaction of hydroxyflavones with zirconium [244-246].

The reactivity of *o*-dihydroxychromenols towards germanium and other metals is attributed to tautomeric conversion of the dyes into anhydro-bases having the structure of *o*-hydroxyquinones [231]. It was finally shown [247] that the *o*-diols 3′,4′-dihydroxyazobenzene-4-sulphonic acid and 3,4-dihydroxynaphthyldiphenylmethanol react with germanium in dilute solutions of strong acids only after conversion into the *o*-hydroxyquinonoid forms, to give complexes GeL and $GeL_2$ (in the case of the first compound) or only GeL (with the second compound).

The composition GeL has been established for the complexes of germanium with hydroxyanthraquinones, formed in sulphuric acid medium [39].

The groups of atoms which, in the molecules of hydroxy--carbonyl compounds, react with germanium in acid medium can be represented by the fragments: (I) — compounds of type A (1)–(5) and (8), and all compounds of type B in the tautomeric form; (II) — A (6); (III) — A′ (7), *o*-hydroxy--phenones and *o*-hydroxy-aldehydes; and (IV) — A (7), benzoin.



(I) (II) (III) (IV)

The groups (I)–(III) are parts of the conjugated bond systems of aromatic nuclei, and in the coloured compounds they are also parts of the chromophoric conjugation systems. The group (IV) of benzoin is not part of an aromatic ring, but the influence of the conjugation systems of the two phenyl radicals on either side of the group gives it an "aromatic" character. In the reaction with the ions of germanium or other multivalent metal, five-membered [groups (I) and (IV)] or six-membered [groups (II) and (III)] cyclic complexes are formed, in which the metal atom is joined to the oxygen atoms of the ligand by non-equivalent bonds — by an ionic bond or almost ionic covalency to the phenolic oxygen, and by a donor–acceptor bond to the carbonyl oxygen. The complexes in which the metal ion replaces only one hydrogen atom in the ligand molecule during ring formation are more stable than the cyclic complexes formed by the dihydric phenols, whose formation involves the replacement of two hydrogen atoms. According to the law of mass action, the influence of hydrogen ions on the equilibrium for the formation of the complex is proportional to the first power of the concentration in the first case and to the square of the concentration in the second case. The nature of the complex-forming bond in the phenylfluoronates of germanium and other metals was examined by Sano [248].

In the colourless addition compounds formed by germanium tetrahalides with acetylacetone and other β-diketones [249], the ligand is present in the keto–enol form; this is to some extent analogous to the case of the complexes formed by germanium with aromatic *o*-hydroxy-carbonyl ligands.

## Nitrogen- and Sulphur-Containing Complexes of Germanium

Apart from the addition products formed by germanium tetrahalides, complexes of germanium with compounds containing nitrogen and sulphur are few in number. It is generally considered that the formation of complexes containing a Ge–N bond is not characteristic of germanium. It has been established, however, that germanium forms a complex with 1,1′-bianthrimide in sulphuric acid [250], analogous to the complex formed by boron with the same reagent, and a complex with ethylenediaminetetraacetic acid ($H_4Y$) in weakly acidic solutions [251], suitable for quantitative analysis. A complex with $H_4Y$ of composition $GeY.2H_2O$ has been isolated in crystalling form by the action of $GeCl_4$ on hot $Na_2H_2Y$ solution [258].

The naturally occurring sulphides of germanium — argyrodite, germanite, and renierite — and also double sulphides [252] of the type $CuS.GeS_2$ are undoubtedly complex compounds. The potassium and sodium thiogermanates $M_6[Ge_2S_7].9H_2O$ isolated by Schwarz and Giese [253] have the structure of dinuclear complexes. Formation of the dinuclear complex thiogermanate $K_2Ge_2S_5$ is used for the iodometric determination of germanium [172]. Among organic thio-compounds, toluene-3,4-dithiol (dithiol), which forms a complex dithiolate, has been described as a reagent for germanium [254]. Germanium reacts with the thiol analogues of hydroxy-carboxylic acids — mercaptoacetic, mercaptosuccinic, and mercaptopropionic — to form di- and tri--basic complex acids [259], whose ionisation constants have been determined.

Potassium and sodium selenogermanates $M_6[Ge_2Se_7].9H_2O$, analogous to the corresponding thiogermanates, have been prepared [255].

## Complex-Forming Germanium Ions.

It is evident that for complexes of bivalent germanium, the complex-forming ion is $Ge^{2+}$, even if it exists in insignificant quantities only as one of the equilibrium forms. It is much more difficult to reach conclusions regarding the nature of the complex-forming ions of quadrivalent germanium, since our knowledge of the state of quadrivalent germanium in solution is inadequate.

It may be taken as established that in the reactions with polyhydroxy-compounds and dihydric phenols, the complex--forming ion is the metagermanate ion $HGeO_3^-$, since complex formation takes place at germanium concentrations which exclude the formation of polymeric forms either in acidic medium or in alkaline medium, where no germanium cations are formed. This agrees with the situation for the analogous complexes formed by boron and arsenic with polyhydroxy-compounds, where the complex-forming ions are assumed to be the singly charged ions of boric and arsenious acids [256]. It may be assumed that, in the reactions with hydroxyanthraquinones in concentrated sulphuric

acid, the complex-forming ion is a germanium cation, since it has been shown for the analogous reactions of boron [257] that the complex-forming ion is a boron cation. In the same way, it may also be assumed by analogy that germanium cations take part in the reactions with *o*-hydroxy-carbonyl compounds and ethylenediaminetetraacetic acid in acidic medium. It is probable that in all complex-formation reactions in acid medium the complex-forming ions are germanium cations, but there are as yet no data for characterising these cations.

It is evident that a successful quantitative study of the chemistry of germanium complexes is possible only if the forms of the components of the complex-formation equilibrium are known. Thus determination of the basic dissociation constants of $GeO_2$ and of the ranges of existence of the individual cations is of primary importance in the chemistry of germanium.


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# THE DIELS–ALDER REACTION WITH MOLECULAR OXYGEN AS DIENOPHILE

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## I. INTRODUCTION

The present review surveys the reactions of conjugated dienes with molecular oxygen to form peroxides.

It has been established that transannular epidioxides are produced by the photosensitised oxidation of alicyclic, aromatic, and heterocyclic homoannular 1,3-dienes. Such dienes undergo the Diels–Alder reaction with maleic anhydride and other dienophiles. Therefore the photooxidation of homoannular 1,3-dienes to transannular epidioxides can be regarded as a photochemical Diels–Alder reaction in which oxygen acts as dienophile.

It has recently been found that homoannular 1,3-dienes are oxidised to transannular epidioxides by molecular oxygen in an excited singlet state. This must be regarded as a diene synthesis with singlet oxygen. It is probable that excited singlet oxygen is the active intermediate also in photosensitised oxidations with molecular oxygen.

The ability of homoannular 1,3-dienes to form transannular epidioxides at low temperatures, and also the ease with which some of the latter rearrange into more stable oxygen compounds or break down again with the liberation of oxygen, suggest that some biological oxidation processes may involve the intermediate formation of transannular epidioxides. This hypothesis has recently been confirmed experimentally.

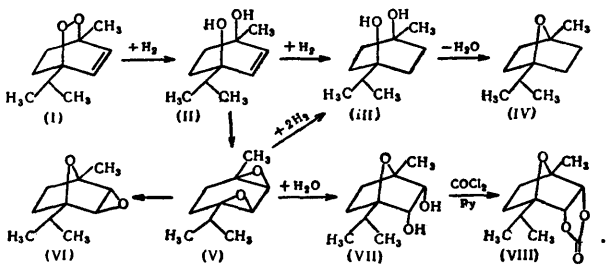
The paper covers the literature published up to 1st March 1965.

## II. REACTION OF MOLECULAR OXYGEN WITH ACYCLIC AND ALICYCLIC 1,3-DIENES

### 1. Ascaridole

In 1908 Gütig[1] isolated an oily substance, having the composition $C_{10}H_{16}O_2$ and boiling at 80–84° (4–5 mm), from chenopodium oil (the essential oil of a species of wormwood, *Chenopodium ambrosioides* var. *anthelminticum*), which possesses an anthelmintic (vermifugal) action. This substance, which is the active principle of chenopodium oil, was termed *ascaridole*. In 1912 Wallach[2,3] established that ascaridole was 1,4-epidioxy-*p*-menth-2-ene (I): catalytic hydrogenation with colloidal palladium gave the previously unknown *p*-menthane-*cis*-1,4-diol (III), dehydration of which with oxalic acid yielded the known 1,4-epoxy-*p*-menthane (IV).

It must be noted that at that time ascaridole was the only known organic compound having a transannular epidioxide structure.



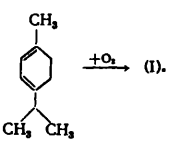

Study of the chemical properties of ascaridole gave interesting results. Catalytic hydrogenation with platinum

oxide[4] or with Raney nickel[5] yielded the diol (III). Reduction with lithium tetrahydroaluminate[6] or with a potassium–sodium alloy in ether[5] produced *p*-menth-2-ene-1,4-diol (II). This unsaturated glycol (II) was also obtained by the catalytic reduction of ascaridole with relatively inactive palladium[4] or nickel[5] catalysts. When heated to 130–150° ascaridole decomposes explosively[2,3]. Nelson[7] found that when heated in *p*-cymene at 150°, ascaridole isomerises to a diepoxy-*p*-menthane. It was found later[6,8] that the thermal isomerisation of ascaridole is more conveniently carried out in boiling xylene, and Schenck[5] showed that ascaridole is converted into this diepoxide by the action of ultraviolet radiation. Nelson[7] assumed that, on being heated, ascaridole is first converted into an unstable isomer, 1,2:3,4-diepoxy-*p*-menthane (V), which then rearranges to the stable isomer, 1,4:2,3-diepoxy-*p*-menthane (VI). In the presence of dilute sulphuric acid, the diepoxide adds on a molecule of water to form 1,4-epoxy-*p*-menthane-2,3-diol (VII). The cyclic carbonate (VIII) has been obtained[9] by the action of carbonyl chloride and pyridine on (VII). Matic and Sutton[6] determined the structure of the thermal isomerisation product of ascaridole by reducing it with lithium tetrahydroaluminate, and isolated the compound (III) and a triol $C_{10}H_{20}O_3$ from the reaction products. The formation of (III) proved the presence of the 1,2:3,4-diepoxide (V) in the product of isomerisation. The triol $C_{10}H_{20}O_3$ could have been formed by reduction of the 1,4:2,3-diepoxide (VI) to 1,4-epoxy-*p*-menthan-2(or 3)-ol, followed by hydration of the latter to *p*-menthane-1,2(or 3),4-triol. It follows from these results that the product of the thermal isomerisation of ascaridole is probably a mixture of the diepoxides (V) and (VI)†. It must be noted that the configuration of 1,4-epoxy-*p*-menthane-2,3-diol (VII) has not been rigorously proved.

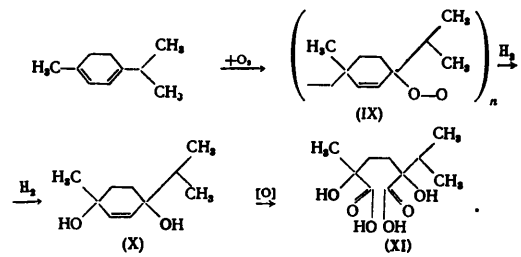
Ascaridole is used in medicine for the treatment of intestinal helminthiases in both adults and children. Chemists use ascaridole as an initiator for radical reactions.

## 2. Autoxidation of Acyclic and Alicyclic 1,3-Dienes

Ascaridole (I) can be regarded as an internal peroxide of *p*-mentha-1,3-diene. In 1933 Bodendorf[4] put forward the hypothesis that autoxidation of the latter compound involves the addition of oxygen to the conjugated system of double bonds at the 1,4 positions to form ascaridole:



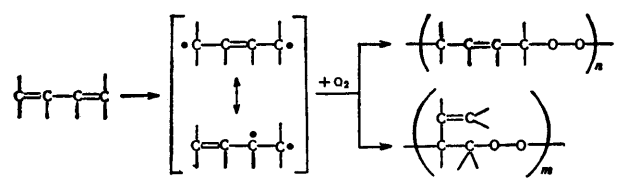
However, experiments undertaken to test this hypothesis showed that molecular oxygen reacts with *p*-mentha-2,3-diene to form, not ascaridole, but an unsaturated polymeric peroxide of low molecular weight. Bodendorf reduced the polyperoxide catalytically, and oxidised the reduction product with potassium permanganate. From the oxidation products he isolated 2,5-dihydroxy-2-isopropyl-5-methyladipic acid (XI). Hence it followed that in the autoxidation of *p*-mentha-1,3-diene the oxygen added on at the 1,4 positions to form the unsaturated polymeric peroxide (IX), catalytic reduction of which yielded the unsaturated glycol (X), and this was oxidised to the dicarboxylic acid (XI):



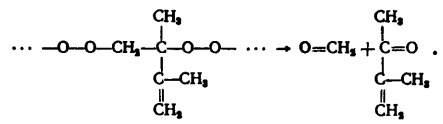
Bodendorf also found that only polymeric peroxides were formed in the oxidation of other diene hydrocarbons (*p*-mentha-1,5-diene, cyclohexa-1,3-diene, isoprene, and 2,3-dimethylbuta-1,3-diene).

Subsequently other investigators have established that polymeric peroxides of low molecular weight are formed in the autoxidation of buta-1,3-diene[13,14], isoprene[15], 2-chlorobuta-1,3-diene[16,17], 2,3-dimethylbuta-1,3-diene[15,16-20], 2,4-dimethylpenta-1,3-diene[21], 2,5-dimethylhexa-2,4-diene[22,23], 2,6-dimethylocta-2,4,6-triene[24-28], cyclopentadiene[15,29], cyclohexa-1,3-diene[15,29,30], *p*-mentha-1,3-diene[31], 1,1′-bicyclohexenyl[32], and methyl octadeca-9,11-dienoate[33].

Study of the structure of copolymers of 1,3-dienes with oxygen has shown that oxygen can add on to dienes in both the 1,2 and the 1,4 positions:



Bodendorf[4] and Kern[15,18] found that thermal decomposition of the polyperoxide of 2,3-dimethylbuta-1,3-diene yields formaldehyde and 3-methylbut-3-en-2-one:

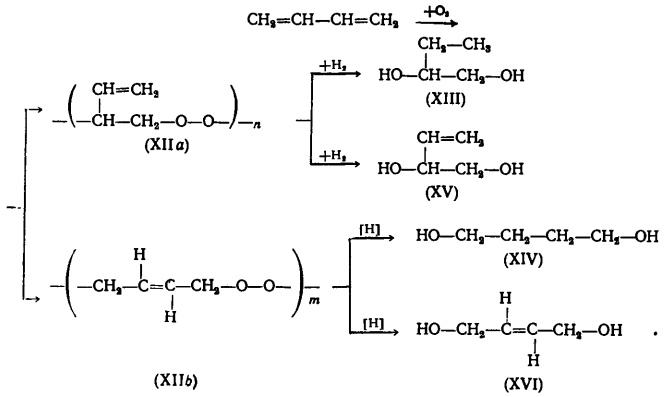


Later Kawahara[20] isolated formaldehyde, the above methylbutenone, αβ-dimethylenebutyraldehyde, and butane-2,3-dione from the decomposition products of this copolymer. Formation of the last two compounds from the copolymer is perhaps explained by the presence in it of 1,4 links as well as the 1,2 links.

Handy and Rothrock[14] established that both 1,2 and 1,4 addition of oxygen takes place in its copolymerisation with buta-1,3-diene, the latter predominating. Catalytic reduction of the polymeric peroxide — (XII*a*) and (XII*b*) — gave

† Other experimental results have been published[10-12] indicating the possible presence of (V) and (VI) in the product of the thermal isomerisation of ascaridole.

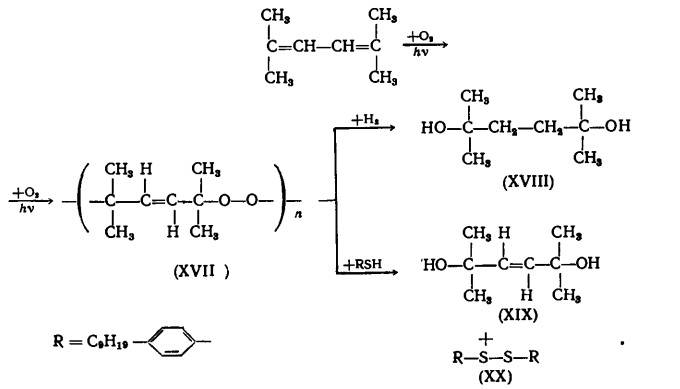
butane-1,2-diol (XIII) and a larger quantity of butane-1,4--diol (XIV), while its reduction with lithium tetrahydroaluminate yielded but-3-ene-1,2-diol (XV) and *trans*-but--2-ene-1,4-diol (XVI).



(XII*a*) (XII*b*) (XIII) (XIV) (XV) (XVI)

Analysis of the infrared spectrum of the copolymer (XII*a*) and (XII*b*) confirmed the chemical evidence of its structure.

Griesbaum et al.[23] have shown that the autoxidation of 2,5-dimethylhexa-2,4-diene is rigorously selective with the formation of a *trans*-1,4-polyperoxide (XVII). The structure and the configuration of this copolymer were proved by an analysis of the nuclear magnetic resonance and infrared spectra. The proton resonance spectrum revealed signals only from vinyl and methyl protons at relative intensities of 1 : 6. Hence it followed that the polyperoxide had the 1,4 structure. Analysis of the infrared spectrum showed that the double bond in the polyperoxide had the *trans* configuration. The *trans*-1,4 structure of the copolymer was confirmed also by a chemical method. Catalytic hydrogenation of the polyperoxide (XVII) produced 2,5-dimethylhexane-2,5-diol (XVIII), whereas reduction of the polyperoxide with *p*-nonylbenzenethiol gave *trans*-2,5-dimethylhex-3-ene-2,5-diol (XIX) and di-*p*--nonylphenyl disulphide (XX)‡:



(XVII) (XVIII) (XIX) (XX)

## 3. Synthesis of Ascaridole

Schenck and Ziegler[5,34-36] suggested that ascaridole is formed in plants by the diene condensation of *p*-mentha--1,3-diene with molecular oxygen under the photosensitising influence of chlorophyll. This hypothesis was verified by shaking a dilute alcoholic solution of *p*-mentha-1,3-diene in the presence of Eosin in an atmosphere of oxygen while exposed to a 300 W lamp. After completion of the photooxidation the solution was reduced in the presence of a palladium catalyst. *p*-Menthane-*cis*-1,4-diol (III) was isolated from the products. In a parallel experiment Schenck distilled off the solvent, and was able to obtain from the residue a preparation melting at 2.5°, a mixture of which with natural ascaridole showed no melting-point depression.

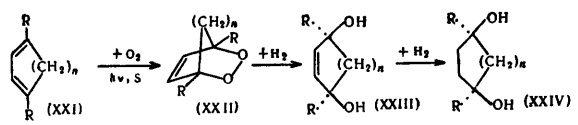
In further experiments Schenck carried out the photochemical diene synthesis of ascaridole in ethanol, propan-2-ol, acetone, and toluene in the presence of various photosensitisers (chlorophyll, Eosin, Erythrosin, Methylene Blue, Fluorescein, Pinacyanol, etc.). The photooxidation of *p*-mentha-1,3-diene in isopropyl alcohol in the presence of Methylene Blue gave a 25% yield of ascaridole. Pure synthetic ascaridole had m.p. 4.2°.

The catalytic hydrogenation of synthetic ascaridole over Raney nickel produced a 96% yield of *p*-menthane--*cis*-1,4-diol (III), whereas the reduction of ascaridole with a potassium–sodium alloy in ether gave a 57% yield of *p*-menth-2-ene-1,4-diol (II).

## 4. Epidioxides of Cyclopentadiene, Cyclohexa-1,3-diene, Cycloheptа-1,3-diene, and Their Derivatives

The photosensitised oxidation of cycloalka-1,3-dienes having five-, six-, and seven-membered rings and their derivatives has been studied by Schenck and other workers.

In 1952 Schenck[35,37,38] obtained a very unstable epidioxide of cyclopentadiene (XXII*a*) (5,6-dioxabicyclo[2,2,1]hept-2--ene) by the photosensitised oxidation of cyclopentadiene (XXI*a*) at -80°. On warming to 0° cyclopentadiene epidioxide decomposes explosively. Catalytic reduction of the epidioxide (XXII*a*) yielded cyclopentane-*cis*-1,3-diol (XXIV*a*), whereas reduction with thiourea at -20° gave cyclopent-4--ene-*cis*-1,3-diol (XXIII*a*).



(XXI) (XXII) (XXIII) (XXIV)

where S is the sensitiser; and for XXI–XXIV:

(*a*) $n = 1$; R = H,
(*b*) $n = 1$; R = $C_6H_5$,
(*c*) $n = 2$; R = H,
(*d*) $n = 3$; R = H,
(*e*) $n = 3$; R = $C_6H_5$.

Schenck[39,40] obtained the epidioxide (XXII*b*) by the photosensitised oxidation of 1,4-diphenylcyclopentadiene (XXI*b*), and reduced the product catalytically to the *cis*-1,3-diol (XXIII*b*). It was found that 1,4-diphenylcyclopentadiene (XXI*b*) can act as a photosensitiser both for its reaction with oxygen and for other diene syntheses of transannular epidioxides (e.g. the synthesis of ascaridole from *p*-mentha--1,3-diene). On heating, the epidioxide (XXII*b*) of 1,4-diphenylcyclopentadiene breaks down into oxygen and the original hydrocarbon (XXI*b*).

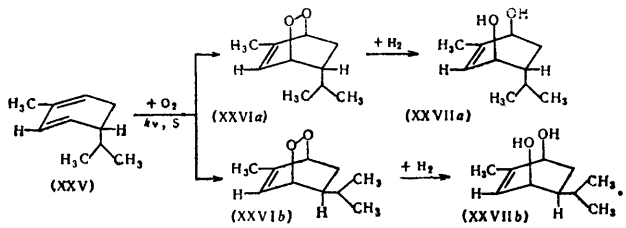
‡ See also Ref. 211 for the structure of the polymeric peroxide of 2,5-dimethylhexa-2,4-diene.

The photosensitised oxidation of cyclopentadienyltriphenyltin at -20° also gave an epidioxide, reduction of which at -20° with thiourea, with sodium tetrahydroborate, or catalytically resulted in an unsaturated *cis*-1,3-diol.[41]

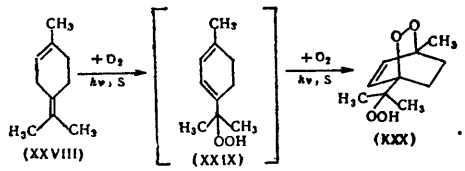
Schenck also found[5,35,37,38,42] that the photosensitised oxidation of cyclohexa-1,3-diene (XXI*c*) forms a crystalline epidioxide of cyclohexa-1,3-diene (XXII*c*) (5,6-dioxabicyclo[2,2,2]oct-2-ene)§.

In 1957 Cope[43] showed that the photosensitised oxidation of cyclohepta-1,3-diene (XXI*d*) involves formation of the crystalline epidioxide (XXII*d*), catalytic reduction of which produced the *cis*-1,4-diol (XXIV*d*). Later Courtot[44,45] established that a crystalline transannular epidioxide (XXII*e*) is formed by the photosensitised oxidation of 1,4-diphenylcyclohepta-1,3-diene (XXI*e*). The product was reduced catalytically to the *cis*-1,4-diol (XXIV*e*).

By the photosensitised oxidation of *p*-mentha-1,5-diene (XXV) Schenck[5,35,38,42] obtained two crystalline stereoisomeric epidioxides (XXVI*a*) and (XXVI*b*), which were reduced to the stereoisomeric unsaturated *cis*-1,4-diols (XXVII*a*) and (XXVII*b*):



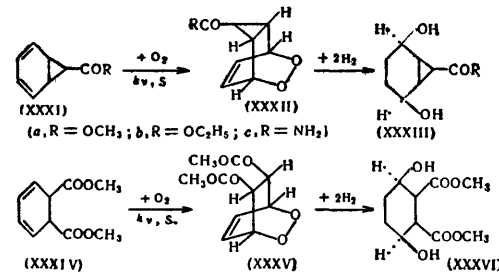
Schenck[38] also showed that the photosensitised oxidation of *p*-mentha-1,4(8)-diene (XXVIII) initially involves migration of the double bond with formation of *p*-mentha-1,3-diene 8-hydroperoxide (XXIX), when then condenses with a second molecule of oxygen by a mechanism of diene synthesis to form the extremely unstable ascaridole 8-hydroperoxide (XXX):



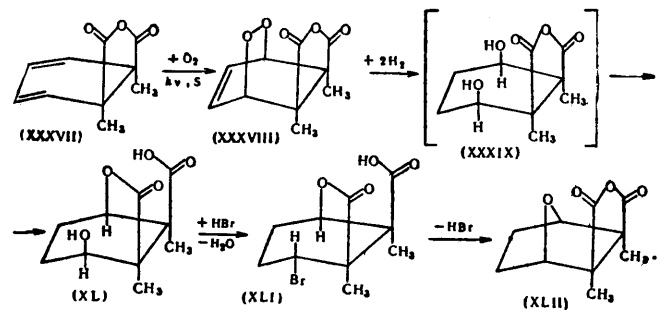
Schenck[35,38,46] studied the photosensitised oxidation of methyl and ethyl norcaradienecarboxylates (XXXI*a*) and (XXXI*b*) and dimethyl 1,2-dihydrophthalate (XXXIV). Oxidation of the first two esters gave the epidioxides (XXXII*a*) and (XXXII*b*), which on catalytic reduction were converted into the saturated 1,4-diols (XXXIII*a*) and (XXXIII*b*). These epidioxides were transformed into the amide (XXXII*c*) by the action of ammonia, the same amide being obtained by the photooxidation of norcaradienecarboxyamide (XXXI*c*).

§ In 1951 Hock established[29,30] that a very small yield of the epidioxide of cyclohexa-1,3-diene (XXII*c*) is formed by the autoxidation of cyclohexa-1,3-diene.

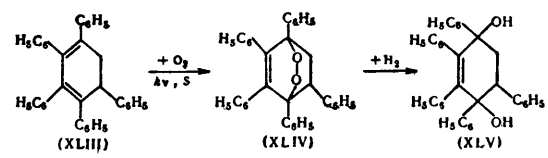
Photooxidation of the ester (XXXIV) enables Schenck to obtain the epidioxide (XXXV), catalytic reduction of which resulted in the saturated 1,4-diol (XXXVI):



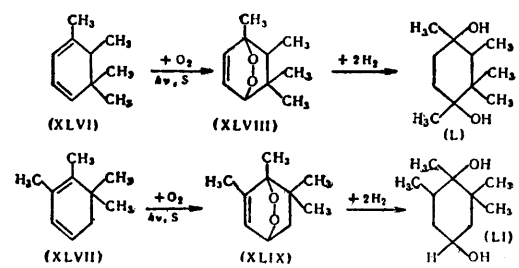
In 1953 Schenck[38,47] accomplished the stereospecific synthesis of cantharidin. The photochemical diene condensation of synthetic dehydrocantharidin (XXXVII) with oxygen gave dehydrocantharidin epidioxide (XXXVIII), in which the peroxide bridge occupies the same spatial position as the ether bridge in natural cantharidin. Catalytic hydrogenation of the epidioxide (XXXVIII) formed the diol (XXXIX), which under the experimental conditions underwent lactonisation to hydrohydroxycantharic acid (XL). The action of hydrogen bromide on the product yielded hydrobromocantharic acid (XLI), thermal decomposition of which gave cantharidin (XLII):



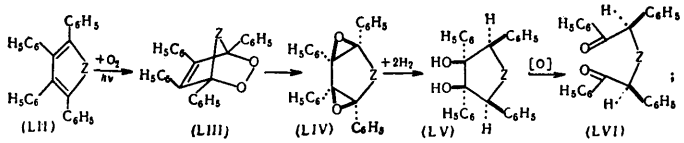
Bergmann[48] studied the photosensitised oxidation of 1,2,3,4,5-pentaphenylcyclohexadiene (XLIII), obtaining the epidioxide (XLIV), catalytic reduction of which gave the unsaturated 1,4-diol (XLV):



Schenck[35,42] investigated the photosensitised oxidation of 1,5,5,6- and 1,2,6,6-tetramethylcyclohexa-1,3-diene (XLVI) and (XLVII). He obtained the corresponding transannular epidioxides (XLVIII) and (XLIX), catalytic hydrogenation of which gave the saturated 1,4-diols (L) and (LI):

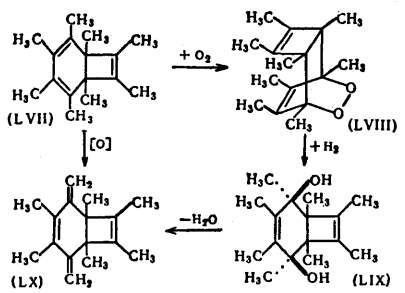


Dufraisse[49] showed that the photochemical oxidation of 2,3,4,5-tetraphenylcyclopentadiene (LII*a*) forms the epidioxide (LIII*a*), which on heating isomerises into the diepoxide (LIV*a*). The structure of the latter was proved by its reduction to the *cis*-1,2-diol (LV*a*), oxidation of which with iodic acid or lead tetraacetate gave 1,2,4,5-tetraphenylpentane-1,5-dione (LVI*a*).

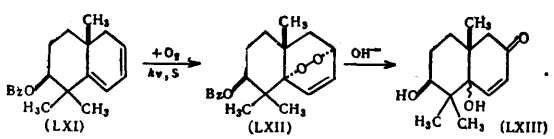


(*a*) Z = >$CH_2$; (*b*) Z = >C = $CH_2$.

Dufraisse[50] also found that the photooxidation of 2,3,4,5-tetraphenylfulvene (LII*b*) gave the epidioxide (LIII*b*), which under the experimental conditions isomerised into the diepoxide (LIV*b*). The latter was reduced with lithium tetrahydroaluminate to the *cis*-1,2-diol (LV*b*), which was oxidised with lead tetraacetate to 3-methylene-1,2,4,5-tetraphenylpentane-1,5-dione (LVI*b*).



In 1962 Criegee[51,52] reported that the 1,2,3,4,5,6,7,8-octamethylbicyclo[4,2,0]octa-2,4,7-triene (LVII) which he had synthesised was oxidised so readily that it could be prepared only when oxygen was completely excluded. In air this hydrocarbon oxidises quantitatively to a crystalline peroxide after a few hours. Examination of the infrared, ultraviolet, and nuclear magnetic resonance spectra of the product showed it to be a transannular epidioxide (LVIII). When a methanolic solution of the hydrocarbon (LVII) was shaken with oxygen for 20 min, exactly one molecule of oxygen was absorbed, the peroxide being formed at the same rate in the light and in the dark. This represents the first case of the formation of an epidioxide in a dark reaction. Nor did addition of inhibitors affect the rate of oxidation of the hydrocarbon (LVII)¶. The epidioxide (LVIII) was reduced to the diol (LIX), dehydration of which yielded the hydrocarbon (LX). The same hydrocarbon was obtained by the oxidation of (LVII) with silver nitrate, chloranil, or benzoquinone. Criegee found that the octamethylbicyclooctatriene (LVII) forms diene adducts with tetracyanoethylene and azoformic ester, but does not react with maleic anhydride or acetylenedicarboxylic ester even at 140°.



Halsall[53,54] established that exposure of a dilute alcoholic solution of 1,2,3,4,5,10-hexahydro-1,1,10β-trimethyl-2β-naphthyl benzoate (LXI) to the light from a 500 W lamp in the presence of Eosin and oxygen results in the formation of the 6α,9α-epidioxide (LXII), which in alkaline medium is converted into an αβ-unsaturated ketone (LXIII). The oxygen bridge in the epidioxide (LXII) must be assumed to have the α configuration, since the 1- and 10-methyl groups prevent attack on the diene (LXI) from the β side.

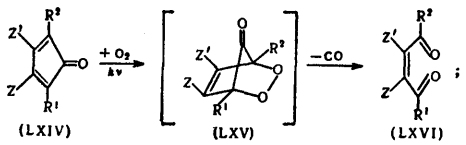
## 5. Photooxidation of Arylated Cyclopentadienones (Cyclones) and Arylated Cyclopentadienols

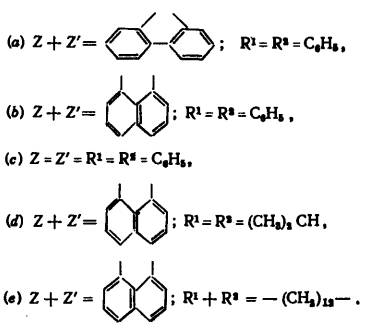
In 1938 Dilthey[55] discovered that, when solutions of phencyclone (LXIV*a*) in pyridine or toluene are exposed to sunlight in the presence of air, 9,10-dibenzoylphenanthrene (LXVI*a*) is formed. In the photochemical oxidation of acecyclone (LXIV*b*) in chlorobenzene medium in air, 1,2-dibenzoylacenaphthylene (LXVI*b*) is obtained[55].

Schenck[56], Dufraisse[57,58], Becker[59], and Wilcox[60] have established the formation of 1,2,3,4,-tetraphenylbut-*cis*-2-ene-1,4-dione (LXVI*c*) and carbon monoxide in the photooxidation of tetracyclone (LXIV*c*).

In 1953 Allen[61] reported that photooxidation of the cyclones (LXIV*d*) and (LXIV*e*) yields the 1,4-diketones (LXVI*d*) and (LXVI*e*).

It must be assumed that the photooxidation of cyclones (LXIV*a–e*) involves the initial formation of unstable diene adducts having an *endo*-carbonyl bridge (LXV*a–e*), which under the experimental conditions break down into carbon monoxide and 1,4-dicarbonyl compounds (LXVI*a–e*)†.



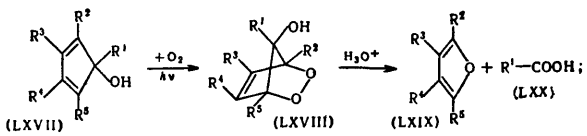


Dufraisse[57,58] and Rio[63] established that in the photooxidation of pentaarylcyclopentadienols (LXVII*a–f*) the corresponding photoperoxides (LXVIII*a–f*) are formed, and these on being heated with acetic acid undergo fission

¶ 1,2,3,4,5,6-Hexamethylcyclohexa-1,3-diene, which was synthesised for comparison, did not oxidise in the dark.

† The mechanism of the photooxidation of cyclones has been discussed by Syrkin and Moiseev[62].

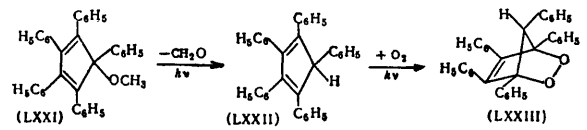
with the formation of tetraarylfurahs (LXIX*a–f*) and aromatic acids (LXX*a–f*):



(LXVII) (LXVIII) (LXIX) (LXX)

(*a*) $R^1 = R^2 = R^3 = R^4 = R^5 = C_6H_5$,
(*b*) $R^2 = R^3 = R^4 = R^5 = C_6H_5$; $R^1 = p\text{-}(CH_3)_2NC_6H_4$,
(*c*) $R^1 = R^2 = R^4 = R^5 = C_6H_5$; $R^3 = p\text{-}(CH_3)_2NC_6H_4$,
(*d*) $R^2 = R^3 = R^4 = R^5 = C_6H_5$; $R^1 = p\text{-}CH_3C_6H_4$,
(*e*) $R^1 = R^3 = R^4 = R^5 = C_6H_5$; $R^2 = p\text{-}CH_3C_6H_4$,
(*f*) $R^1 = R^2 = R^4 = R^5 = C_6H_5$; $R^3 = p\text{-}CH_3C_6H_4$.

The photooxidation of 1-methoxypentaphenylcyclopentadiene (LXXI) at first involves photolysis with production of formaldehyde and pentaphenylcyclopentadiene (LXXII), which undergoes photooxidation to form an epidioxide (LXXIII):[57]



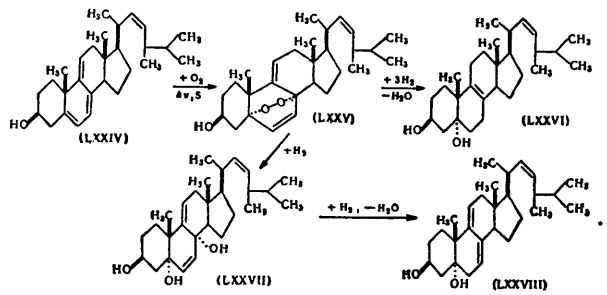
(LXXI) (LXXII) (LXXIII)

## 6. Steroid Epidioxides

In 1928 Windaus[64], while studying the conversion of ergosterol [24-methylcholesta-5,7,22-trien-3β-ol] into vitamin $D_2$ [ergocalciferol], found that irradiation of dilute alcoholic solutions of the former with a 200 W lamp in the presence of a photosensitiser (Eosin, Erythrosin) and air led to the addition of a molecule of oxygen to a molecule of ergosterol, the product possessing the properties of a peroxide and being termed ergosterol peroxide. The photosensitised oxidation of 24-methylcholesta-5,7,9(11),22--tetraen-3β-ol under the same conditions[65–67], produced "9(11)-dehydroergosterol peroxide".

It was subsequently found that other homoannular steroid 1,3-dienes are readily converted into peroxides. Peroxides were prepared from 24-methylcholesta-5,7-dien-3β-ol[68], 3β-acetoxy-24-methylcholesta-6,8(14),9(11),22-tetraene,[69–72] 3-acetoxy-2-methylcholesta-3,5,7,22-tetraene[73], 3-acetoxy-24-methylcholesta-3,5,7,9(11),22-pentaene[73], 3-acetoxy-5α-pregna-6,8(14),9(11)-trien-20-one[71,72], 3β,21-diacetoxy-5α-pregna-6,8(14),9(11)-trien-20-one[71], lumisteryl acetate [3-acetoxy-24-methyl-10α-cholesta--5,7,22-triene][74], [3-acetoxy-24-methyl-10α-cholesta--5,7,9(11),22-tetraene[74], cholesta-5,7-dien-3β-ol[75,77], 3β-acetoxycholesta-5,7-diene[76], cholesta-5,7,24-trien--3β-ol[77], cholesta-2,4-diene[78–80], cholesta-1,3,5-trien--7-one[81], and androsta-5,7-diene-3,17-diol[82].

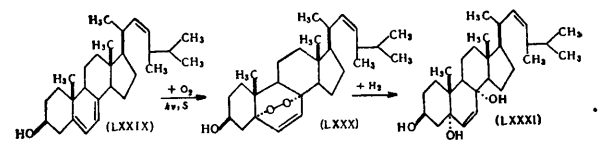
Examination of the ultraviolet spectrum of the peroxide obtained from 24-methylcholesta-5,7,9(11),22-tetraen-3β--ol (LXXIV) showed that it did not contain a conjugated system of double bonds, and on catalytic reduction formed a 24-methylcholestadienediol, for which the structure (LXXVI) was established[67]. From these results it was concluded that the dehydroergosterol peroxide had the structure (LXXV)[67]. The formation of the diol (LXXVI) on catalytic hydrogenation of the transannular epidioxide (LXXV) is explained by initial formation of the 3,5,8-triol, which is dehydrated with formation of a double bond between $C_{(8)}$ and $C_{(9)}$.



(LXXIV) (LXXV) (LXXVI) (LXXVII) (LXXVIII)

When the epidioxide (LXXV) was reduced with zinc and alcoholic alkali, a trienediol was obtained[67,83], whose ultraviolet spectrum showed it to contain two conjugated cyclic double bonds. The trienediol gave no diene adduct with maleic anhydride, so that its conjugated double bonds were present in different rings. On the basis of these results the structure (LXXVIII) was assigned to the trienediol. Its formation probably involved reduction of the epidioxide (LXXV) to the trienetriol (LXXVII) followed by elimination of the 8-hydroxyl and migration of a cyclic double bond to a conjugated position.

In 1950 Fieser[84,85] adduced weighty arguments in support of the α configuration for the oxygen bridge in steroid epidioxides. During 1952–1954 Bladon et al.[86–89] established the α configuration for the oxygen bridge in 24-methylcholesta-5,7,9(11),22-tetraen-3-ol epidioxide (LXXV), and described a method for preparing cortisone from it.

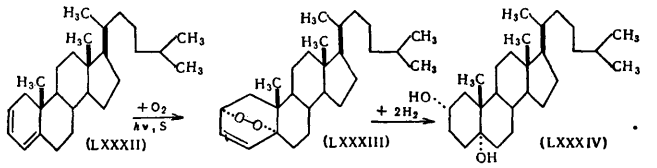


(LXXIX) (LXXX) (LXXXI)

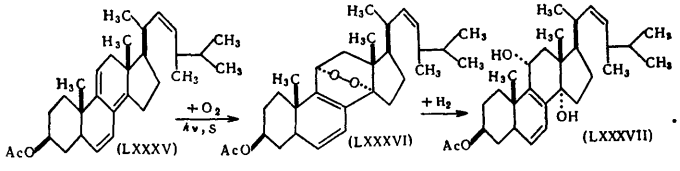
By the photosensitised oxidation of ergosterol (LXXIX) Windaus[64–66] obtained its peroxide, which was reduced with zinc and alcoholic alkali to a dienetriol. Study of the chemical reactions of the latter led Achtermann[90], Müller[67], and Heilbron[91] to conclude that the epidioxide bridge had been attached to $C_{(5)}$ and $C_{(6)}$. However, in 1936 Fieser[92] cited convincing evidence (see also Ref. 85, p. 96) indicating that the reduction product was a 3,5,8-triol (LXXXI), which could be formed only from a transannular epidioxide (LXXX). In 1939 Bergmann[93] agreed with Fieser's view, that the epidioxide of ergosterol had the structure (LXXX). Fieser[84] in 1950 and Henbest and Jones[94] in 1953 showed that the oxygen bridge in the epidioxide had the α configuration.

In 1947 Wieland and Prelog[95] isolated the epidioxide (LXXX) from the mycelia of the mould *Aspergillus fumigatus*, and in 1964 Bauslaugh et al.[96] isolated it from the mycelia of *Trichophyton schönleini*. The epidioxide (LXXX) was identified by the method of mixed melting points with a synthetic specimen[95,96]. The identity of the two samples was confirmed by examination of the infrared, nuclear magnetic resonance, and mass spectra[96].

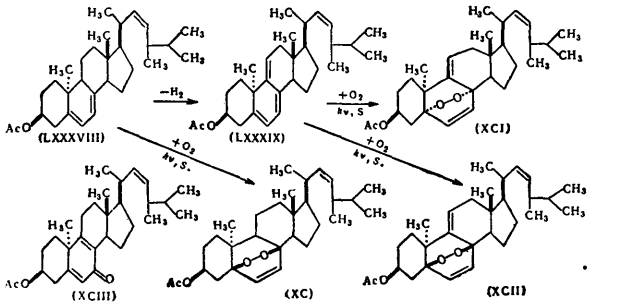
By catalytic reduction of the epidioxide of cholesta-2,4--diene Bergmann[79,80,93] obtained a saturated diol, for which he established the structure (LXXXIV). Hence the product of the photosensitised oxidation of cholesta-2,4--diene (LXXXII) was the epidioxide (LXXXIII). In 1953 he showed[97] that the oxygen bridge in the epidioxide (LXXXIII) had an $\alpha$ configuration.



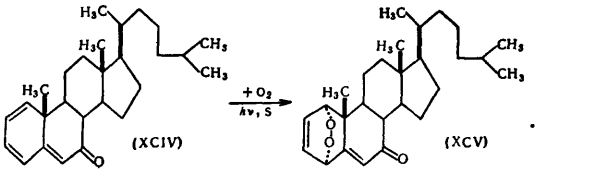
During 1953–1956 Laubach[69,70] established that the photosensitised oxidation of 3$\beta$-acetoxy-24-methylcholesta--6,8(14),9(11),22-tetraene (LXXXV) gives the 11$\alpha$,14$\alpha$-epidioxide (LXXXVI), hydrogenation of which in the presence of Lindlar's catalyst yielded 3$\beta$-acetoxy-24-methylcholesta-6,8,22-triene-11$\alpha$,14$\alpha$-diol (LXXXVII). He developed[98,70] a method for preparing from the epidioxide (LXXXVI) the compound 3-acetoxy-24-methylcholesta--8,22-dien-11-one, from which cortisone can be obtained.



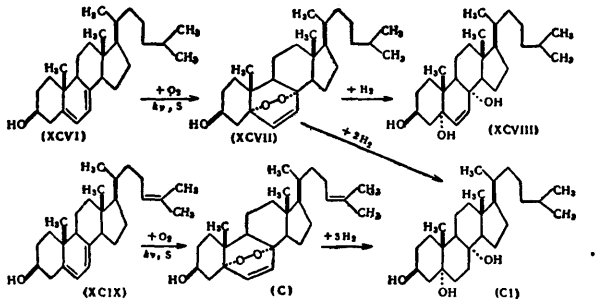
In 1955 Bladon[74] found that the photosensitised oxidation of 3$\beta$-acetoxy-24-methyl-10$\alpha$-cholesta-5,7-22-triene (LXXXVIII) yields 3$\beta$-acetoxy-24-methyl-10$\alpha$-cholesta--5,7,9(11),22-tetraene (LXXXIX), the $\beta$-epidioxide (XC) of (LXXXVIII), the $\alpha$-epidioxide (XCI) of (LXXXIX), the $\beta$-epidioxide (XCII) of (LXXXIX), and 3$\beta$-acetoxy-24--methyl-10$\alpha$-cholesta-5,8,22-trien-7-one (XCIII). Photooxidation of (LXXXIX) gave the $\alpha$-epidioxide (XCI) and the $\beta$-epidioxide (XCII).



In 1956 Henbest[81] reported that the photosensitised oxidation of cholesta-1,3,5-trien-7-one (XCIV) produces the $\alpha$-epidioxide (XCV):



In 1936 Schenck[75] found that the photosensitised oxidation of cholesta-5,7-dien-3$\beta$-ol (XCVI) involves formation of its epidioxide. Reduction of the latter with zinc and alcoholic alkali gave a cholestenetriol. From the results of a study of the structure and chemical reactions of epidioxides of other steroids, the compound formed from (XCVI) was to be regarded as the 5$\alpha$,8$\alpha$-epidioxide (XCVII), and its reduction product as having the structure cholest-6--ene-3$\beta$,5$\alpha$,8$\alpha$-triol (XCVIII). During 1963–1964 Dvornik and Kraml[77,99] prepared epidioxides from cholesta-5,7--dien-3$\beta$-ol (XCVI) and from cholesta-5,7,24-trien-3$\beta$-ol (XCIX), and reduced them catalytically.



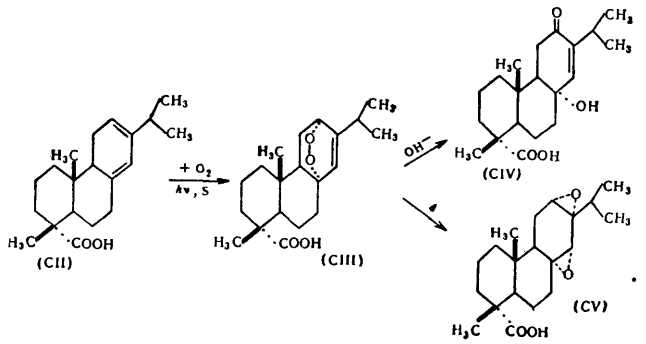
Dvornik and Kraml studied the mechanism of the conversion of lanosterol [4,4,14-trimethylcholesta-8,24-dien-3$\beta$-ol] into cholesterol [cholest-5-en-3$\beta$-ol] during the biochemical synthesis of the latter in cholesterologenic tissues. The method used in this investigation was to inhibit enzymes responsible for individual stages in the biosynthesis of cholesterol. These workers were able to detect in rat blood serum a steroid, examination of whose ultraviolet spectrum showed it to be a homoannular conjugated diene. They isolated from rat's liver a steroid which they identified as a transannular epidioxide (XCVII) of cholesta-5,7--dien-3$\beta$-ol (XCVI). Pig's liver was found to contain a steroid having an ultraviolet spectrum typical of homoannular conjugated diene steroids. The compound was identified by conversion into a transannular epidioxide, which was isolated in an analytically pure form and identified as 5$\alpha$,8$\alpha$-epidioxycholesta-6,24-dien-3$\beta$-ol (C). The structure of the latter was established by catalytic reduction with platinum oxide to cholestane-3$\beta$,5$\alpha$,8$\alpha$-triol (CI), which proved to be identical with a known specimen of this triol, prepared by the photosensitised transannular addition of oxygen to cholesta-5,7-dien-3$\beta$-ol (XCVI) followed by catalytic reduction of the resulting epidioxide (XCVII) to the triol (CI). Examination of the nuclear magnetic resonance spectrum of the epidioxide (C) supported the chemical evidence of its structure.

Dvornik and Kraml's investigation has shown that cholesta-5,7-dien-3$\beta$-ol (XCVI) is an intermediate in the biosynthesis of cholesterol, and that cholesta-5,7,24--trien-3$\beta$-ol (XCIX) is probably a precursor of (XCVI) in this process.

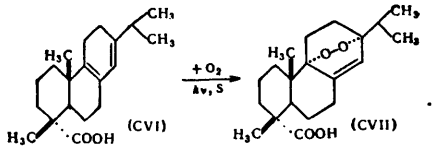
In 1964 Blondin et al.[100] reported that [4-$^{14}$C]cholesta--5,7-dien-3$\beta$-ol is converted into radioactive cholecalciferol in a homogenate of bass liver incubated in the dark. They suggested that 5$\alpha$,8$\alpha$-epidioxycholest-6-en-3$\beta$-ol (XCVII) may be an intermediate in this non-photochemical reaction. An experiment undertaken to verify this hypothesis showed that cholesta-5,7-dien-3$\beta$-ol (XCVI) is converted into the 5$\alpha$, 8$\alpha$-epidioxide (XCVII) in a homogenate of fish liver incubated in the dark.

### 7. Epidioxides of Resin Acids

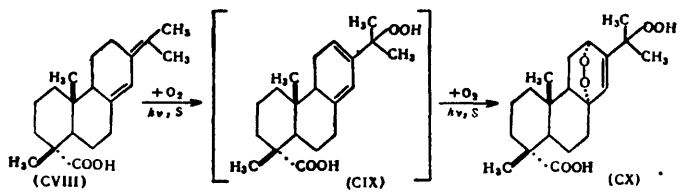
In 1958 Moore and Lawrence[101-104] discovered that the photosensitised oxidation of laevopimaric acid (CII) involves the formation of a crystalline transannular epidioxide — 6α,14α-epidioxy-Δ⁷-dodecahydro-7-isopropyl--1β,12β-dimethylphenanthrene-1α-carboxylic acid (CIII)‡ — which in alkaline medium is converted into Δ⁷-dodecahydro-14α-hydroxy-7-isopropyl-1β,12β-dimethyl-6-oxophenanthrene-1α-carboxylic acid (CIV). When a xylene solution of the epidioxide is boiled, the latter rearranges into 6,7α : 8,14α-diepoxytetradecahydro-7-isopropyl-1β,12β--dimethylphenanthrene -1α-carboxylic acid (CV):[104]



In 1960 Schuller, Moore, and Lawrence[103,104,107] reported that the photosensitised oxidation of palustric acid (CVI) gives a crystalline epidioxide — 7α,13α-epidioxy-Δ⁸-dodecahydro-7-isopropyl-1β,12β-dimethylphenanthrene-1α-carboxylic acid (CVII):



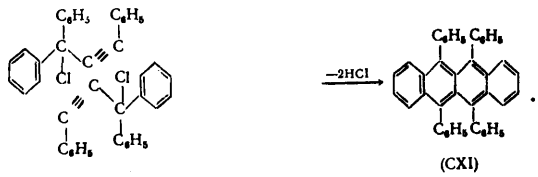
Schuller and Lawrence[104-106] also established that the photosensitised oxidation of neoabietic acid (CVIII) first involves a monoene addition and migration of a double bond to form the 18-hydroperoxy-derivative (CIX) of laevopimaric acid, which reacts further with a second molecule of oxygen by a diene addition mechanism to form a diperoxide — 6α,14α-epidioxy-Δ⁷-dodecahydro-7-(2--hydroperoxyprop-2-yl)-1β,12β-dimethylphenanthrene-1α--carboxylic acid (CX):



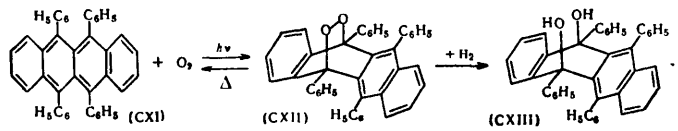
‡ Lawrence[106] attributes an α configuration to the oxygen bridge in the epidioxides of resin acids, since the β-methyl groups prevent attack from the β region on the 1,3-diene system of the resin acids, as in the case of steroids.

## III. REACTION OF MOLECULAR OXYGEN WITH AROMATIC DIENES

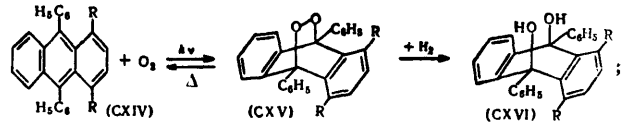
In 1926 Moureu and Dufraisse[108] observed that, when 3-chloro-1,3,3-triphenylprop-1-yne is heated in a vacuum to 100–120°, hydrogen chloride is evolved, and a red hydrocarbon having the composition $C_{42}H_{28}$ is formed. The name of this hydrocarbon is rubrene. These workers established[108] that dilute solutions of rubrene in benzene, carbon disulphide, chloroform, and other solvents rapidly lose their colour on exposure to sunlight or artificial light in the presence of air. A compound possessing the properties of a peroxide and having the composition $C_{42}H_{28}O_2$ was isolated from the decolorised solutions. When rubrene peroxide was heated in a vacuum to 140–150°, it broke down into the original hydrocarbon and oxygen. This decomposition was accompanied by luminescence. It was established[109,110] in 1936 that rubrene was 5,6,11,12-tetraphenylnaphthacene (CXI)§.



In 1937 Dufraisse[112] observed that catalytic reduction of rubrene peroxide gave the 5,12-diol (CXIII), which had been obtained previously by the action of phenyllithium on 6,11-diphenylnaphthacene-5,12-quinone[110] and by the action of potassium permanganate on rubrene[113]. Since rubrene peroxide gave the 5,12-diol (CXIII) on reduction, it must have been a transannular epidioxide (CXII):



By irradiating solutions of 9,10-diphenylanthracene (CXIV*a*) in the presence of air, Dufraisse[114,115] obtained a peroxide of this compound, reduction of which gave the 9,10-diol (CXVI*a*). Consequently the peroxide of 9,10-diphenylanthracene had the transannular structure (CXV*a*). When heated in a vacuum to 180°, the epidioxide of 9,10-diphenylanthracene (CXV*a*) decomposes into oxygen and the original hydrocarbon (CXIV*a*).

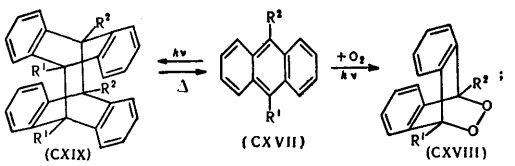


(*a*) R = H; (*b*) R = $OCH_3$.

By the photooxidation of 1,4-dimethoxy-9,10-diphenylanthracene (CXIV*b*) Dufraisse[116,117] obtained the transannular epidioxide (CXV*b*), which slowly dissociated into the original components even at room temperature.

§ For the mechanism of the formation of rubrene from 3-chloro--1,3,3-triphenylprop-1-yne, see Ref.111.

It was also found[118-121] that irradiation in the presence of air of dilute carbon-disulphide solutions of anthracene (CXVII*a*), 9-methylanthracene (CXVII*b*), 9-ethylanthracene (CXVII*c*), 9,10-dimethylanthracene (CXVII*d*), and 9-ethyl-10-methylanthracene (CXVII*e*) yields the transannular epidioxides (CXVIII*a–e*), which when heated in a vacuum decompose violently without the evolution of free oxygen:




(CXIX) (CXVII) (CXVIII)

(*a*) $R^1 = R^2 = H$,
(*b*) $R^1 = H$; $R^2 = CH_3$,
(*c*) $R^1 = H$; $R^2 = C_2H_5$,
(*d*) $R^1 = R^2 = CH_3$,
(*e*) $R^1 = CH_3$; $R^2 = C_2H_5$.

When solutions of anthracene (CXVII*a*), 9-methylanthracene (CXVII*b*), and 9,10-dimethylanthracene (CXVII*d*) in benzene, xylene, glacial acetic acid, and other solvents are exposed at room temperature in the absence of air, photodimers (CXIX*a*), (CXIX*b*), and (CXIX*d*) are formed. This reaction is reversible: the anthracenes are regenerated when the temperature is raised in the dark. Other anthracene derivatives also form photodimers. However, neither 9,10-diphenylanthracene (CXIV*a*) nor rubrene (CXI) undergoes photochemical dimerisation. This may be due to steric hindrance, or else to thermal instability of the photodimers under the experimental conditions[122].

Dufraisse, Clar, Étienne, and other investigators have established that transannular epidioxides are formed by various linear and angular fusion products of anthracene with benzene rings, several of their derivatives, and nitrogen analogues[123-126]. All attempts to prepare photoperoxides of naphthalene, phenanthrene, or acridine were unsuccessful[127,128].

Hence it follows that transannular photoepidioxides are formed only from polycyclic aromatic compounds which contain an anthracene ring system (acenes). These compounds contain a reactive aromatic diene system (an *o*-quinoid grouping), and are capable of undergoing diene synthesis with maleic anhydride, *p*-benzoquinone, azoformic ester, and other dienophiles. The photooxidation of acenes can therefore be regarded as a photochemical diene synthesis with molecular oxygen.

Anthracene, 9,10-diphenylanthracene, rubrene, and other acenes act as sensitisers, and therefore do not require the addition of other photosensitisers for their photooxidation. Acenes can be used also as photosensitisers in the oxidation of other organic compounds. In the presence of rubrene, for examples, *p*-mentha-1,3--diene is oxidised to ascaridole[39,40].

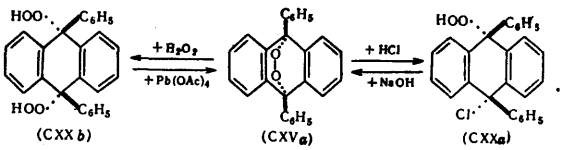
The rate of formation of acene epidioxides is greatly dependent on the nature of the solvent. Thus Dufraisse[129] found the relative rates of photooxidation of rubrene in various solvents to be as indicated in the accompanying Table.

Study of the chemical reactions of the photoperoxides of acenes has given interesting results. For example, Pinazzi[130] established that 9,10-diphenylanthracene photoepidioxide (CXV*a*) reacts with hydrogen chloride to form

TABLE.

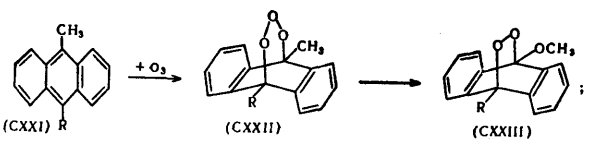
| Solvent | Relative rate of photo-oxidation of rubrene (benzene = 1) |
|---|---|
| Carbon disulphide | 9 |
| Chloroform | 3 |
| Ethyl iodide | 1 |
| Benzene | 1 |
| Acetone | 1 |
| Ether | 0.5 |
| Anisole | 0.4 |
| Pyridine | 0.25 |
| Nitrobenzene | 0.10 |

a chloro-hydroperoxide (CXX*a*), which yields the original peroxide (CXV*a*) on treatment with alkali. He also observed[131] that the epidioxide (CXV*a*) reacts with hydrogen peroxide to form a dihydroperoxide (CXX*b*). Criegee[132] obtained the original 9,10-diphenylanthracene epidioxide (CXV*a*) from the latter by treatment with lead tetraacetate.




(CXX*b*) (CXV*a*) (CXX*a*)

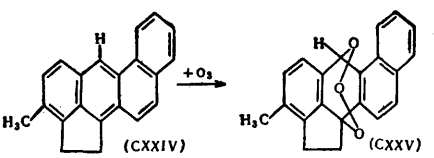
It has recently been found[133,134] that 9,10-dimethylanthracene (CXXI*a*) and 9-methoxy-10-methylanthracene (CXXI*b*) in dichloromethane react at -78° with ozone to form monoozonides. The nuclear magnetic resonance spectra of the latter show them to be transannular-9,10-adducts (CXXII*a*) and (CXXII*b*). In solution these adducts are rapidly converted even at room temperature into the transannular 9,10-epidioxides (CXXIII*a*) and (CXXIII*b*).




(CXXI) (CXXII) (CXXIII)

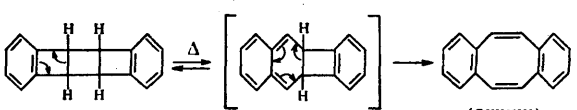
(*a*) R = $CH_3$; (*b*) R = $OCH_3$.

The ozonisation of 3-methylcholanthrene (CXXIV) in dichloromethane at -78° gave a mixture of peroxides, which probably contained the transannular 6,12b-ozonide (CXXV).[135]




(CXXIV) (CXXV)

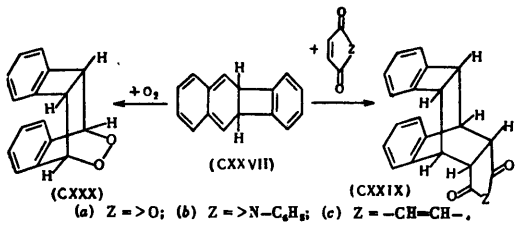
Nenitzescu has shown[136-138] that the linear dimer (CXXVI) of benzocyclobutadiene rearranges on heating to form 1,2 : 5,6-dibenzocyclooctatetraene (CXXVIII). He[137,138] as well as Cava[139] put forward the hypothesis that this change involves two consecutive reactions — (1) reversible isomerisation of (CXXVI) into an unstable hydrocarbon of *o*-quinoid structure (CXXVII), and (2) rearrangement of the latter to (CXXVIII):




(CXXVI) (CXXVII) (CXXVIII)

This mechanism for the rearrangement was confirmed by trapping the intermediate *o*-quinoid compound (CXXVII) with

various dienophiles: heating the hydrocarbon (CXXVI) with maleic anhydride, *N*-phenylmaleimide, and *p*-benzoquinone gave the corresponding diene adducts (CXXIX*a–c*) [137–139].

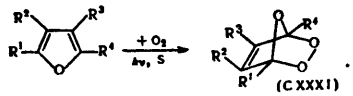



(*a*) Z = >O; (*b*) Z = >N–$C_6H_5$; (*c*) Z = –CH=CH–.

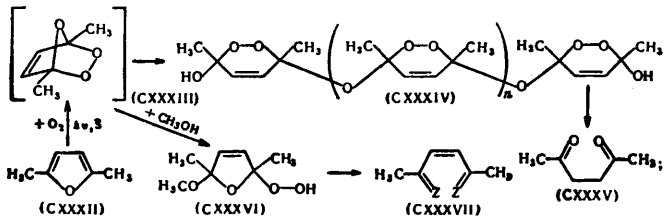
Nenitzescu [137,138] also found that, when a stream of oxygen is passed through an ethereal solution of dibenzotricyclooctadiene (CXXVI), a crystalline peroxide is formed, to which he attributed the transannular structure (CXXX). This peroxide is sparingly soluble in the usual solvents, and Nenitzescu does not exclude the possibility that it may be a polymeric compound. Catalytic reduction of the peroxide yields, instead of the expected diol, a hydrocarbon having the composition $C_{16}H_{16}$.

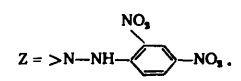
## IV. REACTION OF MOLECULAR OXYGEN WITH 1,3-DIENES CONTAINING HETEROATOMS

In 1952 Schenck [35,38,140–142] reported that furan and its derivatives on exposure to light in the presence of a photosensitiser, react with molecular oxygen by a mechanism of diene synthesis to form extremely unstable adducts of ozonide structure (CXXXI), which cannot be isolated¶:



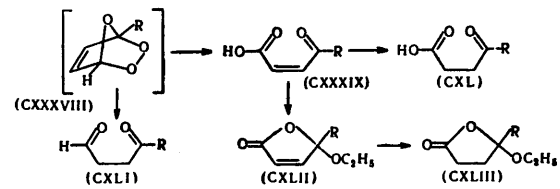

The first attempt at photosensitised oxidation was undertaken with 2,5-dimethylfuran (CXXXII). A dilute alcoholic solution of this compound containing Eosin was shaken in an atmosphere of oxygen while exposed to a 300 W lamp for 10 days. The photooxidation product possessed peroxide properties, and from it was isolated a crystalline polymeric peroxide, catalytic hydrogenation of which gave a quantitative yield of hexane-2,5-dione (CXXXV). Hence, in the photosensitised oxidation of 2,5-dimethylfuran, the oxygen had added on at the 2,5 positions to form a readily polymerisable diene adduct of ozonide structure (CXXXIII). Schenck assumes that the polymeric peroxide which he isolated had the structure (CXXXIV).




In 1964 Foote [147] established that the photosensitised oxidation of 2,5-dimethylfuran (CXXXII) in methanol gives a 74% yield of a crystalline peroxide having the composition $C_7H_{12}O_4$. Examination of the infrared and nuclear magnetic resonance spectra of this peroxide showed it to be 2,5-dihydro-2-hydroperoxy-5-methoxy-2,5-dimethylfuran (CXXXVI). This was converted into the known bis-2,4-dinitrophenylhydrazone of hex-*cis*-3-ene-2,5-dione (CXXXVII). Foote assumes that the photooxidation of (CXXXII) involves the initial formation of a diene adduct of ozonide structure (CXXXIII), which then reacts with the methanol to form the hydroperoxide (CXXXVI).

By the photosensitised oxidation of 2-methylfuran Schenck [140] obtained a peroxide of ozonide structure (CXXXVIII*a*), catalytic hydrogenation of which gave γ-oxovaleraldehyde (CXLI*a*) and γ-oxovaleric acid (CXL*a*). The latter was formed by rearrangement of the peroxide (CXXXVIII*a*) to 4-oxopent-*cis*-2-enoic acid (CXXXIX*a*) followed by hydrogenation. The rearrangement of the adduct (CXXXVIII*a*) to (CXXXIX*a*) readily occurs in alcoholic solution in the presence of vanadium pentoxide. Under these conditions 2-methylfuran gave a 76% yield of the ethyl ether (CXLII*a*) of the lactol form of the acid (CXXXIX*a*), catalytic reduction of which formed the ethyl ether (CXLIII*a*)†.




(*a*) R = $CH_3$; (*b*) R = H; (*c*) R = COOH.

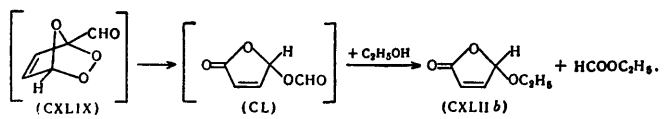
Schenck [140] obtained by the photosensitised oxidation of furan an adduct of ozonide structure (CXXXVIII*b*), which rearranged rapidly to 4-oxobut-*cis*-2-enoic acid (CXXXIX*b*), catalytic reduction of which formed γ-oxobutyric acid (CXL*b*). When rearrangement of the adduct (CXXXVIII*b*) was carried out in ethanol medium, the ethyl ether (CXLII*b*) of the lactol form of (CXXXIX*b*) was obtained, and was reduced to the ethyl ether (CXLIII*b*) of the lactol form of (CXL*b*).

By the photosensitised oxidation of 2-furoic acid and furfural in ethanolic medium Schenck [140] obtained high yields of the ethyl ether (CXLII*b*) of the lactol form of 4-oxobut-*cis*-2-enoic acid. In the former case the intermediate diene adduct (CXXXVIII*c*) is immediately decarboxylated with formation of the adduct (CXXXVIII*b*), which is then converted into the pseudo-ester (CXLII*b*). In the second case the reaction probable involves the initial formation of a diene adduct (CXLIX), which then rearranges to the mixed anhydride (CL) of the lactol form of 4-oxobut-*cis*-2-enoic acid and formic acid, and this undergoes

¶ For the autoxidation of furan and its derivatives in the absence of photosensitisers, see Refs. 140 and 143–146.

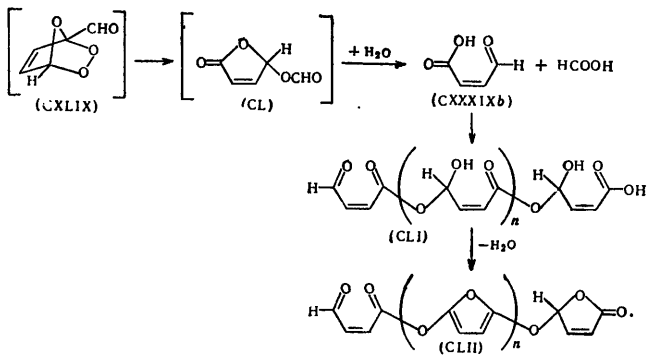
† Holeček and Horák [148] found that 4-oxopent-2-enoic acid (CXXXIX*a*) was formed by the photooxidation of 2-methylfuran in acetone medium in the presence of protoporphyrin IX.

alcoholysis to the pseudo-ester (CXLII*b*) and ethyl formate‡:



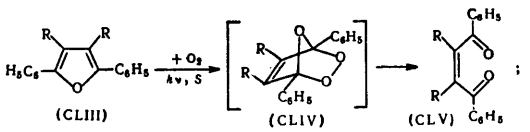
(CXLIX) (CL) (CXLII *b*)

Dunlop[153,154] studied the autoxidation of furfuraldehyde, which on standing in the air darkens and acquires an acid reaction. The investigation showed that the autoxidation involves the formation of formic acid, 4-oxobut-2-enoic acid and its polymer, and small amounts of 2-furoic acid. Dunlop assumed the first stage of the reaction to be formation of a 2,5-adduct of ozonide structure (CXLIX), which hydrolysed with the production of formic acid and the unstable 4-oxobut-2-enoic acid (CXXXIX*b*), the latter being converted into the polymeric acids (CLI), and (CLII), responsible for the brown colour of oxidised furfuraldehyde:



(CXLIX) (CL) (CXXXIX*b*) (CLI) (CLII)

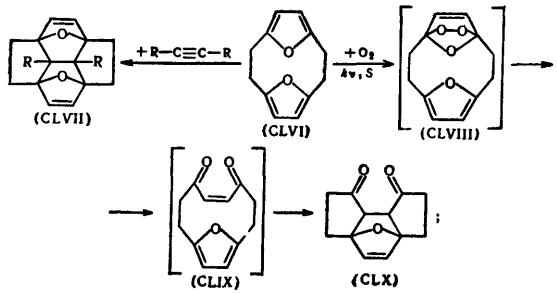
Martel[155] reported that the photochemical oxidation of 2,5-diphenylfuran (CLIII*a*) involves the formation of an unstable adduct of ozonide structure (CLIV*a*), which could not be isolated but whose structure was established by reduction with potassium iodide and acetic acid to 1,4-diphenylbut-*cis*-2-ene-1,4-dione (CLV*a*).



(CLIII) (CLIV) (CLV)

(*a*) R = H; (*b*) R = $C_6H_5$.

Martel[155], Wasserman[156], and Lutz[157] found that the photooxidation of 2,3,4,5-tetraphenylfuran (CLIII*b*) was accompanied by the formation of an unstable peroxide (CLIV*b*), which was reduced with potassium iodide and acetic acid to 1,2,3,4-tetraphenylbut-*cis*-2-ene-1,4-dione (CLV*b*).



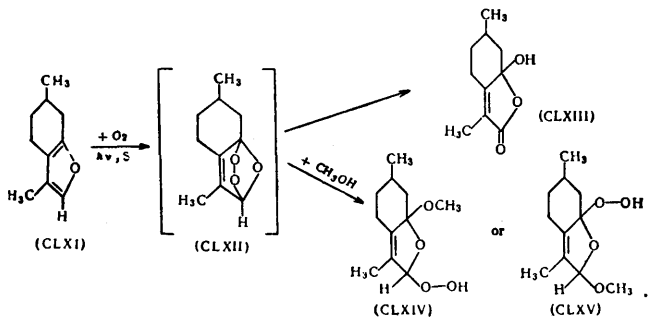
(CLVII) (CLVI) (CLVIII) (CLIX) (CLX)

R = $-COOCH_3$.

Cram[158] has shown that 1,4 : 7,10-diepoxydodeca-1,3,7,9-tetraene (CLVI) reacts with dimethyl acetylenedicarboxylate by a mechanism of diene synthesis to form an adduct (CLVII), whose configuration was not established.

Wasserman[159] established that the photosensitised oxidation of the heterocyclophane (CLVI) in alcoholic solution yields a 1,4-diketone (CLX), the reaction probably occurring in three stages: (i) oxidation of (CLVI) to the monoepidioxide (CLVIII); (ii) reduction of (CLVIII) to an unsaturated 1,4-diketone (CLIX); (iii) intramolecular diene condensation of (CLIX) to (CLX).

In 1958 Schenck and Foote[160] found that the photosensitised oxidation of menthofuran (CLXI) gives a 40% yield of the pseudo-acid (CLXIII). The unstable diene adduct of ozonide structure (CLXII) formed as an intermediate in this reaction could not be isolated even when the experiment was carried out at -20°§.



(CLXI) (CLXII) (CLXIII) (CLXIV) (CLXV)

The photooxidation of menthofuran in methanol medium gave an addition product of a methanol molecule to the epidioxide (CLXII), whose structure was not established. In 1964 Foote[147] reported that the product of the methanolysis of the epidioxide (CLXII) was a hydroperoxide (CLXIV) or (CLXV).

In 1946 Dufraisse[162] showed that, when dilute solutions of 1,3-diphenylisobenzofuran (CLXVI)¶ undergo photooxidation at -40°, an extremely unstable diene adduct of ozonide structure (CLXVII), which explodes at ~18°, is

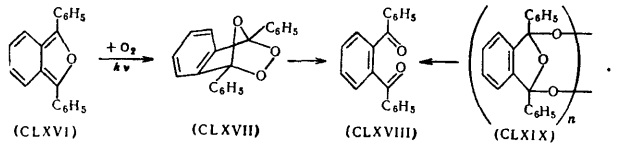
‡ Schenck[149,150], Ogura[151], and Alder[152] have worked out a method for preparing the pseudo-ester (CXLII*b*) from furfuraldehyde.

§ In 1950 Woodward[161] had investigated the autoxidation of menthofuran, and isolated a 15% yield of the pseudo-acid (CLXIII) from the oxidation products.

¶ 1,3-Diphenylisobenzofuran, which contains a reactive aromatic 1,3-diene system (*o*-quinoid grouping), readily undergoes diene condensation with maleic anhydride, acrylaldehyde, *p*-benzoquinone, and other dienophiles[163].

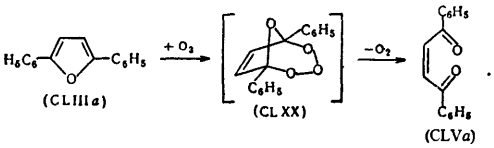
formed. In solution this adduct is rapidly converted at room temperature into *o*-dibenzoylbenzene (CLXVIII).

In 1963 Le Berre[164] shook a benzene solution of 1,3-diphenylisobenzofuran (CLXVI) in an atmosphere of oxygen in the dark, and obtained a polymeric peroxide (CLXIX), which decomposed explosively when heated above 100°; quinol inhibits the autoxidation of 1,3-diphenylisobenzofuran. When the polyperoxide (CLXIX) was reduced with potassium iodide and and acetic acid, *o*-dibenzoylbenzene (CLXVIII) was obtained†.



(CLXVI) (CLXVII) (CLXVIII) (CLXIX)

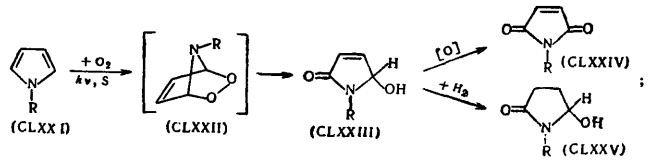
It was established in 1957 that[166] the ozonisation of 2,5-diphenylfuran (CLIII*a*) in acetone or methanol at -40° involves the formation of 1,4-diphenylbut-*cis*-2-ene-1,4-dione (CLV*a*). It is probable that in this case, too, the first stage in the process is 2,5 addition of an ozone molecule to 2,5-diphenylfuran to form the monoozonide (CLXX), the second stage being conversion of the $O_3$-adduct (CLXX) into *cis*-1,2-dibenzoylethylene (CLV*a*):



(CLIII*a*) (CLXX) (CLV*a*)

In 1939 Bernheim and Morgan[167] showed that illumination of an aqueous, alcoholic, or acetone solution of pyrrole in the presence of a photosensitiser (Methylene Blue, Eosin) and oxygen results in the formation of a crystalline substance melting at 102°. The structure of this substance was not determined.

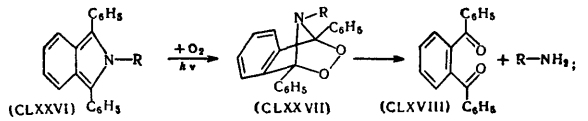
These experiments were repeated by de Mayo and Reid[168] in 1962, who found that, if a 0.1% aqueous solution of pyrrole (CLXXI*a*) was shaken with Eosin in an atmosphere of oxygen while exposed to a 100 W lamp, one molecular equivalent of oxygen was rapidly absorbed. A photooxidation product of composition $C_4H_5NO_2$ and m. p. 102° was isolated in 32% yield from the reaction mixture. Under the same conditions 1-methylpyrrole (CLXXI*b*) gave a 48% yield of a crystalline substance $C_5H_7NO_2$ melting at 85°. These workers assume that the photosensitised oxidation involves the initial formation of unstable diene adducts (CLXXII*a*) and (CLXXII*b*), which then rearrange to the compounds melting at 102° and 85°, for which the formulae (CLXXIII*a*) and (CLXXIII*b*) are proposed. These suggested structural formulae were confirmed by examination of the infrared spectrum of the substance melting at 102° and of the nuclear magnetic resonance spectrum of that melting at 85°. Oxidation of the photooxidation products (CLXXIII*a*) and (CLXXIII*b*) with active manganse dioxide gave respectively maleimide (CLXXIV*a*) and *N*-methylmaleimide (CLXXIV*b*), and catalytic hydrogenation of the photooxidation product of pyrrole (CLXXIII*a*) gave the dihydro-derivative (CLXXV*a*).



(CLXXI) (CLXXII) (CLXXIII) (CLXXIV) (CLXXV)

(*a*) R = H; (*b*) R = $CH_3$.

During 1955–1957 Theilacker and Schmidt[169] studied the oxidation of several derivatives of isoindole, and found that 2-methyl-1,3-diphenylisoindole (CLXXVI*a*) readily forms a diene adduct with maleic anhydride‡. Passage of a stream of air through a boiling solution of 2-methyl-1,3-diphenylisoindole (CLXXVI*a*) in aqueous butanol produced *o*-dibenzoylbenzene (CLXVIII). These workers assume the intermediate formation of an epidioxide (CLXXVII*a*), which is then hydrolysed with the formation of *o*-dibenzoylbenzene, methylamine, and hydrogen peroxide.

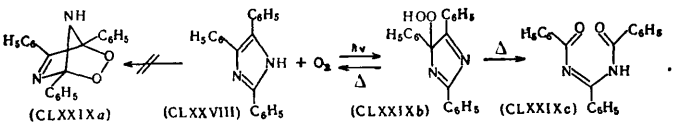


(CLXXVI) (CLXXVII) (CLXVIII)

(*a*) R = $CH_3$; (*b*) R = $C_6H_5$.

The photooxidation of dilute carbon-disulphide solutions of 1,2,3-triphenylisoindole (CLXXVI*b*), which is the nitrogen analogue of 1,3-diphenylisobenzofuran (CLXVI), gives a good yield of a diene adduct (CLXXVII*b*), which decomposes at 80–90°. Reduction of the adduct (CLXXVII*b*) with zinc and acetic acid produced a high yield of 1,2,3-triphenylisoindole (CLXXVI*b*), whereas reduction of (CLXXVII*b*) with sodium sulphite gave *o*-dibenzoylbenzene and aniline.

In 1957 Dufraisse[170–172] reported that the photooxidation of dilute solutions of lophine, 2,4,5-triphenylimidazole (CLXXVIII), in carbon disulphide at 18° involves the formation of a crystalline peroxide, which when heated to 170° decomposes into lophine (CLXXVIII), oxygen, and *NN'*-dibenzoylbenzamidine (CLXXIX*c*). He assumed the lophine peroxide which he had obtained to be a diene adduct (CLXXIX*a*), but an examination of its ultraviolet, infrared, and nuclear magnetic resonance spectra undertaken in 1964 has shown that it is a hydroperoxide (CLXXIX*b*)[173,174].



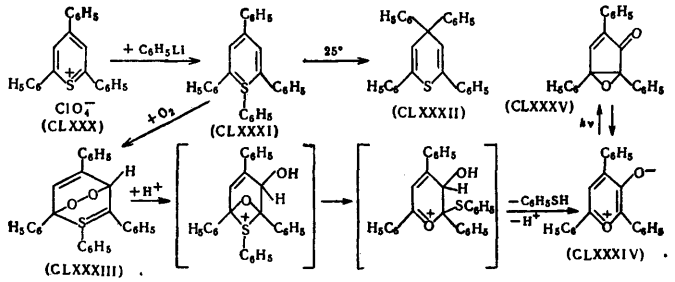
(CLXXIX*a*) (CLXXVIII) (CLXXIX*b*) (CLXXIX*c*)

In 1962 Suld and Price[175] reported that phenyllithium reacts in ether with 2,4,6-triphenylthiapyrylium perchlorate (CLXXX) to form the unstable 1,2,4,6-tetraphenylthiabenzene (CLXXXI), which was isolated as an ether complex, a purple amorphous mass. At room temperature (CLXXXI) isomerises to the colourless crystalline 2,4,4,6-tetraphenylthiapyran (CLXXXII). If oxygen is admitted to the reddish violet ethereal solution of tetraphenylthiabenzene (CLXXXI), the solution is rapidly decolorised with formation of an extremely unstable "transannular epidioxide" of 1,2,4,6-tetraphenylthiabenzene

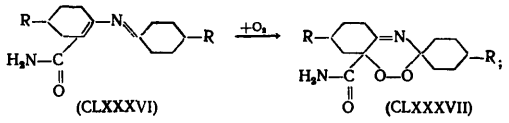
† As early as 1906 Guiot and Catel[165] had observed the formation of *o*-dibenzoylbenzene when benzene or alcoholic solutions of 1,3-diphenylisobenzofuran were in contact with air. They also noted that the oxidation of 1,3-diphenylisobenzofuran is more rapid in the light than in the dark.

‡ For diene syntheses with isoindoles, see Ref. 163, p. 554.

(CLXXXIII), which could not be isolated. In ethereal solution the "epidioxide" (CLXXXIII) reacts rapidly with hydrogen chloride to form benzenethiol and 2,4,6-triphenylpyrylium 3-oxide (CLXXXIV), consisting of dark red crystals. In 1963 Ullman[176] showed that, when an acetonitrile solution of (CLXXXIV) is illuminated, the latter undergoes reversible photochemical conversion into a valency tautomer, 4,5-epoxy-2,4,5-triphenylcyclopent-2-en-1-one (CLXXXV)§.



During 1961–1964 McKay[178–180] investigated the condensation of alicyclic ketones with urea. It was found that, when the latter was heated with cyclohexanone, 4-methylcyclohexanone, and 4-t-butylcyclohexanone, the corresponding condensation products (CLXXXVI*a–c*) were formed. In the purfication of these products it was noted that they absorbed oxygen very readily. One molecular equivalent of oxygen was absorbed when chloroform solutions of (CLXXXVI*a–c*) were stirred at room temperature and normal pressure in an atmosphere of pure oxygen for 1 h, and in the presence of 0.1% of cobalt naphthenate this occurred within 5 min. The oxidation products were crystalline peroxides, which were shown to have the structures (CLXXXVII*a–c*). Hence they had been formed by 1,4 addition of oxygen to the conjugated "diene" system of the condensation products (CLXXXVI*a–c*).



(*a*) R = H; (*b*) R = $CH_3$; (*c*) R = $(CH_3)_3C$.

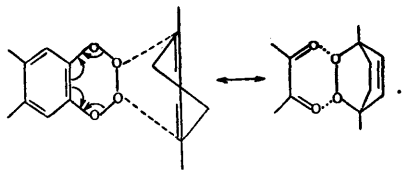
## V. MECHANISM OF PHOTOSENSITISED OXIDATION; OXIDATION WITH SINGLET OXYGEN

On absorbing radiation, molecules pass into an excited electronic state, from which they return to the normal state with the emission of radiation (fluorescence). This excitation energy can be used for chemical reactions. The excited molecule can either react with a molecule which collides with it, or else transmit its energy to another molecule, which will then become a centre for photochemical reaction. In the latter case the molecule which absorbs the radiation acts solely as a sensitiser, and undergoes no change during the reaction (sensitised photochemical reaction)[181]. The problem of the nature of the intermediate products in the photosensitised oxidation of olefins and conjugated dienes has been discussed by several investigators.

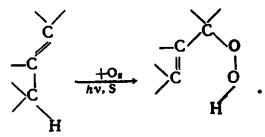
According to the ideas developed by Schönberg[182,183], Schenck[38,40,184–188], and Bowen[189,190], a sensitiser (S), on absorbing light energy, passes into a diradical (.S.), which adds on a molecule of oxygen to form a peroxy-radical (.S–O–O.). The labile oxygen in the peroxy-radical is then transferred to an acceptor A with formation of the peroxide $AO_2$ and the original sensitiser. Schönberg[183] assumes that the transfer of oxygen to the acceptor takes place either in a reaction aggregate or by breakdown of the peroxy-radical into the original sensitiser and active (nascent) oxygen.

$$S \xrightarrow{h\nu} \cdot S \cdot,$$
$$\cdot S \cdot + O_2 \rightarrow \cdot S{-}O{-}O \cdot$$
$$\cdot S{-}O{-}O \cdot + A \rightarrow AO_2 + S.$$

On the basis of Schenck's concepts, Schuller et al.[107] suggested that in the case of the photosensitised oxidation of laevopimaric acid (CII) and palustric acid (CVI) (see Section II, 7) the transition state can be represented (with *o*-benzoquinone as sensitiser) as follows

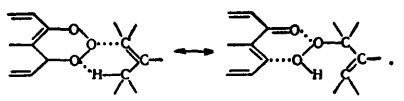


Schenck[35,38,184,191–200] and other workers[201–203] have established that the photosensitised oxidation of olefins involves migration of an allyl hydrogen atom to the oxygen with displacement of the double bond to a neighbouring position, i.e. by a mechanism of monoene addition. The reaction products are allyl hydroperoxides (CLXXXVIII)¶:



(CLXXXVIII)

Thus the first stage in the photosensitised oxidation of *p*-mentha-1,4(8)-diene (XXVIII) and neoabietic acid (CVIII) is their conversion into the allyl hydroperoxide (XXIX) and (CIX) (see Sections II, 4 and II, 7). Schuller and Lawrence[105,106] assume that in this case the transition state can be represented (with a 1,4-naphthaquinone derivative as sensitiser)



A different reaction mechanism was suggested for photosensitised oxidation by Kautsky[204–206], who regarded the oxidation as caused by photoactive oxygen. According to him the sensitised oxidation comprises two stages — light and dark: the light energy absorbed by a sensitiser

§ In 1964 Dunston and Yates[177] established that 4, 5-epoxy-2,3,4,5-tetraphenylcyclopent-2-en-1-one and 2,4,5,6-tetraphenylpyrylium 3-oxide are also photochemical valency tautomers.

¶ In the case of fused cyclic systems, the reaction occurs stereospecifically; it is the quasi-axial allyl hydrogen atom located in the *cis* position with respect to the newly formed C–O bond which migrates.

molecule is first transferred to an oxygen molecule; and in the second stage, for which illumination is not required, the excited oxygen molecule reacts, in one of two theoretically possible metastable singlet states $^1\Delta_g$ or $^1\Sigma_g$, with the acceptor A to form a peroxide product $AO_2$:

$$S \xrightarrow{h\nu} S^*,$$
$$S^* + O_2 \rightarrow O_2^* + S,$$
$$O^*_2 + A \rightarrow AO_2.$$

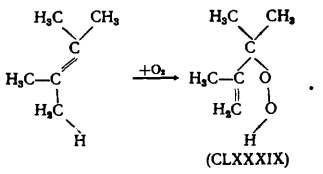
As an experimental demonstration of the correctness of his suggested reaction mechanism for photosensitised oxidation, Kautsky prepared separately peroxides of the sensitiser (Trypaflavine) and of the acceptor (the leuco base of Malachite Green), and illuminated mixtures of the two adsorbates (the experiments were carried out at low oxygen pressures). Under these conditions the leuco base was oxidised to the dye. This result provided a convincing proof of the correctness of Kautsky's suggested reaction mechanism.

A similar phenomenon has been observed by Rosenberg[207] in a study of the interaction of oxygen with photoexcited Acriflavine deposited on silica gel.

In 1964 Foote[147] and Corey[208] simultaneously published brief communications describing new methods for the oxidation of cyclic 1,3-dienes to transannular epidioxides with molecular oxygen in an excited singlet state.

Foote[147] obtained singlet oxygen *in situ* by the action of sodium hypochlorite on hydrogen peroxide. The technique of oxidation is very simple: to a solution in methanol of the substance to be oxidised are added 30% hydrogen peroxide, and then 1 M sodium hypochlorite solution with stirring and cooling. Foote's method is suitable for the preparation of epidioxides from cyclic 1,3-dienes and of allyl hydroperoxides from olefins. By the oxidation of cyclohexa-1,3-diene (XXI*c*) was obtained an epidioxide (XXII*c*, yield 20%) previously synthesised by Schenck (see Section II, 4). The oxidation of tetracyclone (LXIV*c*) gave 1,4-diphenylbut-*cis*-2-ene-1,4-dione (LXVI*c*, yield 50%), which had previously been obtained by the photooxidation of tetracyclone (see Section II, 5). The oxidation of 2,5-dimethylfuran (CXXXII*c*) in methanol gave a hydroperoxide (CXXXVI, yield 84%) identical with that obtained by Foote by the photosensitised oxidation of 2,5-dimethylfuran in methanol (see Section IV).

Foote reported that, according to preliminary results, rubrene and other acenes are also oxidised by singlet oxygen to transannular epidioxides. Oxidation of olefins containing allyl hydrogen atoms by means of singlet oxygen yields, with displacement of the double bond, allyl hydroperoxides. Thus the oxidation of 2,3-dimethylbut-2-ene led to 3-hydroperoxy-2,3-dimethylbut-1-ene (CLXXXIX, yield 63%), previously obtained by Schenck[196] by the photosensitised oxidation of 2,3-dimethylbut-2-ene.



(CLXXXIX)

Foote[209] regards his results as indicating that singlet oxygen may be the reactive intermediate in the photosensitised oxidation, too.

Corey[208] has employed the method of transforming molecular oxygen to the singlet state by means of an electric discharge, first described in 1956 by Foner and Hudson[210]. By this method ~10% of the molecular oxygen is converted to the $^1\Delta_g$ metastable state, and only ~0.01% passes into the $^1\Sigma_g$ metastable state. Corey carried out the oxidation of 1,3-dienes at 0° in bromobenzene, chlorobenzene, nitrobenzene, and other solvents. The oxidation of *p*-mentha-1,3-diene resulted in ascaridole (I), previously synthesised by Schenck (see Section II, 3). By the oxidation of 1,3-diphenylisobenzofuran (CLXVI) a high yield of *o*-dibenzoylbenzene (CLXVIII) was obtained. 9,10-Diphenylanthracene (CXIV*a*), anthracene (CXVII*a*), and 9,10-dimethylanthracene (CXVII*d*) were converted into the corresponding epidioxides (CXV*a*), (CXVIII*a*), and (CXVIII*d*), identical with specimens obtained by the photooxidation of these hydrocarbons (see Section III).

Attempts to oxidise 2,3-dimethylbut-2-ene, cyclohex-1-enylbenzene, pin-2-ene, and cholest-4-en-3β-ol to allyl hydroperoxides did not give positive results.

Corey's method cannot yet be employed to prepare transannular epidioxides from cyclic 1,3-dienes. The generator of metastable oxygen which he used enabled only a few millimoles of substances to be oxidised: for example, the oxidation of 100 mg of 9,10-dimethylanthracene to the 9,10-epidioxide lasted 19 h.

## NOTE ADDED IN PROOF

Foote[212] has recently made a comparative stereochemical study of the reaction of *p*-mentha-1,8-diene with singlet oxygen and of the photosensitised oxidation of this compound. The results show that identical intermediates are formed in the two cases. Thus Foote's earlier suggestion[209], that singlet oxygen is formed as intermediate in the photooxidation of alkenes and dienoid compounds, has been confirmed experimentally.


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# THE EXTRACTION OF HETEROPOLY--COMPOUNDS AND ITS APPLICATION IN INORGANIC ANALYSIS

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## I. INTRODUCTION

In recent years, in the analytical determination of silicon, phosphorus, and arsenic, small quantities of which are most reliably determined by photometric measurements on their heteropoly-acids, increasing use has been made of the extraction of these heteropoly-acids by organic solvents.

The increasing introduction of the extraction method in the field of heteropoly-compounds cannot be attributed entirely to the general and nowadays widely known advantages of this method. Certain particular advantages of the extraction method are shown to a greater extent by heteropoly-compounds than by any other types of compounds. In this connection it is sufficient to mention two features.

A serious disadvantage of all analytical methods based on photometric measurements on molybdenum heteropoly--compounds (particularly their reduced blue forms) is the superposition of the light absorption of the reagent itself — molybdate; the use of extraction makes possible the ready and reliable elimination of the influence of molybdate, since isopolymolybdate, unlike heteropolymolybdates, is generally not extracted by organic solvents.

Another frequent obstacle to the analytical application of heteropoly-compounds is the instability of the light absorption of the solutions taken for the photometric measurements. This is due to the existence of complex equilibria in aqueous solutions of the heteropoly-compounds, which are extremely sensitive to very small changes in the conditions. The solutions obtained as a result of extraction of the heteropoly-compound by organic solvents are much more stable than the aqueous solutions.

The study of the extraction behaviour of heteropoly--compounds, apart from its analytical value[1-4], is also of undoubted interest from other viewpoints.

The most important method for the preparation of the heteropoly-acids of most elements is the ether method, based on separation of the heteropoly-acids from acidified solutions of their salts by means of diethyl ether[4].

Extraction may provide a valuable method for studying the physicochemical properties of heteropoly-compounds, for which reliable experimental methods are still urgently required[5].

The combination of the most varied properties in a single chemical individual, so characteristic of heteropoly--compounds, is a favourable factor in obtaining useful and concentrated information on the theory of extraction when these compounds are chosen as objects for study (models).

## II. BRIEF HISTORICAL REVIEW

The first information on the behaviour of heteropoly-compounds towards organic solvents appeared in papers by Marignac[6], Parmentier[7], and Sobolev[8], who studied various physicochemical properties of tungstosilicic, molybdophosphoric, and tungstophosphoric acids, including their solubility in diethyl ether.

Drechsel[9] was the first to make use of the solubility of heteropoly-acids in diethyl ether for their isolation in the free state. The ethereal extraction method for the preparation of heteropoly-acids became a classical method, and was later studied in detail by Scroggie[10], who showed the possibility of replacing diethyl ether by other oxygen-containing organic solvents.

The first views on the mechanism of the extraction of heteropoly-acids by diethyl ether were put forward by Rosenheim[11], and the composition of the compound extracted (for the case of molybdophosphoric acid) was first studied by Copaux[12]. A detailed study of the quaternary system molybdophosphoric acid–sulphuric acid–water–diethyl ether was made by Souchay[13]. Extensive studies of equilibria in the systems formed by saturated heteropoly-acids with organic solvents were made by Nikitina and her coworkers; the results of these studies are described in a recently published monograph[4].

The analytical application of the extraction of heteropoly-acids by organic solvents was begun in work by Denigès[14], who pointed out the possibility of making use of the extraction of the reduced forms of molybdophosphoric and molybdoarsenic acids by diethyl ether or pentanol for the qualitative detection of phosphorus and arsenic†. The extraction of heteropoly-acids was first used for quantitative analysis by Copaux[12], who determined the concentration of phosphorus in native phosphates by measuring the volume of an ethereal extract of molybdophosphoric acid. The first extraction–colorimetric method of analysis using heteropoly-compounds was developed by Shneerson[16] for the determination of phosphorus in steels: the method involves the extraction of reduced molybdophosphoric acid by diethyl ether, followed by colorimetric measurements on the extract using a standard series. The use of extraction for the quantitative separation of elements as the heteropoly-acids was first carried out by Alekseev[17] in the analysis of phosphate–arsenate–silicate mixtures. Of considerable importance for the development of extraction methods for the separation and determination of elements as their heteropoly-compounds were the ideas of Keggin[18], and also the work of Berenblum and Chain[19], Allen[20], Proctor and Hood[21], and Wadelin and Mellon[22].

Bibliographies on the extraction of heteropoly-compounds and its use in chemical analysis are to be found in monographs[4,23] and reviews[3,24-29] on the chemistry of heteropoly-compounds, in a monograph[2] and reviews[1,30-42] on the extraction of inorganic compounds, in textbooks on the photometric determination of elements[43-46], in reviews of the analytical chemistry of phosphorus[47-51] and silicon[52-54], and also in a number of original papers[22,55-62].

As far as we are aware, the present review is the first attempt to systematise the available published material.

† Earlier, Jacobs[15] had made use of the extraction of molybdophosphoric acid by pentanol to remove this acid from the mother-liquor after the precipitation of tungstophosphates, but this work was preparative rather than analytical.

## III. GENERAL CHARACTERISTICS OF THE EXTRACTION OF HETEROPOLY-COMPOUNDS

Heteropoly-acids and their salts are extracted from acidified aqueous solutions by oxygen-containing organic solvents (alcohols, ethers, esters, ketones, and aldehydes)[2-4,10,17,18,22-29,49,53,62-73]. They are not extracted by solvents containing no oxygen (hydrocarbons, halogenohydrocarbons, carbon disulphide, petroleum ether), but solutions of nitrogen-containing compounds (amines) in non-polar solvents (benzene or chloroform) are excellent extracting agents for heteropoly-compounds[57,74,75]. Thus the effective extraction of heteropoly-compounds requires the presence of a basic oxygen or nitrogen atom in the molecule of the organic extractant.

Of the binary heteropoly-acids of molybdenum, the most readily extracted is molybdophosphoric acid; the ease of extraction of the heteropoly-acids studied decreases in general in the order: molybdophosphoric > molybdoarsenic > molybdosilicic > molybdogermanic. It is difficult as yet to say anything definite about the extraction behaviour of other known heteropoly-acids of molybdenum, since they have been little studied in this connection (there are only a few data on the extraction of molybdoceric[76,77], molybdotitanic[78], and molybdozirconic[78] acids).

The behaviour of binary heteropoly-acids of tungsten towards organic solvents is in general similar to that of their molybdenum analogues. This is indicated by the scant but fairly convincing experimental data on the extraction of tungstophosphoric (diethyl ether[8,15,79,80] and pentanol[15,79]), tungstosilicic (diethyl ether[6,9,10], ethyl acetate, etc.[10]), and tungstogermanic (diethyl ether[81], butanol[82], ethyl acetate[82]) acids.

The appearance of a third element in the structure of the heteropoly-complex (in addition to the two necessary elements other than oxygen and hydrogen) also produces no fundamental change in the behaviour of the heteropoly-complex towards organic solvents. The available published data on the extraction of molybdovanadophosphoric[83-93], tungstovanadophosphoric[71,94,95], tungstoarsenophosphoric[96], molybdovanadogermanic[81,82,97], tungstovanadogermanic[81,82], molybdotitanophosphoric[73,98,99], and molybdoniobophosphoric[100,101] acids indicate that ternary heteropoly-compounds are in general readily extracted by oxygen-containing solvents, but are not extracted by solvents containing no oxygen. The ternary heteropoly-acids, for example molybdoniobophosphoric[100], molybdotitanophosphoric[73], and telluromolybdophosphoric[102] acids, however, are not extracted by certain oxygen-containing solvents, in particular butyl acetate. The extraction behaviour of ternary heteropoly-acids possibly depends on whether the third component is the central atom in the structure of the complex or is present in the ligand part of the complex.

The extraction behaviour of reduced heteropoly-compounds, judging from the few data relating to this field[57,69,70,72,75], does not differ in principle from that of the unreduced heteropoly-compounds. This is a further indication that the structures of the reduced (blue) and unreduced (yellow) forms of the heteropoly-compounds are identical[103].

The extraction of heteropoly-compounds, like any process, depends to a marked extent on the conditions, and is influenced by various factors, of which the most important — the nature of the compound being extracted, the nature of the solvent, the acidity of the aqueous phase, the con-

centration of the compound being extracted in the aqueous phase, the presence of neutral salts, and the temperature — are of considerable significance for the utilisation of the extraction of heteropoly-compounds in chemical analysis, and will be examined in more detail below.

The physicochemical properties of extracts of heteropoly-compounds have been little studied: only a few data relating to their optical characteristics are available. The extracts of both reduced and unreduced heteropoly-compounds retain the colour characteristic of their aqueous solutions (blue and yellow respectively). The general appearance of the absorption spectra of the extracts remains unchanged in both cases[21,22,58,59,67,72,82,104-116], but the light-absorption maxima for the heteropoly-compounds in organic solvents are generally displaced slightly towards shorter wavelengths compared with the maxima of the same heteropoly-compounds in aqueous solutions. For example, unreduced molybdophosphoric acid in aqueous solution shows a light-absorption maximum at 345 mμm[49], and the reduced form shows maxima at 630 and 735 mμm[49]; the corresponding maxima for the same acid in organic solvents lie at 310 mμm[22,59,109,110], or 625 and 725 mμm[21,104,109,111]. Unreduced molybdosilicic acid in aqueous solution has an absorption maximum at 350–355 mμm[53], and the reduced form a maximum at 800–820 mμm[53]; the corresponding maxima for the same acid in organic solvents lie at 330 mμm[22,58], or 630 and 720 mμm[112].

The composition of the forms in which the heteropoly--acids are extracted (the extractable forms) has not been specially studied. Fairly convincing experimental data indicate, however, that at a comparatively low acidity ($< 2\ N$), when the possibility of the extraction of isopolymolybdate is excluded, the stoichiometric composition of molybdophosphate in ethyl acetate[117], butyl acetate[59], and butanol–chloroform[118] extracts corresponds to a constant P : Mo ratio of 1 : 12; this ratio remains unchanged even for the extraction of molybdophosphoric acid with insufficient molybdate[117]. These data indicate that the molybdophosphate complex enters the organic phase in the form of the dodecamolybdophosphoric acid or its salt. An interesting feature is that sodium is extracted into ethyl acetate together with phosphorus and molybdenum in the proportions Na : P : Mo = 2.1 : 1 : 11.9 and 0.7 : 1 : 11.19, depending on the acidity[177]; it is possible that in this case an acid sodium salt of molybdophosphoric acid is extracted.

The increase in the distribution coefficient, for molybdophosphoric and molybdosilicic acids between aqueous solution and butanol, with dilution of the aqueous heteropoly-acid solutions indicates indirectly that the monomeric form of the heteropoly-acids enters the organic solvent during extraction[119,120], since dilution of aqueous solutions of the heteropoly-acids leads to depolymerisation of these acids to forms of low molecular weight. The increase in the extractability of molybdophosphoric and molybdosilicic acids with increase in the hydrogen-ion concentration in the aqueous phase may indicate the preferential extraction of these acids in the undissociated (molecular) form in accordance with the equilibrium[119]

$$\begin{array}{l}(H_nA)_m \rightleftarrows mH_nA \rightleftarrows nH^+ + A^{n-}\ \text{(in water)},\\ \quad\downarrow\uparrow\\ \quad H_nA\qquad\ \text{(in butanol)}.\end{array} \qquad (1)$$

The results of experiments on light-scattering by solutions of tungstophosphoric acid in various organic solvents[121] are of interest in this connection. The molecular weight of tungstophosphoric acid in ethanol and allyl alcohol, determined by the light-scattering method, was found to have the values 2600 and 2900 respectively, showing good agreement with the formula weight for $H_3PW_{12}O_{40}$ (2880) and indicating that tungstophosphoric acid is monomeric in these solvents.

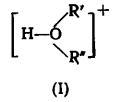
It is quite probable that the formation of a true (molecular) solution as a result of the extraction of heteropoly--compounds by organic solvents is one of the reasons for the greater stability of the organic extracts of heteropoly--compounds (particularly the reduced forms) compared with their aqueous solutions, which, according to some authors[115,122,123], are colloidal solutions and thus have a tendency to undergo gradual decomposition on standing (particularly at high concentrations).

## IV. MECHANISM OF THE EXTRACTION OF HETEROPOLY-COMPOUNDS

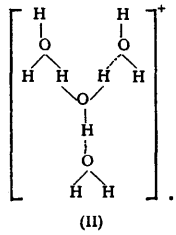
Various suggestions have been made regarding the mechanism of the extraction of heteropoly-compounds by organic solvents, but none has been confirmed by special experimental studies.

The earliest suggestion was that oxygen-containing organic solvents (in particular diethyl ether) extract heteropoly-compounds from acidic solutions with the formation of alkyl-substituted oxonium salts (etherates)[11]. If the acidity is not too high, or the solvent present in large excess, only part of the oxygen-containing solvent enters the oxonium salt and the latter dissolves in the excess of solvent, to which it is structurally similar. This mechanism, known as the oxonium mechanism, accounts well for the most important necessary conditions for the extraction of heteropoly-compounds — the presence of an acid medium and of an oxygen-containing solvent.

The oxonium-mechanism theory, previously used to explain many other examples of extraction[30], has recently been subjected to serious criticism. The main assumption in this theory, that the proton of the acid is attached directly to the oxygen atom of the organic solvent with the formation of an oxonium (solvonium) cation (I) is unjustified in a number of cases. Experimental data which have accumulated in recent years on the extraction of strong acids suggest that the main reaction in this case is attachment of the proton of the acid to the oxygen atom of water, with the formation of a hydroxonium cation, which in turn is hydrated by several water molecules (II); the organic solvent is attached to the water molecules polarised in the field of the hydroxonium ion. This extraction mechanism, which has been called the hydrate–solvate mechanism[124,125], has unfortunately not yet been verified for heteropoly-compounds.



(I)



(II)

According to another suggestion, the extraction of heteropoly-compounds with oxygen-containing solvents is

accompanied by formation of a coordination compound between a molecule of the organic solvent (as electron donor) and the anion of the heteropoly-acid (as electron acceptor)[65]; the compound formed in this way is covalent, and dissolves more readily in the organic solvent than in water. In the formation of coordination compounds of this type, a direct part is apparently played by the electronegative oxygen atom of the organic solvent and a molybdenum atom of the heteropoly-anion, which in this case shows a coordination number of 8. This mechanism readily explains cases of the extraction of heteropoly-compounds by non-polar solvents (chloroform or benzene) using amines and other compounds with marked basic (electron-donating) properties[74].

Both of these suggestions regarding the mechanism of the extraction of heteropoly-compounds are based on the assumption that a donor–acceptor interaction takes place between the heteropoly-compound and the extracting agent; the difference lies in which part (cationic or anionic) of the heteropoly-compound reacts with the extracting agent.

Another suggestion is based on the assumption that the extraction of heteropoly-compounds involves physical distribution, in which the heteropoly-compounds are distributed between the aqueous phase (in ionised form) and the organic phase (in molecular form) as a result of the difference in their solubilities in water and the organic solvent, without the formation of saltlike compounds with the latter[30]. This mechanism explains fairly simply certain regular features observed in the extraction of heteropoly--compounds, for example the salting-out action of salts.

Finally, it is also possible that the extraction of heteropoly-compounds involves a so-called colloid-chemical mechanism, in which the compound being extracted is transferred from the aqueous phase to the organic phase in the form of highly dispersed colloidal particles[126].

The data at present available on the mechanism of the extraction of heteropoly-compounds do not make it possible to give preference to any of the above mechanisms. Most of the experimental facts relating to the extraction of heteropoly-compounds are explained equally satisfactorily on the basis of any of these mechanisms; at the same time there are a number of facts which are explained by none of them. For example, the extractability of heteropoly-compounds by amines of high molecular weight dissolved in inert solvents can be interpreted in terms of any of the above mechanisms, but it can also be understood without recourse to them, simply on the basis of the generally accepted anion-exchange mechanism of extraction with amines[127].

## V. CHIEF FACTORS INFLUENCING THE EXTRACTION OF HETEROPOLY-COMPOUNDS

### 1. Nature of the Compound Being Extracted

The extractability of binary heteropoly-compounds (of molybdenum and tungsten) depends to a considerable extent on the nature of the central atom (phosphorus, arsenic, silicon, germanium, etc.). The difference in the extraction behaviour of heteropoly-compounds is revealed as a difference in the percentage extraction for the same solvent and differences in the number of solvents suitable for the extraction.

Heteropoly-acids having quinquevalent elements (phosphorus and arsenic) as central atoms are extracted much more readily than those with quadrivalent elements (silicon, germanium, cerium, etc.). For example, the degree of extraction of molybdophosphoric acid by organic solvents from aqueous solutions of pH 1, is 100% for pentyl acetate, 70% for dibutyl ether, 54% for hexyl butyrate, 50% for diethyl ether, 8% for isopentyl acetate, and 5% for ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, and isobutyl acetate; molybdosilicic acid undergoes almost no extraction by any of these solvents under the same conditions[68].

Comparison of the extractability of molybdophosphoric and molybdoarsenic acids (Table 1) shows clearly that the former acid is more readily extracted.

Comparison of the molybdenum heteropoly-acids of quadrivalent elements, for example with respect to their behaviour towards diethyl ether, reveals a clearly defined order: silicon > germanium > titanium > zirconium > > cerium > thorium[78]. The heteropoly-acids of the first three elements are prepared by the ether method: i.e. they are extracted by diethyl ether. But the heteropoly-compounds of the last three elements cannot be prepared by the ether method, since they are not extracted by diethyl ether. The poor extractability of molybdoceric acid (compared with molybdosilicic and molybdogermanic acids) has also been demonstrated for other solvents[76,77].

It is difficult on the basis of data at present available to follow the difference in extraction behaviour between binary heteropoly-acids of tungsten and molybdenum. In the case of the ternary heteropoly-acids, however, it can be definitely stated that the introduction of a third component into the molecule of the heteropoly-acid generally leads to a decrease in the ability of the acid to undergo extraction by organic solvents. Even with molybdovanadophosphoric and tungstovanadophosphoric acids, the range of solvents is slightly restricted (compared with that for the binary acids of phosphorus), and acids such as molybdoniobophosphoric[100], molybdotitanophosphoric[73], and telluromolybdophosphoric[102] acids are not extracted at all, for example, by butyl acetate or isobutyl acetate. Here, of course, a significant feature is the part played by the newly introduced third component, i.e. whether it is the central atom or part of a ligand.

The regular features of the influence of the nature of the central atom have also been observed for reduced heteropoly-acids[69]. The reduced heteropoly-compounds are apparently extracted slightly more readily than their unreduced analogues[69,70,72]. In this case an important part is undoubtedly played by the nature of the reducing

TABLE 1. Extraction of molybdophosphoric and molybdoarsenic acids by various solvents[62].

| Solvent | Percentage extraction | |
|---|---|---|
| | P–Mo | As–Mo |
| Ethyl acetoacetate | 100.00 | 96.67 |
| Butanol + chloroform (1 : 4) | 94.97 | 4.74 |
| Ethyl acetate | 79.92 | 29.46 |
| Butyl acetate | 73.58 | 8.49 |
| Isobutanol + benzene (1 : 1) | 72.63 | 36.76 |
| Isobutanol | 67.21 | 86.05 |
| Butanol | 60.63 | 87.91 |
| Octanol | 29.86 | 14.39 |
| Chloroform | 00.00 | 00.00 |
| Benzene | 00.00 | 00.00 |

agent; recent data[128] suggest that organic solvents are extremely sensitive to the slightest changes in the process of heteropoly-compound reduction and to the reduction products.

The extractability of heteropoly-acids (reduced and unreduced) increases sharply when basic substances (for example amines) are introduced into the system[87,74,75], i.e. when conditions are created for the formation and extraction of the salts of the heteropoly-acids with organic bases (sometimes called "addition products"). As noted above, in this case inert solvents of the benzene and chloroform type may act as extractants for heteropoly--compounds.

## 2. Nature of the Solvent–Extractant

According to Alekseev[17], organic solvents can be divided into two groups — light (sp. gr. $< 1$) oxygen-containing solvents (alcohols and ethers), and heavy (sp. gr. $> 1$) solvents containing no oxygen (chloroform and carbon tetrachloride) — according to their behaviour towards heteropoly-compounds. Such compounds dissolve much more readily in solvents of the first group than in water, and are therefore readily extracted by these solvents from aqueous solutions; heteropoly-acids are almost insoluble in solvents of the second group. The extracting power of solvents of the first group decreases when solvents of the second group are added; the decrease is proportional to the quantity of inert solvent added, and is different for different heteropoly-acids.

The results of a large number of studies[17,22,55,60–73,114] show that, for heteropoly-compounds, alcohols are the most effective extractants and ethers the most selective. Of the aliphatic alcohols, the best extracting properties are shown by those containing 4–8 carbon atoms: lower alcohols do not extract heteropoly-compounds quantitatively from aqueous solutions, and higher alcohols from stable emulsions, which are difficult to remove, at the phase boundary.

The addition of a second solvent (usually inert) to the main solvent (usually containing oxygen), in addition to changing the solvent power of the main solvent, sometimes ensures a distinct boundary of separation between the phases, decreases the mutual solubility of the solvents in the extraction system, improves certain operating parameters of the extracting agent, etc. These advantages of mixed solvents are of course not specific for heteropoly--compounds, but are nevertheless of considerable interest for the application of the extraction of heteropoly-compounds in chemical analysis, and they will be examined in more detail below.

## 3. Acidity of the Aqueous Phase

The extraction of heteropoly-compounds is sensitive to change in the acidity of the aqueous phase (Table 2). At low acidities, heteropoly-compounds are extracted only to a slight extent or not at all; their solubility in organic solvents generally increases with increase in the acidity of the aqueous phase. The upper limit of acidity is determined by the stability of the given heteropoly-complex at high acidities, although the optimum range of acidity for extraction does not always overlap the optimum range of acidity for stability of the heteropoly-complex, and is usually wider.

TABLE 2. Influence of acidity on the extraction of molybdoarsenic acid by butanol[129].

| 10 M HCl added, ml | Optical density of extract (400 μg As) at 370 mμm | | |
|---|---|---|---|
| | for test soln. ($D_1$) | for blank soln. ($D_0$) | true ($D_1 - D_0$) |
| 0.25 | 0.735 | 0.401 | 0.334 |
| 0.50 | 0.556 | 0.146 | 0.410 |
| 0.75 | 0.536 | 0.031 | 0.505 |
| 1.00 | 0.559 | 0.027 | 0.532 |
| 1.33 | 0.569 | 0.029 | 0.540 |
| 1.50 | 0.573 | 0.029 | 0.544 |
| 1.67 | 0.574 | 0.032 | 0.542 |
| 2.00 | 0.570 | 0.025 | 0.545 |
| 2.50 | 0.139 | 0.015 | 0.124 |
| 5.00 | 0.031 | 0.011 | 0.020 |

The optimum acidity for the extraction of heteropoly--acids by different solvents varies considerably for the different cases studied: the range corresponds to 0.01–2.0 $N$ with respect to a strong acid in the aqueous phase for molybdophosphoric acid[16,19,58,59,66,67,106,109,117,118,130–133], pH 1.0–1.3 for molybdoarsenic acid[130,134], 0.25–6.0 $N$ for molybdosilicic acid[58,67,74,108,112,114,135], 0.8–3.0 $N$ for molybdogermanic acid[107], 0.4–1.6 $N$ for molybdovanadophosphoric acid[89,90], 0.3–0.8 $N$ for tungstovanadophosphoric acid[95], 0.5–1.0 $N$ for tungstovanadosilicic acid[136], and 3.6–5.4 $N$ for molybdovanadogermanic acid[97].

If it is assumed that the organic solvent extracts the monomeric form of the heteropoly-acid, and that the heteropoly-acid dissociates to form ions only in aqueous solution, it is possible to examine theoretically the dependence of the distribution coefficient for the heteropoly-acid on the hydrogen-ion concentration in the aqueous phase[60].

If we denote the heteropoly-acid by $H_nA$, its dissociation constant by $K_i$, and the distribution constant by $P$, we obtain

$$K_i = \frac{[H^+][H_{n-i}A^{i-}]}{[H_{n-i+1}A^{-i+1}]} \qquad (1)$$

and

$$P = \frac{[H_nA]_{org}}{[H_nA]_{aq}}. \qquad (2)$$

The distribution coefficient is

$$D = \frac{[H_nA]_{org}}{\sum_{i=0}^{n} [H_{n-i}A^{i-}]_{aq}}. \qquad (3)$$

Putting $i = p$ in Eqn. (1) and making use of (2), we find that

$$[H_{n-p}A^{-p}]_{aq} = \frac{1}{P} \times \frac{\prod_{i=1}^{p} K_i}{[H^+]^p_{org}} \times [H_nA]_{org}. \qquad (4)$$

Substitution of (4) in (3) gives finally

$$D = \frac{P}{1 + \sum_{p=1}^{n} \frac{\prod_{i=1}^{p} K_i}{[H^+]^p}}. \qquad (5)$$

When the values of $K_i$ and $P$ are fixed (for a given heteropoly-acid), $D$ is thus a function of $[H^+]$: i.e.

$$\log D = f(pH). \qquad (6)$$

Despite the fact that in the derivation of formula (5) no allowance was made for the influence of ionic strength, the mutual solubility of the solvents, temperatures, polymerisation, and other factors, the observed extraction

behaviour of molybdophosphoric and molybdosilicic acids conforms to the relationships predicted on the basis of this formula[60].

The nature of the acid used has no significant influence on the extraction of molybdophosphoric[117] and molybdoarsenic[137] acids, but in the case of molybdosilicic acid[135] the optimum range of acidity for extraction is different with hydrochloric, nitric, and sulphuric acids. The dependence of the extraction on the nature of the acid is even more marked with ternary heteropoly-acids; for example, tungstovanadophosphoric acid is extracted quantitatively by ethyl methyl ketone from hydrochloric and sulphuric acids, but is incompletely extracted from nitric acid, and is not extracted at all from perchloric acid medium[95].

## 4. Concentration of Compound Being Extracted

In the extraction of heteropoly-acids by organic solvents from relatively dilute aqueous solutions, the distribution coefficient at first increases, and then decreases, with increase in the concentration of the heteropoly-acid in the aqueous phase[119,120]. These observations can be explained on the assumption that the organic solvents extract the undissociated monomeric forms of the heteropoly-acids. The initial increase in the distribution coefficient is apparently due to the gradual suppression of the dissociation of the heteropoly-acid with increase in its concentration in the aqueous phase, and the subsequent decrease in the distribution coefficient is due to the increase in the polymerisation of the acid.

At a comparatively high concentration of heteropoly--acid, e.g. molybdophosphoric acid, in the aqueous phase, the extraction (for instance by diethyl ether) gives a heavy oily liquid (a saturated solution of the heteropoly-acid in ether), which is usually present in a three-layer system in equilibrium with the pure organic solvent (ether) and water (or aqueous mineral acid solution)[6,7,14,15]. The addition of crystalline heteropoly-acid to this three-layer system leads to the gradual disappearance of the liquid ethereal phase; further addition of the solid heteropoly--acid leads to mixing of the aqueous and etherate phases, with the formation of a single liquid phase in equilibrium with the solid heteropoly-acid, which separates in the form of a hydrate with 14 molecules of water[13].

## 5. Presence of Neutral Salts (Electrolytes)

Neutral salts (NaCl, $NaNO_3$, $Na_2SO_4$, etc.) in low concentrations (1–3%) have no significant influence on the extraction of heteropoly-compounds[138]. The distribution coefficients of molybdosilicic and molybdophosphoric acids decrease at moderate concentrations ($< 1$ M) of NaCl[60] or $NaNO_3$.[120]

At high concentrations, neutral salts increase the distribution ratios of heteropoly-acids, apparently as a result of a salting-out effect[119,120]. The salt effect depends on the pH of the aqueous phase[60,139], but is apparently independent of the nature of the heteropoly-acid. This last feature often leads to a levelling of the extraction of different heteropoly-acids in the presence of large quantities of salts; for example, the ratio of the distribution coefficients for molybdophosphoric and molybdosilicic acids (the separation factor) is quite favourable for their separation by butanol in the absence of salts ($10^2 : 10^{-2}$ at pH 2.5), but decreases considerably when neutral salts are added[139].

In a number of cases, the mechanism of the influence of neutral salts on the extraction of heteropoly-compounds is not quite clear. In this connection it may be noted again that, in the extraction of molybdophosphoric acid by ethyl acetate in the presence of NaCl, partial extraction of sodium together with the heteropoly-acid takes place[117]. Since sodium undergoes almost no extraction with molybdate in the absence of phosphate (or with phosphate in the absence of molybdate)[117], this can be regarded as an example of coextraction[140].

Of particular importance in the examination of the extraction of molybdenum heteropoly-compounds is the question of the influence of an excess of molybdate (sodium or ammonium) on the extraction. The results of special studies[60,120] indicate that the extraction of molybdosilicic or molybdophosphoric acid by butanol begins to decrease even at a low concentration ($> 0.1$ M) of molybdate in the aqueous solution. This cannot be attributed entirely to the influence of the presence of molybdate on the acidity of the aqueous phase and hence on the extraction; the influence of molybdate (sodium or ammonium) as a neutral salt evidently plays some part.

## 6. Temperature

Slight changes in temperature have no appreciable influence on the extraction of heteropoly-compounds[21,60,70,89,141]. In the examination of the influence of temperature, however, allowance must be made for the fact that the equilibria in aqueous solutions of heteropoly-compounds may show a marked dependence on temperature (and on pH). With molybdophosphoric acid, for example, certain authors[142–145] assume that in aqueous solution an equilibrium is established between the colourless and yellow forms of the acid. This equilibrium depends to a marked extent on temperature: at low temperature the colourless form predominates, and at high temperature the yellow form[144,145]. Recent studies have shown that organic solvents (isopentyl acetate) extract only the yellow form of molybdophosphoric acid[146]; thus at low temperatures ($< 9°$) — in the range of stability of colourless molybdophosphoric acid — extraction takes place extremely slowly, whereas at high temperatures ($> 50°$) the extraction is almost instantaneous, as a result of rapid formation of the yellow form.

Analogous equilibria exist in aqueous solutions of other heteropoly-acids. The very interesting equilibrium between the $\alpha$ and $\beta$ forms of molybdosilicic acid, which also depends on temperature[147,148], has unfortunately not been studied from the extraction viewpoint; there are merely reports of the possibility of stabilisation of the $\beta$ form of molybdosilicic acid by extraction with a solution of tridecylamine in toluene[74].

Equilibria are known to be established in the reduction of heteropoly-acids. It may be noted, for the case of molybdosilicic acid, that the different products of the reduction of a given heteropoly-acid are extremely sensitive and specific in their behaviour towards organic solvents[128], Since the equilibrium involving these reduction products is usually markedly temperature-dependent, even slight changes in temperature in this case may lead to marked changes in extraction.

## VI. ANALYTICAL APPLICATION OF THE EXTRACTION OF HETEROPOLY-COMPOUNDS

### 1. Separation of Elements by Extraction

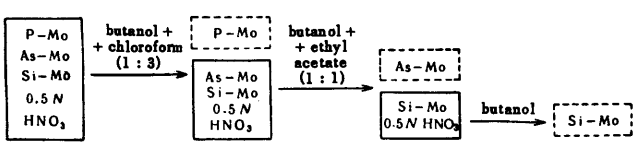
The extraction of heteropoly-compounds by organic solvents provides a valuable method for the separation of mixtures containing phosphorus, arsenic, silicon, and germanium. Such separations are possible in principle for all elements forming heteropoly-compounds.

The separation of elements by extraction as their heteropoly-compounds is based on the creation of conditions for selective behaviour of these compounds towards the organic solvents. This is achieved by changing the acidity of the aqueous phase, by selecting the solvents and combinations of solvents, by using complex-forming reagents, etc. All these cases are well illustrated by three typical examples of the separation of mixtures: scheme *1* for P + As + Si,[17] scheme *2* for P + Si + As,[138] and scheme *3* for P + As + Si + Ge [106] (in these separation schemes the full lines denote aqueous phases, and the broken lines organic phases).

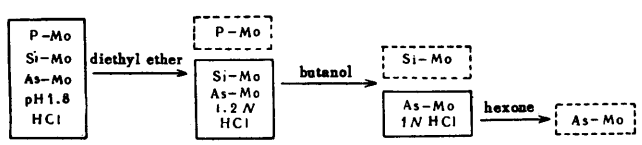
The extraction of molybdophosphoric acid has been used by various workers for the separation of phosphorus from silicon (isobutanol[67,108], diethyl ether[69,138], ethyl acetate[68,130,149,150], butyl acetate[151], isopentyl acetate[68,105], butanol + chloroform[17,58,120], butanol + benzene[60,139], and isobutanol + chloroform[106]), phosphorus from arsenic (pentanol[66,152], diethyl ether[138], ethyl acetate[150], isopentyl acetate[105], butanol + chloroform[17,62,129,137,153,154], isobutanol + chloroform[106], and ethyl acetate + butyl acetate[155]), phosphorus from vanadium (ethyl acetate[117] and ethyl acetate + butyl acetate[155]), phosphorus from calcium and magnesium (butanol + chloroform[156]), molybdophosphate from molybdate (isobutanol + diethyl ether[132]), and molybdophosphate from molybdotitanophosphate (butyl acetate[73,98,99]). Thanks to the ease of extraction of molybdophosphoric acid, it is not difficult to choose an effective and at the same time selective solvent for this compound; from the practical viewpoint, however, it is more convenient in this case to use a mixture of butanol with chloroform or benzene.

The extraction of molybdoarsenic acid has proved suitable for the separation of quinquevalent arsenic from tervalent arsenic (isobutanol[134]), arsenic from silicon (isopentyl acetate + ethanol[105], butanol + ethyl acetate[17], and butanol + ethyl acetate + chloroform[106]), and arsenic from germanium (butanol + ethyl acetate + chloroform[106]); the extraction of molybdosilicic acid for the separation of silicon from arsenic (butanol[138], butanol + chloroform[153], and butanol + ethyl acetate[153]), silicon from phosphorus (isobutanol[67,108]), and molybdosilicate from molybdate (pentanol + diethyl ether[136]); the extraction of molybdogermanic acid for the separation of germanium from arsenic (isopentanol[82,107] and butanol + ethyl acetate[82,107]); the extraction of molybdoniobophosphoric acid for the separation of niobium from titanium and tantalum (butanol[101]); and the extraction of molybdotitanophosphoric acid for the separation of titanium from chromium, copper, nickel, cobalt, manganese, iron, aluminium, lead, tantalum, and hafnium (pentanol + cyclohexanol[73]).

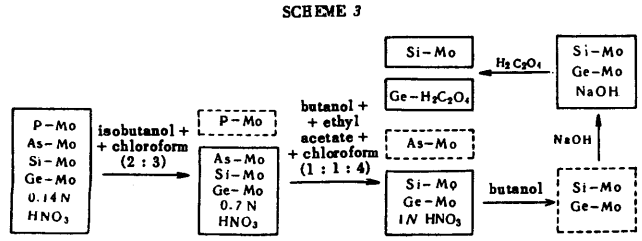
SCHEME *1*




SCHEME *2*




SCHEME *3*




### 2. Extraction–Photometric Determination of Elements

The extraction–photometric method has been used to determine phosphorus, silicon, arsenic, vanadium, and germanium as the reduced or unreduced heteropoly-compounds; it is also possible to determine molybdenum, titanium, cerium, thorium, zirconium, niobium, etc. The chief advantages of the extraction method over other methods are in this case high sensitivity and selectivity and the ease of prevention of interference.

High sensitivity in the extraction–photometric determination of elements as heteropoly-compounds is achieved not only as a result of the usual factors associated with extraction, but also by certain characteristic methods. One such method is the use for the photometric measurements of the decomposition products of the heteropoly--compounds, since these exhibit intense light absorption in the ultraviolet range of the spectrum; the preliminary separation of the heteropoly-compounds from the excess of analytical reagent, identical with the decomposition products, is achieved by extraction. The sensitivity of the determination in this way of, for example, phosphorus[132] and silicon[136] is characterised by molar absorption coefficients of 57 400 and 59 000 respectively.

Direct photometric measurements on the actual heteropoly-compound are avoided also in another original method: after separation of the heteropoly-complex from the excess of reagent by extraction, photometric measurements are made on one of its components, for which sensitive analytical reactions are available. For example, the sensitivity of the determination of phosphorus by photometric determination of the molybdenum from molybdophosphoric acid based on the thiocyanate reaction is characterised by a molar absorption coefficient of 185 000 (calculated as phosphate)[118].

An exceptionally high sensitivity is achieved in the determination of elements by photometric measurements on salts of the corresponding heteropoly-acids with organic bases, which are extractable even by inert solvents of the benzene and chloroform type. Silicon, for example, is

determined with a sensitivity reaching 1 μg litre$^{-1}$ (calculated as $SiO_2$) in the form of the blue polyoxyethyldodecylammonium molybdosilicate, extracted by chloroform[57,75]; the sensitivity of the extraction–photometric determination of phosphorus as the molybdophosphate of safranine[157] is characterised by a molar absorption coefficient of 190 000.

An extremely important feature in the extraction–photometric determination of elements as heteropoly-compounds is the ease of eliminating the interfering influence of an excess of the reagent, e.g. of molybdate when molybdenum heteropoly-acids are used. The non-extractability of unreduced isopolymolybdate under the conditions of the analytical application of heteropoly-compounds is well known and has been convincingly demonstrated in many experiments. Data on the extractability of reduced isopolymolybdate are contradictory, but there is no doubt that by altering the conditions it is possible to achieve complete suppression of the extraction of this form of molybdate also. For well-known reasons, separation from the excess of molybdate helps considerably the attainment of reliable and reproducible results in the determination, since it decreases the size of the blank specimen and opens up new possibilities for increasing the sensitivity of the analysis.

The process of extraction in the photometric determination of elements as heteropoly-compounds has interesting possibilities in connection with the stabilisation of the necessary analytical forms. For example, the main difficulties and errors in the determination of silicon as β-molybdosilicic acid are associated with the instability of this form of molybdosilicic acid in aqueous solution and its gradual conversion into the more stable α form; the extraction of β-molybdosilicic acid by organic solvents contributes appreciably to the solution of this problem, since the β form is stabilised in the organic solvent[74].

In the extraction–photometric determination of phosphorus, n-butanol or isobutanol is most frequently used as solvent. The use of butanol for the extraction of phosphorus as molybdophosphoric acid, with subsequent reduction and photometric determination of the latter in the organic phase, has been used successfully to determine phosphorus in biological materials[19,56,132,158-161], natural waters[21,61,162-167], plant materials[104,141], steels[109,168], aluminium alloys[169,170], vanadium[171], technical products[108], iron ores[168], petrol[172], and artificial mixtures[67]; photometric measurements on a butanol extract of molybdophosphoric acid without preliminary reduction can be used for the determination of phosphorus in biological materials[173].

The use of other alcohols instead of butanol gives no fundamental advantages, although some authors note increased sensitivity in the determination of phosphorus on extraction with isopentanol[174,175] or n-hexanol[176], better separation of the layers when pentanol is used[66], a lower degree of extraction of isopolymolybdate with n-octanol[64] and isopentanol[115], and also the greater availability of isopentyl alcohol[177] compared with butanol.

Extraction properties much better than those of butanol are shown by mixtures of n-butanol with chloroform[17,22,58,110,118,120,154,178-180], isobutanol with chloroform[106,181], and, more particularly, isobutanol with benzene[60,63,133,139,182-186]. This last mixture always has a component ratio of 1 : 1; the composition of the mixtures of butanol with chloroform, used in different cases, varies considerably (from 1 : 1 to 1 : 10), but most authors consider that the optimum butanol : chloroform ratio is ~1 : 3.

Other solvents suitable for the extraction of molybdophosphoric acid in the photometric determination of phosphorus include diethyl ether[55,138,187-197], ethyl acetate[117,130,149], butyl acetate[59,198], isopropyl acetate[199], isopentyl acetate[146,200,201], isobutyl methyl ketone[111], and mixtures of butanol with diethyl ether (1 : 1)[202] and of ethyl acetate with butyl acetate (7 : 3)[203,204].

Butanol is also the solvent most frequently used for the extraction of molybdoarsenic and molybdosilicic acids in the photometric determination of arsenic[129,134,137,153] and silicon[17,58,67,106,108,117,138,179]. The best extractants, however (particularly as regards selectivity), are — for molybdoarsenic acid, isobutyl methyl ketone (hexone)[113,138] and mixtures of butanol with ethyl acetate (1 : 1)[17,107,154,171,179], isopentyl acetate with ethanol (5 : 1)[105], and butanol with ethyl acetate and chloroform (1 : 1 : 4)[106]; and for molybdosilicic acid, n-pentanol[205,206], isopentyl alcohol[135,207], and isobutyl methyl ketone[112].

Butanol[106], isopentyl alcohol[82,107], and a mixture of butanol with ethyl acetate (1 : 1)[82,107] are suitable for the extraction–photometric determination of germanium as molybdogermanic acid.

Extraction of the reduced forms of heteropoly-acids is little used in photometric analysis. The only determinations described are those of phosphorus by extraction as the reduced molybdophosphoric acid (n-butanol[56,208], isobutanol[20,209], isopentanol[115], diethyl ether[16,69,210], isobutyl methyl ketone[211], acetophenone[70], and a mixture of isopentanol with diethyl ether[175]), the determination of arsenic by extraction as reduced molybdoarsenic acid (isopentanol[212-214] and a mixture of isopentanol with diethyl ether[215]), and the determination of silicon by extraction as reduced molybdosilicic acid (isopentanol[207,216]).

The extraction of ternary heteropoly-acids has recently been used successfully for the photometric determination of various elements, Thus for example, the extraction of molybdovanadophosphoric, tungstovanadophosphoric, molybdotitanophosphoric, molybdoniobophosphoric, and molybdovanadogermanic acids has been used for the determination respectively of phosphorus[84,86-93], vanadium[71,94,95], titanium[73,98,99], niobium[101], and germanium[97].

## 3. Other Examples of the Use of the Extraction of Heteropoly-Compounds

The extraction of heteropoly-compounds can be used not only in photometric methods but also in combination with other methods — gravimetric[150], titrimetric[155], spectroscopic[217], and radiometric[62,218,219].

For the determination of comparatively large quantities of phosphorus[12,65,220,221] and arsenic[222], some workers have used a method based on measurement of the volume of the oily layer obtained on extraction of the heteropoly-acid with diethyl ether. The extraction of heteropoly-acids also forms the basis of highly sensitive and selective methods for the detection of phosphate[14,223], arsenate[14,223,224], germanate[224], vanadium[225], and molybdenum[225].

In conclusion, brief mention may be made of other applications of the extraction of heteropoly-acids (other than analytical). The preparative importance of the extraction of heteropoly-compounds is well known: the use of extraction for the preparation of heteropoly-acids has been described in a monograph on heteropoly-compounds[4].

The extraction method is being used successfully to investigate the formation and reduction of heteropoly-complexes [110,128,142,146], and to study their composition [72,96], redox properties [226], etc. [177,189,212,227].

The further study of the extraction behaviour of heteropoly-compounds will undoubtedly facilitate investigation of the structure and nature of the bonding in the molecules of heteropoly-complexes, and will also extend the range of their practical application.


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# THE STRUCTURE AND EXTRACTIVE POWER OF AMINES AND THEIR SALTS

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## I. INTRODUCTION

In recent years a large number of papers have been published dealing with the use of amines of high molecular weight as extractants. The extraction of acids with amines and amine salts has attracted the greatest attention[1-40]; the extraction of metal salts by amine salts from hydrochloric-acid[1,17,23,41-84], sulphuric-acid[85-96], and nitric-acid[8,22,97-132] solutions and other media[133-144] has also attracted attention.

High-molecular-weight amines extract acids because, being bases, they are neutralised on contact with aqueous solutions of acids, and the amine salts formed pass into the organic phase.

In the presence of a sufficient excess of acid, the amines are almost completely present as the corresponding salts. Therefore, in the extraction of acids and salts from acid solution, the part of extractant is played in the majority of cases not by the amines themselves, but by their salts.

The relation between the structure of amines and the extractive power of their salts has attracted great attention. The possibility of predicting the extractive properties of amine salts is of great practical importance in the selection of extractants for different purposes. A considerable number of experimental results on the extractive power of amine salts have now been published. The object of the present review is to systematise these results and to interpret them from the point of view of information in the literature on the structure of amine salts. Extraction by amine salts may take place by different mechanism. Therefore, possible mechanisms for the extraction of acids and metal salts by amine salts are first briefly considered.

## II. BRIEF INFORMATION ON THE MECHANISM OF EXTRACTION OF ACIDS AND METAL SALTS BY AMINE SALTS

The extraction of acids by amine salts may proceed with the formation of addition products or by anion-exchange mechanism. The extraction of nitric acid with tri-n-octyl-[3], di-n-octyl-,[4] tri-n-nonyl-,[8] tri-n-decyl-[8], or tri-n-dodecyl-ammonium[129] nitrates is an example of extraction by an addition mechanism; the reaction is of the type†

$$\mathrm{AmineHNO_3}_{org} + \mathrm{H^+}_{aq} + \mathrm{NO_3^-}_{aq} \rightleftharpoons [\mathrm{AmineHNO_3}]\mathrm{HNO_3}_{org}. \quad (1)$$

Examples of the anion-exchange mechanism are provided by the extraction of oxalic acid by tri-n-octylammonium nitrate[6,7]

$$\mathrm{AmineHNO_3}_{org} + \mathrm{HC_2O_4^-}_{aq} \rightleftharpoons \mathrm{AmineH_2C_2O_4}_{org} + \mathrm{NO_3^-}_{aq}, \quad (2)$$

the extraction of nitric acid by an amine perchlorate[106]

$$\mathrm{AmineHClO_4}_{org} + \mathrm{NO_3^-}_{aq} \rightleftharpoons \mathrm{AmineHNO_3}_{org} + \mathrm{ClO_4^-}_{aq}, \quad (3)$$

and the extraction of technetium(VII)[34] by the reaction

$$\mathrm{AmineHNO_3}_{org} + \mathrm{TcO_4^-}_{aq} \rightleftharpoons \mathrm{AmineHTcO_4}_{org} + \mathrm{NO_3^-}_{aq}. \quad (4)$$

Metal salts $MA_m$ are extracted by amine salts AmineHA because compounds are formed that pass into the organic phase; their composition may be expressed by the formula $(\mathrm{AmineHA})_n.MA_m$.[100]‡ The structure of these compounds is more closely represented by the formula $(\mathrm{AmineH})_n[MA_{n+m}]$, since interaction of the molecules of amine with the metal atom is not effected directly but through the system AmineH–A–M, and the absorption spectra indicate the presence of the complex anions $MA_{n+m}^{n-}$ in the molecules of the extracted compounds[97,99,106]. The sum $n+m$ is usually equal to the coordination number of the central atom M.

The formation of the extractable compounds of metal salts may be represented by the addition reaction

$$MA_{m\,aq} + n(\mathrm{AmineHA})_{org} \rightleftharpoons (\mathrm{AmineH})_n[MA_{n+m}]_{org}, \quad (5)$$

by the anion-exchange reaction

$$MA_{n+m\,aq}^{n-} + n(\mathrm{AmineHA})_{org} \rightleftharpoons (\mathrm{AmineH})_n[MA_{n+m}]_{org} + nA_{aq}^-, \quad (6)$$

or by a number of simultaneous addition and anion-exchange reactions

$$MA_{i\,aq}^{(m-i)+} + n(\mathrm{AmineHA})_{org} \rightleftharpoons (\mathrm{AmineH})_n[MA_{n+m}]_{org} + (i-m)A_{aq}^-, \quad (7)$$

where the minimum value of $i$ is 0 and the maximum corresponds to the coordination number of the ion $M^{m+}$.[60,99,100]

Since for reactions (5)–(7), corresponding to different values of $i$, the reaction product is identical but the metal compounds in the aqueous phase are in dynamic equilibrium with one another, the position of the extraction equilibrium for any given composition of the phases does not depend on the reaction by which the compound is formed. For this reason, in spite of the extensive experimental information available on extraction equilibria, there were until recently no convincing arguments in the literature on how to find out by which of the above reactions the extraction of metal salts by amine salts occurs in any individual case.

Investigation of the mechanism of the extraction of uranyl sulphate by an $^{35}S$-labelled amine sulphate showed that, under conditions such that anionic uranyl complexes predominate in the aqueous solution, extraction occurs mainly by an anion-exchange mechanism; but when anionic complexes are not present in solution, extraction by addition reactions predominates[145]. This rule appears to be valid also for the extraction of salts of other metals by amine salts with like anions.

The ability of amine salts to extract acids and metal salts by an addition mechanism depends on the stability of the extractable addition compounds formed by their interaction. The ability of amine salts to extract anions by an anion-exchange mechanism, however, depends on the relation between the stability of the initial amine salt and of the compound formed after anion exchange. If the amine salt is to have the properties of a strong extractant, it is also necessary that this salt and the extracted compound should, as far as possible, be slightly soluble in the aqueous phase, and on extraction should go practically completely into the organic phase. It is usual to employ amine salts with a quite high molecular weight. Compounds of these amines pass practically completely into the organic phase during extraction, and therefore extractive power is largely determined by the stability of the compound extracted.

In this review the main factors connected with the structure of amines that determine the extractive power of their

† The initial amine salt and the addition product may be present in the solutions as polymers[5,19,36-38].

‡ The compound extracted may be solvated by solvent molecules including AmineHA molecules[117].

salts are considered. Since the extractive power of amine salts insoluble in water is determined by the stability of the extractable compounds that they form, the relation between the stability of these compounds and the structure of the amine salts used as extractants will first be considered.

## III. THE EFFECT OF THE STRUCTURE OF AMINE SALTS ON THE STABILITY OF THE COMPOUND EXTRACTED BY DIFFERENT EXTRACTION MECHANISMS

### 1. Extraction of Acids by an Addition Mechanism

A large number of addition products of acids and salts have been described in the literature[146-162]. In 1908 a product of the addition of HCl to tetramethylammonium chloride $(CH_3)_4NCl.HCl$ was isolated[147,148]. There are other reports of the preparation of compounds of this type[149-154]. After these reports, many papers appeared on the formation of acid–salt addition products in solution. It was established that molecules of the acids combine with anions of the salts; on dissociation of the latter this leads to the formation of complex anions of the type $FHF^-$,[155,156] $ClHCl^-$,[157-159] $PiHPi^-$ [160] (Pi = picrate ion), and $HSO_4^-.H_2SO_4$.[161,162] Van Looy and Hammett found that the sulphates of some amines, dissolved in nitromethane, can add on molecules of sulphuric acid with the formation of compounds $(AmineH_2SO_4).2H_2SO_4$, in which these molecules are linked by hydrogen bonds to oxygen atoms of the anions[146]. Frolov and Sergievskii have reported the probable formation of an addition product of sulphuric acid with an amine hydrogen sulphate, $(TOA.H_2SO_4)H_2SO_4$ [163] [TOA = = tri-n-octylamine (Ed. of Translation)]. Recently the addition of hydrohalic acids to anions of halide salts has been studied in detail by McDaniel and Vallee[164], Harmon and Gebauer[165], and Lipovskii and Nikitina[166], who show that the addition of acid molecules to salt anions is due to the formation between them of hydrogen bonds involving the protons of the acid.

It is to be expected that the stability of the hydrogen bond between a given acid and a salt anion will increase with increasing electron-donor properties (basicity) of the atoms forming the anion[167]. Obviously, the electron-donor properties of each anion increase with the displacement of the negative charge of the salt towards this anion, i.e. with the polarity of the salt of which the anion forms part. McDaniel and Vallee[164] determined the free energies and heats of formation of the addition products of HCl, HBr, and HI with corresponding halide salts of the type $R_4NHal$(R = alkyl) of different polarity. The results show, as would be expected, that more polar salts form more stable addition products with acids. For example, the value of $-\Delta H$ for the compound of HCl with the least polar of the salts $(CH_3)_4NCl$ was 11.3 kcal mole$^{-1}$, for the more polar $(C_2H_5)_4NCl$ the value was 13.7, and for the still more polar $(C_4H_9)_4NCl$ it was 14.2 kcal mole$^{-1}$.

From the data presented it would be expected that, in the extraction of acids by amine salts by the addition mechanism, the stability of the extracted compounds (AmineHA)HA will also increase when amines whose salts are more polar are used; and, therefore, in a series of salts of different amines with the same anions, greater extractive power will be shown by salts of more polar structure.

### 2. Extraction of Metal Salts by an Addition Mechanism

The extraction of metal salts by an addition mechanism is due to the formation of complex compounds of the type $(AmineH)_n[MA_{n+m}]$ when an amine salt AmineHA interacts according to Eqn. (7) with various molecules or ions $MA_i^{(m-i)+}$ $(i \leq m)$ present in aqueous solution. In reactions of this type, of which reaction (5) is a particular case, a necessary condition for the formation of the compound to be extracted is the addition to the central atom M of the $M^{(m-i)+}$ group of supplementary anions $A^-$ of the amine salt in quantity sufficient to form the complex anion $MA_{n+m}^{n-}$. The addition of anions of the amine salt to the given central atom M with the formation of a coordinate bond will occur more readily the higher the electron-donor power (basicity) of these anions. As has been noted, the basicity of the anion increases with increasing polarity of the amine salt containing the anion. It could therefore be expected that, as in the extraction of acids, the stability of the extracted compounds of metal salts with amine salts should increase, in a series of salts having the same anion, in the sequence of salts of increasingly polar structure.

After formation of the complex being extracted, the substituted ammonium cation that has entered into the composition of the amine salt occurs in the external coordination sphere. Outer-sphere cations may have considerable influence on the stability of the complex anions linked with them and of the compound as a whole[168-173]. Recently, Sinitsyn and Zvyagintsev made a detailed study of the effect of the properties of outer-sphere cations on the stability of the complex anions linked to them[174]; as an example they used compounds of the type $K_2[RuCl_5NO]$, where K is a singly charged cation. They showed that the stability of the bond to Cl ions in the complex anion increases in the order $Na^+ < K^+ < NH_4^+ < Rb^+ < Cs^+$. For the compounds $(AmineH)_2[RuCl_5NO]$ the effect of the outer-sphere cations increases in the order: primary amine < secondary amine < tertiary amine. Sinitsyn and Zvyagintsev note that an increase in the stability of the Ru–Cl bonds occurs because of a redistribution of electron density in the compounds and particularly because of a displacement of electron density along the line $K \ldots Cl \rightarrow Ru$ in the direction of the Ru atom. Obviously, the more polar the K–Cl bond, the greater will be the displacement towards the Ru atom. This kind of bond may also be expected for compounds of those amines, the salts of which $AmineH^+Cl^-$ are also more polar.

It follows from the foregoing that in a series of amine salts with the same anions, salts of a more polar structure should have a greater extractive power for metal salts by an addition mechanism, as in the extraction of acids.

### 3. Extraction by an Anion-Exchange Mechanism

In extraction by an anion-exchange mechanism, represented by Eqns. (2)–(4) and (6), "ready made" and mostly stable anions take part in the reactions, and the effect of outer-sphere substituted ammonium cations on the stability of the complex anions that form the compounds extracted usually has no material effect on the stability of these compounds. In this case, the stability of the extracted compound is mainly determined by the stability of the bond between the cation and the anion. Factors affecting the stability of such bonds have been widely described[175-185]; they include ionisation potentials, electron affinity and

charge of cation and anion, the sizes of cation and anion, their polarisability, and the energy of interaction with the surrounding medium. The extraction equilibrium depends on the relation between the stability of the initial amine salt and that of the salt formed by exchange of anions.

A special feature of extraction by the anion-exchange mechanism is that the stability of the initial amine salt and that of the amine salt formed after extraction are connected with the properties not only of the cation but also of the anion. In this case, when the two exchanging anions have similar properties, a change in the structure of the amine can affect to the same degree the stability of the salts formed by both anions, and therefore will not materially affect the extraction equilibrium.

A considerable influence of the structure of the amine on the anion-exchange equilibrium may be observed when the stability of the salts of different anions undergoing exchange changes in a different way when the structure of the amine changes. Such different behaviour of anions may be observed in the presence of specific factors affecting the structure and stability of the salts, including steric factors, differences in the power of anions to form hydrogen bonds with different cations, etc. These factors are described in greater detail in the following Section, on the dependence of the structure of amine salts on the nature of the amines. Also, since the polarity of amine salts has a great effect on extraction by an addition mechanism, we shall first consider structural factors of amines that determine the polarity of their salts.

## IV. PRINCIPAL STRUCTURAL FACTORS OF AMINES DETERMINING THE STRUCTURE OF THEIR SALTS

The interaction of amine salts with acids leading to the formation of salts is connected with the presence on the nitrogen atom of an unshared pair of electrons capable of forming a coordinate bond with electron-acceptor atoms and ions[189-191]. A coordinate bond of the nitrogen atom with positive hydrogen ions, which are strong acceptors of a pair of electrons, is particularly easily formed. This explains the basic properties of amines and their ability to form compounds with acids.

The structure of compounds formed by amines with acids depends on the properties of the acid, the base, and the medium in which interaction occurs[192-199]. The structure of amine salts has been studied by many workers in the field of acid–base theory and also by those studying the electrical conductivity of non-aqueous solutions. When sufficiently strong acids and bases (amines) interact, there is complete transfer of a proton from the acid to the base and salts with a polar structure $AmineH^+ \ldots A^-$ are formed[194,198-204]. When the amine is a weak base, i.e. has only a slight tendency to add on protons, or if the acid is relatively weak, i.e. liberates a hydrogen ion with difficulty, interaction between them to form an addition product may involve merely the formation of a hydrogen bond between the amine nitrogen atom and the acid, without transfer of the proton from the acid to the nitrogen atom. The structure of such a product may be schematically represented by the formula Amine ... HA. It has been shown by infrared spectroscopy, by conductivity and dielectric constant measurements, and also by measurements of refraction and dipole moments that e.g. the following compounds have such a structure — tribenzylamine with picric acid[205,206], pyridine with acetic acid[207], aniline with phenol[208], aniline and *p*-nitroaniline with acetic and formic acids[209], hexamethylenetetramine with phenol[199], and ethylamine with *m*-nitrophenol, *p*-nitrophenol, pentachlorophenol, and 2-bromo-5-nitrophenol[210].

When the strength of the base or the acid is increased, a more stable bond is formed between the proton of the acid and the amine nitrogen atom, the link with the anion of the acid is weakened[194,209,211], and the polarity of the salts formed increases. For example, the dipole moments of compounds of pyridine with acetic, chloroacetic, and trichloroacetic acids are respectively 2.98, 4.67, and 7.78 D: i.e. the polarity of these compounds increases appreciably with the strength of the acid[198]. In contrast to the weak acetic acid, hydrochloric acid forms a polar salt with *p*-nitroaniline involving complete transfer of the proton of the acid to the nitrogen atom of the amine[209]. In contrast to the very weak acid *m*-nitrophenol, the stronger acids 2,4-, 2,5-, and 2,6-dinitrophenols form ion-pairs with triethylamine; these contain the $O^- \ldots HN^+$ bond. The weaker base pyridine forms compounds with these phenols without the transfer of a proton to the nitrogen atom[210]. The polarity of the compound of a relatively strong base, tri-n-butylamine, with a strong acid, $HClO_4$, is much higher than the polarity of the compound of a weak base, aniline, with the relatively weak picric acid[192,208]. Detailed information on the effect of the strength of acids and bases on the polarity of the salts formed is given in Shatenshtein's book[194].

In many cases in which the acid proton is transferred to the amine nitrogen atom, the bond between the cation and the anion does not remain purely ionic, and in addition to electrostatic interaction between them, non-coulombic forces may also play a part. For example, in many alkyl- and aryl-ammonium halides the substituted ammonium ions are linked to the anions not only by ionic bonds but also by hydrogen bonds[212-219]. Sato, who studied the infrared spectra of tri-n-octylammonium nitrate $R_3NH^+ \ldots NO_3^-$ in different solvents, found that the frequency of the $N^+-H$ stretching vibrations was strongly displaced towards the long-wave side[32]; he explains this by the presence of a strong hydrogen bond between the cation and the anion of the amine salt.

Hydrogen bonds of substituted ammonium cations are most easily formed with anions of weak acids; they are formed with far greater difficulty with the anions of strong acids[216,217]. The possibility of the formation of a hydrogen bond by a substituted ammonium cation and an anion in compounds of amines with complex salts is greatly reduced, since the negative charges are displaced from the peripheral atoms of the complex anions towards the central atom of the latter[216-219]. Nevertheless, the existence of intramolecular hydrogen bonds has been noted in salts of some complex acids, for example $(R_3NH)[UO_2(NO_3)_3]$ and $(R_3(NH)_2[PuO_2Cl_4]$, and in compounds containing other complex anions of the actinide elements[220-227].

The relation between the dipole moments of salts and the structure of the amines forming them has not been systematically investigated. A considerably greater amount of systematic information has accumulated on the study of the relation between the basicity of amines and their structure[188]. Since it has been established that the polarity of amine salts increases with their basicity, data on the basicity of amines may be used within certain limits to predict how the polarity of amine salts will depend on their structure. However, the basicity of an amine determined in some solvent is not a universal quantitative characteristic of the ability of the amine to form polar

salts with acids under any conditions; for the basicity depends on the nature of the solvent, and the order of basicity of amines of different structure may change with change of solvent[193-196]. It is therefore more rational to consider (using quantitative data obtained in the determination of the basicity of amines of different structure) factors connected with the structure of amines that directly influence the structure (polarity) of their salts. The most important of these factors are the electron-donor power of amines, the formation of intramolecular hydrogen bonds in the amine salt molecules, the solvation of amine salt cations and anions by molecules of solvent, steric factors, and the effect of "inert" non-solvating solvents.

## 1. Electron-Donor Power of Amines

From the point of view of electronic theory, the power of amine molecules to coordinate protons and form polar compounds with acids depends on the mobility of the unshared electron pair on the nitrogen atom[176,177,186-189].

The greater the displacement of electron density in the amine molecule towards the nitrogen atom, the greater will be the mobility of the electron pair of the nitrogen atom capable of forming a donor–acceptor bond. The shift in electron density towards the nitrogen atom depends on the inductive effects of the radicals attached to this atom. Aliphatic radicals have a positive inductive effect, or a greater power of repelling electrons compared with the hydrogen atom. For this reason, the mobility of electrons of the nitrogen atom is greater in alkylamines than in ammonia.

When the number of identical substituents on the nitrogen atom increases, their total inductive effect increases. For the aliphatic amines this leads to an increase in the electron-donor properties of nitrogen in the order — primary < secondary < tertiary amines — which corresponds to a decrease in the ionisation potentials of the amines in this order. Values of the ionisation potentials, which indicate the mobility of the unshared pair of electrons on the nitrogen atom, determined[228,229] for some alkylamines, show (Table 1) that, when the number of alkyl substituents or their length is increased, the ionisation potentials are reduced.

Because of the negative inductive effect of the aryl radicals in aromatic amines, the electron density is displaced from the nitrogen atom in the direction of these radicals, and the unshared pair of electrons on the nitrogen atom is less mobile than in ammonia[215]. The general inductive effect of the substituents in aromatic amines also increases in the order — primary < secondary < tertiary — which reduces the electron-donor power of the nitrogen atom (and the ability of the amines to form polar salts) in the same order.

As mentioned above, the power of amines to form polar salts parallels their power of adding protons (their basicity). Much has been published on the determination of basicity, which confirms how substituents on the nitrogen atom affect the electron-donor power of the amines and their ability to form polar compounds with acids[188]. For aqueous solutions the basicity is expressed quantitatively by the basicity constant

$$K_b = \frac{[\text{AmineH}^+][\text{OH}^-]}{[\text{Amine}]}. \quad (8)$$

For organic systems in aprotic solvents the basicity constant directly characterises the power of the amine to form a polar salt on reaction with an acid. For such solutions this value is given by the formula

$$K_b = \frac{[\text{AmineH}^+ \ldots \text{A}^-]}{[\text{Amine}][\text{HA}]}. \quad (9)$$

The quantities necessary for the calculation of $K_b$ in aqueous solution are mainly determined by means of indicators or by potentiometric and other methods connected with the measurement of hydrogen-ion concentration[232]. The degree of conversion of HA to $A^-$, necessary for the determination of $K_b$ in aprotic solvents, is usually determined spectrophotometrically[210].

The basicity constants of some alkylamines determined in water are given in Table 2. In aqueous solutions, because of the effect of other factors besides electron-donor power of amines (mainly solvation of cations), the expected dependence of $K_b$ on the number of substituents is not observed throughout the series of alkylamines with different substituents. However, Table 2 shows that the basicity of all alkylamines is greater than that of ammonia. The basicity of primary and secondary amines changes little as the length of the alkyl chain is increased; in the tertiary amine series there is a tendency for the basicity to increase as the alkyl chain in lengthened. The basicity constants of the dialkylanilines increase with the length of the alkyl chain. For example, the value for dimethylaniline is $4.5 \times 10^{-10}$, and that for diethylaniline $165 \times 10^{-10}$.[234] The basicity of aromatic amines is lower than that of ammonia, and decreases as the number of aromatic substituents increases. The basicity constant of aniline in water is $3.8 \times 10^{-10}$; that of diphenylamine is $7.6 \times 10^{-14}$.[234]

In aprotic organic solvents, in contrast to aqueous solution because of the relatively weak solvation effect the basicity of amines is in many cases determined by the electron-donor power of the nitrogen atom alone, and the order of basicity expected from the inductive effects of

TABLE 1. Ionisation potentials (eV) of amines[228] (ammonia, 10.15 eV).

| No. of C in alkyls | Primary amines | Secondary amines | Tertiary amines |
|---|---|---|---|
| 1 | $CH_3NH_2$—8.97 | $(CH_3)_2NH$—8.24 | $(CH_3)_3N$—7.82 |
| 2 | $C_2H_5NH_2$—8.86 | $(C_2H_5)_2NH$—8.01 | $(C_2H_5)_3N$—7.50 |
| 3 | $C_3H_7NH_2$—8.78 | $(C_3H_7)_2NH$—7.84 | $(C_3H_7)_3N$—7.23 |
| 4 | $C_4H_9NH_2$—8.71 | $(C_4H_9)_2NH$—7.69 | |

TABLE 2. Basicity constants of some alkylamines in water[233,234] at 25° (ammonia ~ $1.8 \times 10^{-5}$).

| No. of C in alkyls | Primary amines | Secondary amines | Tertiary amines |
|---|---|---|---|
| 1 | $CH_3NH_2 \sim 4.4 \cdot 10^{-4}$ | $(CH_3)_2NH \sim 5.2 \cdot 10^{-4}$ | $(CH_3)_3N \sim 5.4 \cdot 10^{-5}$ |
| 2 | $C_2H_5NH_2 \sim 3.4 \cdot 10^{-4}$ | $(C_2H_5)_2NH \sim 9.6 \cdot 10^{-4}$ | $(C_2H_5)_3N \sim 5.6 \cdot 10^{-4}$ |
| 3 | $C_3H_7NH_2 \sim 4.7 \cdot 10^{-4}$ | $(C_3H_7)_2NH \sim 1.02 \cdot 10^{-3}$ | $(C_3H_7)_3N \sim 5.5 \cdot 10^{-4}$ |
| 4 | $i\text{-}C_4H_9NH_2 \sim 3.1 \cdot 10^{-4}$ | $(i\text{-}C_4H_9)_2NH \sim 4.8 \cdot 10^{-4}$ | — |
| 5 | $i\text{-}C_5H_{11}NH_2 \sim 5 \cdot 10^{-4}$ | $(i\text{-}C_5H_{11})_2NH \sim 9.6 \cdot 10^{-4}$ | — |

the substituents is fully observed. It has been shown that in chlorobenzene the strength of amines varies in the order tributylamine > dibutylamine > monobutylamine[210,235,236]. The same order has been established for the ethylamines[237,238], methylamines[238,239], octylamines[46], decylamines[46], and some other amines. Pearson and Vogelsong, who have studied the relation between basicity and structure in the greatest detail, showed that in chlorobenzene and dichloroethane the basicities of tributyl-, triethyl-, and trimethyl-amines are higher than those of the corresponding secondary amines[240]. It has also been shown that the introduction into aromatic amines of substituents with a positive inductive effect, for example alkyl groups, also leads to an increase in basicity[219,241]. Because inductive effects of substituents in amines often have a definite influence on the polarity of salts of these amines, Hall was able to establish a quantitative relationship between the basicity constants $K_b$ and Taft's constants, which characterise the inductive effects[242,243]. Taft proposed the use of a number of parameters (induction constants) $\sigma^*$ which characterise the inductive effects of various substituents attached to a reactant atom or group, and showed that for a number of reactions the following relationship holds§

$$\log k/k_0 = \rho^*\sigma^*, \qquad (11)$$

where $k$ is the equilibrium constant for the substituted compound, $k_0$ is the constant for the reference compound, and $\rho^*$ represents coefficients constant for each type of reaction[244-250].

Hall[242,243] and also Hansson[251] have shown that this equation is applicable to the calculation of the basicity constants of amines. Logarithms of the basicity constants of 46 primary, secondary, and tertiary amines investigated by Hall (except for amines with considerable steric hindrance round the nitrogen atom) depend linearly on $\Sigma\sigma^*$, i.e. the sum of Taft's induction constants for all the substituents attached to the nitrogen atom. A number of other primary, secondary, and tertiary amines show an analogous linear dependence[242,252,253].

Therefore, the order of the basicity of amines of different structure has been confirmed in a great number of cases by consideration of the influence of the inductive effects of substituents on the mobility of the unshared electron pair of the amine nitrogen atom¶. Therefore values of $\sigma^*$, which characterise these inductive effects, may be used to estimate the probable polarity of salts formed by amines of different structure. Values of $\sigma^*$ for some substituents are given in Table 3.

The use of Taft's induction constants to calculate the effect of bulky substituents, e.g. long alkyl chains, is limited by steric effects; apparently they are most successfully applied to evaluate the polarity of primary alkylamine salts.

TABLE 3. Values of Taft's induction constants $\sigma^*$ for some substituents[250,251,255].

| Substituent | $\sigma^*$ | Substituent | $\sigma^*$ |
|---|---|---|---|
| $NO_2$ | +5.3 | $O_2N(CH_2)_2$ | +0.50 |
| $Cl_3C$ | +2.65 | H | +0.430 |
| $CH_3OOC$ | +2.00 | $(C_6H_5)_2CH$ | +0.405 |
| $Cl_2CH$ | +1.94 | $(C_6H_5)(C_6H_4)CH$ | +0.040 |
| $CH_3CO$ | +1.65 | $CH_3$ | 0.000 |
| HO | +1.55 | cyclo-$C_6H_{11}CH_2$ | −0.060 |
| $ClCH_2$ | +1.050 | $C_2H_5$ | −0.100 |
| $BrCH_2$ | +1.030 | n-$C_3H_7$ | −0.115 |
| $C_6H_5OCH_2$ | +0.850 | n-$C_4H_9$ | −0.130 |
| $C_6H_5(OH)CH$ | +0.765 | i-$C_4H_9$ | −0.125 |
| $CH_3COCH_2$ | +0.600 | t-$(C_4H_9)CH_2$ | −0.140 |
| $C_6H_5$ | +0.600 | i-$C_3H_7$ | −0.200 |
| $C_6H_5CH_2$ | +0.225 | $(C_2H_5)_2CH$ | −0.225 |
| $(C_6H_5)(CH_3)_2$ | +0.020 | t-$(C_4H_9)CH_2CH$ | −0.285 |
| $HOCH_2$ | +0.555 | t-$(C_4H_9)$ | −0.320 |
| $CH_3OCH_2$ | +0.520 | | |

TABLE 4. Values of the constants $\sigma$ in Hammett's equation for some substituents in the *para*-position[255,256].

| | Substituent | $\sigma$ | | Substituent | $\sigma$ |
|---|---|---|---|---|---|
| Amino- -groups | $NH_2$ | −0.660 | Hydroxy- and alkoxy- -groups | OH | −0.357 |
| | $NHCH_3$ | −0.592 | | $OCH_3$ | −0.268 |
| | $N(CH_3)_2$ | −0.600 | | $OC_2H_5$ | −0.250 |
| | $NHNH_2$ | −0.550 | | $OC_3H_7$ | −0.268 |
| | NHOH | −0.339 | | $OCH(CH_3)_2$ | −0.286 |
| Carboxy- -groups | COOH | +0.265 | | $OC_4H_9$ | −0.320 |
| | $COOC_2H_5$ | +0.522 | | $OC_5H_{11}$ | −0.340 |
| | CHO | +0.216 | | $O(CH_2)_5CH(CH_3)_2$ | −0.265 |
| | $COCH_3$ | +0.516 | | $OCH_2C_6H_5$ | −0.415 |
| | $COC_6H_5$ | +0.459 | | $OC_6H_5$ | −0.028 |
| | $COO^-$ | +0.132 | Alkyl groups | $CH_3$ | −0.170 |
| | CN | +0.628 | | $C_2H_5$ | −0.151 |
| Other groups | $NO_2$ | +0.778 | | $C_3H_7$ | −0.126 |
| | NO | +0.123 | | $CH(CH_3)_2$ | −0.151 |
| | F | +0.062 | | $C_4H_9$ | −0.161 |
| | Cl | +0.227 | | $CH_2CH(CH_3)_2$ | −0.115 |
| | Br | +0.232 | | $CH(CH_3)C_2H_5$ | −0.148 |
| | I | +0.276 | | $C(CH_3)_3$ | −0.198 |
| | $CF_3$ | +0.551 | | $(CH_3)_2CH(CH_2)_2$ | −0.225 |
| | $CH_2Cl$ | +0.184 | | $C(CH_3)_2C_2H_5$ | −0.190 |

The effect of nuclear substituents in aromatic amines is determined by Eqn. (11) with the aid of Hammett's $\sigma$ constants[254-257], which are less sensitive to steric hindrance if the substituent is in the *para*- or *meta*- position. Values of $\sigma$ for some substituents are given in Table 4. Values of $\rho^*$ for calculating the basicity constants from Eqn. (11) are negative. It may therefore be concluded from the data in Table 3 that all amines in which there are substituents on the nitrogen atom with positive values of $\sigma^*$, exceeding the value of $\sigma^*$ for H, must have a lower electron-donor power (basicity) than ammonia. These amines are less likely to form polar salts with acids. It cannot therefore be expected that salts of amines containing these substituents ($Cl_3C$, $CH_3COO$, $CH_3CO$, $CNCH_2$, $C_6H_5$, etc.) would form stable extraction compounds with acids and metal salts where extraction is by an addition mechanism. Replacement of hydrogen atoms in ammonia by substituents with a value of $\sigma^*$ less than 0.430 should lead to increased electron-donor power and to increased basicity. Values of $\sigma^*$ for substituents having negative inductive effects decrease considerably when a $CH_2$ group comes between them and the nitrogen atom. It follows from the data in Table 3 that the polarity of salts should increase in the order $C_6H_5NH_2 < C_6H_5CH_2NH_2 < C_6H_5[CH_2]_3NH_2$; the polarity of salts of this last amine and the stability of the compounds extracted should be comparable with the stability and polarity of alkylamine salts. It also follows from the data in Table 3

§ A similar relationship

$$\log k/k_0 = \rho\sigma \qquad (10)$$

was previously proposed by Hammett for calculating the effect of substituents in aromatic rings on the reaction constants of different functional groups attached to these rings[254].

¶ In a later paper Mead also established quantitative relationships between the heats of neutralisation of some amines with trichloroacetic acid in benzene and Taft's parameters[258]. Recently Kuča, with the aid of induction constants $\sigma^*$, has established a quantitative relationship between the extractive power of a large number of organophosphorus compounds and their structure[259].

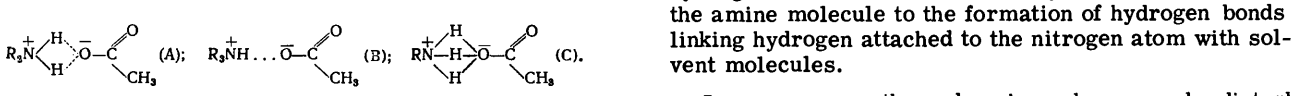
that the polarity of salts and the stability of the extracted compounds of alkylamines should increase with increase in length, number, and degree of branching of alkyl chains linked to the nitrogen atom.

The data in Table 4 show that introduction into the benzene and other aromatic groups of aromatic amines, of such substituents as Cl, $NO_2$, NO, and COOH should lead to a decrease in the electron-donor power (basicity) of the amines and to a reduction in the polarity of their salts. When such substituents as OH, alkoxy-groups, or alkyl groups are introduced into the *para*-position, the basicity of the aromatic amines should increase. Therefore, the polarity of their salts and the stability of compounds extracted by an addition mechanism should also increase.

The data in Tables 3 and 4 may be used for a preliminary evaluation of the probable changes in polarity and extractive power of amine salts when some substituents are replaced by others. However, the electron-donor power of amines is not the only factor that determines the structure of their salts. A number of other factors, considered below, must also be taken into account.

## 2. Intramolecular Hydrogen Bonding

The formation of intramolecular hydrogen bonds in amine salts may have a material effect on the structure of these salts. As has been mentioned above, the anions of weak acids show a tendency to form hydrogen bonds with the hydrogen atoms of substituted ammonium cations. The number of possible intramolecular hydrogen bonds increases with the number of hydrogen atoms attached to the nitrogen atom, the number being greater in primary amines than in secondary, and greater in secondary than in tertiary amines. Barrow and Yerger showed that in chloroform the stability constants of compounds of acetic acid with dibutylamine and diethylamine are higher than with the corresponding tertiary amines[260,261]. They explained this by an increase in the number of intramolecular hydrogen bonds in the compound of the secondary amine (A) in comparison with the compound of the tertiary amine (B). According to these authors, three intramolecular hydrogen bonds are formed in compounds of the primary amine (C):[261]




The presence of hydrogen bonds in these compounds has been confirmed by infrared spectroscopy[261]. Davis[262,263] noted that in solvents that do not solvate cations the absorption spectra of acid indicators change differently in reactions with primary, secondary, and tertiary amines. He explained these differences also by the formation of different numbers of intramolecular hydrogen bonds. Ryan, having compared the absorption spectra of the compounds $Cs_2[UO_2Cl_4]$, $[(C_4H_9)_4N]_2[UO_2Cl_4]$, and $[(C_4H_9)_3NH_2][UO_2Cl_4]$, established that the spectrum of the last compound differs from the spectra of the first two[220,221]; this can also be explained by the presence of an hydrogen bond between the cation $R_3NH^+$ and the anion $[UO_2Cl_4]^{2-}$. Similar spectral differences were observed in compounds of secondary amines $[(C_2H_5)_2NH_2]_2[UO_2Cl_4]$, the differences being more marked in these. According to Ryan's results, the melting points of salts of secondary amines with $[UO_2Cl_4]^{2-}$ are much lower than those of salts of the corresponding tertiary amines; in the author's opinion this also indicates the greater part played by non-coulombic forces in the bond between the anion and the secondary alkylammonium cations. A hydrogen bond is also assumed to be present in compounds of primary amines $[RNH_3]_2[UO_2Cl_4]$.[220] Similar effects, indicating the formation of internal hydrogen bonds, have also been noted in analogous chloride compounds of uranium(IV).[221] Vdovenko, Lipovskii, and coworkers have demonstrated the presence of intramolecular hydrogen bonds in a number of salts of long-chain alkylamines[166,225-227].

The formation of intramolecular hydrogen bonds promotes the approach of the anion and the cation, and therefore the polarity of the amine salt is reduced; this leads to a reduction in the dissociation constants of the amine salts in polar organic solvents and to a decrease in the electrical conductivity of solutions of these salts. According to Kraus[192] the conductivity constants of tetra-, tri-, di-, and mono-butylammonium picrates in nitrobenzene are $>2 \times 10^{-1}$, $1.9 \times 10^{-4}$, and $1.6 \times 10^{-4}$ respectively; the distances between the centres of gravity of the positive and negative charges in these salts of picric acid are: tetrabutylammonium salt (intramolecular hydrogen bond) about 6.29 Å, tributylammonium salt (one hydrogen bond) 1.02 Å, dibutylammonium salt (two hydrogen bonds) 0.977 Å, and monobutylammonium salt (three hydrogen bonds) 0.992 Å. Differences in the polarity of salts of secondary and tertiary amines, due to the greater power of secondary amines of forming intramolecular hydrogen bonds with anions, have also been noted by other workers[211,212].

It follows from the foregoing that the formation of intramolecular hydrogen bonds, just like changes in the electron-donor power, leads (in the absence of other forces affecting the structure of amine salts, considered below) to the polarity of the alkylamine salts varying in the order: tertiary > secondary > primary.

The most favourable conditions for the formation of hydrogen bonds between cation and anion occur when the molecules of solvent do not form hydrogen bonds with hydrogen atoms of substituted ammonium cations. Intramolecular hydrogen bonds are therefore usually observed in such solvents as carbon tetrachloride, chloroform, benzene, xylene, etc. The formation of intramolecular hydrogen bonds is also favoured by steric hindrance in the amine molecule to the formation of hydrogen bonds linking hydrogen attached to the nitrogen atom with solvent molecules.

In some cases, the order given above may be disturbed by solvation of the cation and the effect of steric factors.

## 3. Solvation of Cations of Amine Salts by Solvent Molecules

An example of the effect of solvation of a substituted ammonium cation on the basicity of amines and the polarity of their salts is provided by the disturbance in aqueous solutions of the order of their basicity to be expected from the electron-donor power of the amines. Data in Table 2 show that in aqueous solutions secondary amines have a higher basicity than the corresponding tertiary amines, although tertiary amines have the higher electron-donor power. This deviation is explained in the following way. According to Izmailov's theory[197] ionisation of molecules of acids or bases takes place because of interaction with molecules of bases or acids

respectively, or because of interaction with solvent molecules. Ionisation of an amine in water may be represented by the equations

$$\text{Amine} + \text{aq.} \rightleftharpoons \text{Amine.aq.}, \quad (12)$$

$$\text{Amine.aq.} \rightleftharpoons \text{AmineH}^+\text{.aq.} + \text{OH}^- \quad (13)$$

$$\text{Amine} + \text{aq.} \rightleftharpoons \text{AmineH}^+\text{.aq.} + \text{OH}^- \quad (14)$$

From these equations it follows that the total energetic effect of the ionisation reaction and the equilibrium constant $K_b$ that characterises it are determined, not only by the mobility of the free electron pair of the amine nitrogen atom, but also by the differences in the solvation (hydration) energies of the amine molecules and the corresponding substituted ammonium ions. The higher basicity of secondary and primary alkylamines in comparison with tertiary amines in aqueous solution is explained by the fact that the hydration energy of mono- and di-alkylammonium ions is considerably higher than that of the corresponding trialkylammonium ions[238]. At the same time, the heats of hydration of the unionised amines are considerably lower than those of the ions, and have no material effect on the energy balance of the ionisation reaction. The heats of hydration of ammonium ions are as high as 85 kcal mole$^{-1}$, but the heats of hydration of unionised amines do not exceed 10–11 kcal mole$^{-1}$.[238,264,265]

The increased solvation of incompletely substituted ammonium ions was established by a number of workers as early as the 1920s;[266-268] it is due to the presence in these ions of a greater number of hydrogen atoms linked directly to the nitrogen atom than in completely substituted alkylammonium ions, these hydrogen atoms being capable of forming hydrogen bonds with water molecules. It is assumed that the hydrated ions of primary, secondary, and tertiary amines in water have respectively the structures $RN(H_3O)_3^+$, $R_2N(H_3O)_2^+$, and $R_3N(H_3O)^+$.[238]

The higher solvation of mono- and di-substituted ammonium ions compared with the corresponding trialkylammonium ions makes the ionisation of hydrates of primary and secondary amines energetically more favoured than the ionisation of tertiary hydrates[268]. This rule is followed in aqueous solutions not only by amines having hydrocarbon substituents but also by other aliphatic amines, for example the derivatives of hydroxylamine $NH_2OH$, $NH(CH_3)OH$, and $N(CH_3)_2OH$, and also by the compounds $NH_2OCH_3$, $NH(CH_3)OCH_3$, and $N(CH_3)_2OCH_3$.[269]

In both organic and aqueous solvents, aliphatic amines show a number of deviations from the order to be expected on the basis of electronic interpretations, for the basicity of amines of different structure[244,270]. According to a number of authors, primary and secondary amines are the strongest in several organic solvents as well as in water. Izmailov and Mozharova showed that disturbances of the normal order of amine basicity occur in organic solvents that strongly solvate substituted ammonium cations, for example in alcohols; this can be explained, as for aqueous solutions, by solvation effects[270]. It has also been shown[240] that the addition of alcohols and other diluents capable of forming bonds with hydrogen atoms attached to amine nitrogen atoms has a great effect on basicity constants of amines in aprotic solvents, whereas the addition of alcohols has practically no effect on the basicity or the polarity of salts of tertiary amines, with no free hydrogen directly linked to nitrogen; the strongest effect is obtained with primary amines, which have two such atoms in the molecule. For example, the basicity constant of the tertiary amine $(C_2H_5)_3N$, which is 2680 in chloroform, does not change on the addition of 4–5 mole % of ethanol[240]; the basicity constant of the corresponding secondary amine increases from 1230 to 12 700 (approximately tenfold) when the same amount of alcohol is added to the solution, and the corresponding change in basicity of the primary amine is from 35 to 5830 (~150 times).

Bayles and Taylor have given detailed data (including values of $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$) for the acid–base interaction of amines of different structure in different diluents[271]. As a rule, in pure alcohols the strongest bases are the primary amines, followed by the secondary and tertiary amines.

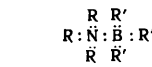
A change in the expected basicity sequence of amines occurs also because solvation of the cation prevents formation of intramolecular hydrogen bonds. In such solvents as ethyl acetate or alcohol, the oxygen atoms may form hydrogen bonds with the alkylammonium cations. The participation of hydrogen atoms linked to nitrogen in the formation of hydrogen bonds prevents the formation of hydrogen bonds between the cation and the anion. As mentioned above, the absorption spectra of some anions of substituted ammonium salts in benzene changed according to whether tertiary or primary amines were used; this was explained by the different power of the primary amines to form intramolecular hydrogen bonds. In water, however, the absorption spectra of these anions show little difference[262,263]: the hydrogen atoms which would have formed bonds with the anions now form bonds with solvent molecules. Thus, solvation of the substituted ammonium cation leads to an increase in the polarity of amine salts also by eliminating intramolecular hydrogen bonds.

Because of stronger solvation of the cations, the salts of primary amines may be more polar than the salts of secondary and tertiary amines. It is therefore to be expected that, in solvents capable of solvating ammonium cations, the compounds of primary and secondary amines extracted by an addition mechanism will be more stable than the corresponding compounds of tertiary amines. The greatest power of forming bonds with amine hydrogen atoms, and therefore of solvating cations of amine salts, is possessed by molecules of compounds that are electron donors — oxygen-containing organic solvents (alcohols, ethers, esters, ketones, phosphine oxides, alkylphosphonates, etc.)[272-275] and also organic bases (amines, nitriles of organic acids[276-280], dioxan, nitrobenzene[281], etc.).

The solvation of anions in amine salts may take place in solvents the molecules of which have electron-acceptor properties, such as alcohols and carboxylic acids, or in compounds of the chloroform type. Solvation of the anion, like that of the cation, may well lead to some increase in the polarity of the salt. But, since the molecules of extracted compounds attach themselves to the anion, solvation of the anion hinders the formation of compounds to be extracted by an addition mechanism. Solvation of the anions by alcohol molecules[282-284] appears to be the cause of the reduction in the extractive power of amine salts observed when alcohols are added to solutions of these extractants[54,129]. Similar solvation is probably also the main cause of the reduction of partition coefficients when chloroform is added to solutions of amine salts[123,285].

4. Steric Factors

Steric factors also affect the basicity of amines and the polarity of their salts. The effect of these factors on the formation of addition products with amines by acidlike compounds (in Shatenshtein's terminology[193,194]) has been studied in greatest detail. The interaction of amines of different structure with acidlike compounds of the type $BR'_3$ – $B(CH_3)_3$, $B(C_2H_5)_3$, etc. – which are strong electron acceptors, has been studied in detail by Brown and his coworkers[286-294]. The structure of the compounds of $BR'_3$ with $NR_3$ may be represented by the formula



To form a coordinate bond in this compound, the molecules of the two compounds must approach each other sufficiently closely; because of the relatively large volume of the $BR'_3$ molecules, steric factors begin to play an important part. The ability of methylamines to combine with $B(CH_3)_3$ varies in the order $NH_3 < CH_3NH_2 < (CH_3)_2NH \gg \gg (CH_3)_3N$. In this case the tertiary amine is the least basic because of steric hindrance due to the presence of three methyl groups on the nitrogen atom. The order of the strength of the other methylamines is that to be expected from the inductive effects of the substituents. The following order of basicity holds for the interaction of $B(CH_3)_3$ with ethylamines, which have more bulky alkyl groups: $NH_3 < C_2H_5NH_2 > (C_2H_5)_2NH \gg (C_2H_5)_3N$. When the volume of the molecule of acidlike compound increases (as with tributylboron), steric hindrance increases still further, and the stability of compounds of different amines varies in the order: $NH_3 < CH_3NH_2 > (CH_3)_2NH \gg (CH_3)_3N$; $NH_3 > C_2H_5NH_2 \gg (C_2H_5)_2NH > (C_2H_5)_3N$. Thus, when ethylamines react with tributylboron, the order of basicity of the amines is, because of steric hindrance, opposite to that to be expected from the inductive effects of the alkyl groups. The ability of tertiary alkylamines to form addition products with methanol decreases as the alkyl chain is lengthened[20], although the electron-donor power of the amines increases. Other examples of the effect of steric hindrance on basicity include the reducted reactivity with $B(CH_3)_3$ of 2-methylpyridine compared with pyridine itself (Brown and Taylor[286]), the diminished stability of the compound of $SO_3$ with triethylamine compared with the trimethylamine compound[295,296], and of the compounds of $SO_3$ with *o*-substituted compared with *p*-substituted aromatic amines[297], and the decreased stability of iodine complexes with aromatic amines when substituents are introduced in the *ortho*-position[298].

In the reaction of amines with proton acids, steric hindrance due to the alkyl groups is less significant because of the small volume of the proton, than in the reaction of amines with methylboron or with alcohols, and obviously could be important only with amines having sufficiently long hydrocarbon chains.

Hall noted that calculation of the basicity constants of amines on the basis of Taft's induction constants gives accurate results only when there is no steric hindrance to the reaction of the acid with the base[242]. If the alkyl groups attached to the amine nitrogen atom are considerably branched, the basicity constants of the amines are much lower than those calculated by formulae allowing only for the inductive effect of substituents.

Forman and Hume[299] evaluated the effect of steric hindrance on the basicity of amines by comparing values of the basicity calculated with the aid of Taft's induction constants with experimental values from the literature[300,301]. For primary and unbranched secondary amines the calculated values were close to the experimental. For secondary amines with sufficiently long and branched alkyl radicals, and for tertiary amines with long alkyl radicals, the experimental basicity constants were lower than the calculated values. Recently, Chremos and Zimmerman have attempted to allow for steric factors in the calculation of basicity constants by the introduction of a new scale of values for $\sigma^*$, representing both the polar and the steric effects of substituents[252].

When the length of the hydrocarbon chains of amines increases beyond a certain limit it is to be expected that the ability of the amines to add on protons and to form polar compounds with acids will be reduced; the length of the alkyl chain (or volume of other substituent having a positive inductive effect), corresponding to maximum polarity of the salts formed and maximum stability of the compounds extracted, is probably greater for primary than for secondary and tertiary amines.

In considering the effect of steric factors on the polarity of amine salts, it must be noted that these factors affect also the interaction of amines with the solvent, especially the solvation of the cations, and this in turn affects the basicity. It has been noted that, with long-chain primary and secondary amines, solvation of the substituted ammonium cations by alcohol molecules (especially higher alcohols) is made difficult by the formation of hydrogen bonds with hydrogen atoms attached to the amine nitrogen atom[242]. It is to be expected that the role of the solvation of substituted ammonium cations and its effect on the basicity of amines and the polarity of their salts will decrease as the hydrocarbon chains of the amine become longer.

5. Effect of "Inert" Solvents

At present, the field of study of "inert" solvents has considerably contracted, because it has been shown that most solvents investigated are not inert, but are capable of specifically solvating cations or anions of dissolved salts[281,302-304]. As has been shown above, the solvation of cations and anions of amine salts by molecules of solvent has a considerable effect on the structure of these salts, and therefore on their extractive power. Here we shall consider as "inert" non-polar solvents the molecules of which have no fundamental groups capable of forming stable hydrogen bonds with cations or anions of amine salts and also cannot appreciably solvate molecules and ions of amine salts by dipole–dipole interaction, but they may solvate them mainly by dispersion forces[304]. Pearson and Vogelsong established that in non-polar "inert" solvents of the n-heptane type the order of basicity of primary, secondary, and tertiary amines is changed in a similar way to that described above for solvents that solvate the cation[238,240]. Thus, in n-heptane the polar compounds of tri-n-butylamine with the acid indicator 2,4-dinitrophenol are formed with greater difficulty than the corresponding compounds of di-n-butylamine. It is assumed that this order for non-polar solvents which do not form bonds with the cation and anion of the salt may be explained as follows. The energy of interaction of molecules of amine salts with such non-polar solvents is much lower than with the analogous moderately polar solvents, and

apparently far lower than the energy of interaction of the amine molecules themselves with these non-polar solvents[82]. It may therefore be assumed that the difference in the solvation energies of the amines and their salts in such solvents is determined for various amines largely by the differences in the energies of solvation of the amines themselves. In such a case it may be expected that the greater the energy of solvation of the amine molecule, the more energetically unfavourable will be the formation of a polar salt by interaction of the amine with the acid. Because of the greater number of hydrocarbon chains, the energy of interaction of molecules of tertiary aliphatic amines with non-polar hydrocarbon solvents is higher than the energy of solvation of molecules of the corresponding secondary and primary amines[240]. It has been suggested that, on the basis of the variation in solvation energy, the formation of polar salts of tertiary amines in hydrocarbon solvents is less favoured than the formation of such salts of the corresponding secondary and primary amines[240]. The influence of opposing factors — solvation and the inductive effects of the alkyl groups of the amine — is probably the cause of secondary amines having a greater power of forming polar salts than have tertiary amines in non-polar aprotic solvents. When the alkyl chains are lengthened it is probable that the differences in the solvation energies of secondary and tertiary amines in such solvents will decrease, and the main factors determining the structure of the amine salt may be the inductive effect of substituents and steric factors.

Up to now, few papers have been published on the study of amine salts in solvents of this type, because of the very slight solubility of most amines in such solvents, which makes such systems of little practical importance.

## V. THE EFFECT OF THE STRUCTURE OF AMINES ON THE EXTRACTIVE POWER OF THEIR SALTS WITH EXTRACTION BY AN ADDITION MECHANISM

In the extraction of acids and metal salts by the addition mechanism the stability of the compounds being extracted should increase when the structure of the amine is altered in such a way that the polarity of the amine salts is increased. When the structure of an amine changes, there should be a corresponding change in extractive power. When the effect of the various factors mentioned above is taken into account, it is possible to explain published results on the extractive power of amines of different structure.

A number of papers contain data that enable the extractive power of primary, secondary, and tertiary amines to be compared. Shevchenko and his coworkers showed that the nitrate of a tertiary amine (tri-n-octylamine) extracts nitric acid much more strongly than does the nitrate of the secondary amine (di-n-octylamine)[3,4]. These results were confirmed by Skavdahl and Mason[18]. Sinitsyn, Zvyagintsev, and their coworkers showed that the extraction of ruthenium nitroso-complexes by amines from hydrochloric-acid[65,174] and nitric-acid[104] solutions increases when the number of alkyl chains in the amine is increased. Laskorin and Yuzhin established that chlorides of tertiary amines extract gallium(III) better from hydrochloric-acid solutions than do those of secondary amines[49]. Winchester and Maraman showed that the extraction of $Pu^{IV}$, $U^{VI}$, and $Th^{IV}$ from nitric-acid solutions by amine nitrates is greater with secondary and tertiary than with primary alkylamines[98]. Good and his coworkers, having systematically studied the dependence of the extractive power of amines on their structure, found that the extraction of $Fe^{III}$, $Co^{II}$, $Ga^{III}$, and $In^{III}$ by solutions of amine chlorides in benzene is also greater on passing from primary to secondary and then to tertiary alkylamines[61-63,68,305,306]. The same order was established for the extraction of a number of other elements[73,125]. Nemodruk showed that the extraction of uranyl acetate by solutions of amine acetates in a solvent that does not solvate cations is greater with dialkylaniline than with aniline[307]. The order established for the extractive power of primary, secondary, and tertiary amines is in agreement with the order of increasing polarity of salts of these amines and stability of the compounds extracted, which are formed by an addition mechanism.

A deviation from the usual order of the extractive power of primary, secondary, and tertiary amines is observed when solvents capable of solvating cations are used. For example, it was shown[307] that replacement of the non-solvating solvent by isobutyl methyl ketone, which solvates alkylammonium cations, led to a significant increase in the extraction of uranyl from acetic solutions of the primary amine, aniline; as a result, in this solvent aniline became a stronger extractant than the tertiary amine dialkylaniline. This increase in the extractive power of the primary amine may be explained by solvation of the cation of the amine salt by solvent molecules, leading to an increase in the polarity of the amine salt and in the stability of the extracted compound.

Many workers have noted[138] that the introduction into the amines of substituents with negative inductive effects leads to a reduction in extractive power. Thus, amines with aromatic substituents directly attached to the nitrogen atom are relatively weak extractants. This also agrees with the data given above on the reduction of the polarity of salts and the stability of compounds when such substituents are introduced. According to the data in Table 3, the value of $\sigma^*$ is lower for the cyclohexyl and benzyl groups than for the aryl group $C_6H_5$, and even lower than for a hydrogen atom. This explains the relatively high extractive power of benzylamines[44,72,309] and cyclohexylamines[309].

The effect of the length of alkyl chains on the extractive power of symmetrical tertiary n-alkylamines was studied by Wilson, who observed an increase in the extraction of plutonium from nitric-acid solutions when the number of carbon atoms in the alkyl chain was increased to eight[97]. This is in agreement with what would be expected from increased inductive effects in the substituents. With further increase in the chain length the extractive power of the alkylamines begins to decrease. Zvyagintsev and Frolov[26,33,40], Zvyagintsev and Sinitsyn[104,174], Timoshev[275], Baroncelli[310], and their coworkers have described a similar dependence of the extractive power of amines on the length of the alkyl chains. The increase in the extractive power of the trialkylamines when the number of carbon atoms in the chain increases to eight is in agreement with the increase, mentioned above, in the inductive effect of alkyl chains when their length is increased. Timoshev points out that one of the causes of the increase in extractive power with increasing alkyl chain length in amines of low molecular weight is also the reduction in the solubility of the extracted compound in the aqueous phase[275]. The reduction in extractive power with further increase in chain length appears to be due to steric hindrance, which becomes the main factor determining the structure and stability of the extracted compounds[311-313].

Comparison of data on the extraction of nitric acid and uranyl nitrates by tertiary n-alkylamines with more than eight carbon atoms in the chain shows that their extraction is reduced by increasing the length of the amine alkyl chains[8,24,129]. The effect of steric factors also appears in the reduction of the extractive power of amine salts with alkyl chains which branch near the nitrogen atom; this has been observed by many workers[138].

From the foregoing it is clear that the extractive power of amine salts in extraction by an addition mechanism is determined by a number of the same factors as effect their polarity. With substituents of relatively small volume and solvents that do not solvate cations, the extractive power changes with changes in the inductive effect of the substituents. When diluents that solvate cations are used, the effect of cation solvation and rupture of intramolecular hydrogen bonds becomes evident. When very bulky substituents are introduced into the amine molecule, steric factors begin to play a predominating part.

## VI. THE EFFECT OF THE STRUCTURE OF AMINES ON THE EXTRACTIVE POWER OF THEIR SALTS WITH EXTRACTION BY AN ANION-EXCHANGE MECHANISM

Up to now little information has been published on the effect of amine structure on the extraction of simple acids with amine salts by an anion-exchange mechanism. Data on the extraction of metal salts by an anion-exchange mechanism[94,96,308,314] show that the rules governing the effect of the structure of amines on the extractive power of their salts cannot materially differ from the rules governing extraction by an addition mechanism.

The extraction of thorium by tri-n-octylammonium sulphate from aqueous sulphate solutions, in which thorium is present as anionic complexes, is an example of the extraction of a metal salt by an anion-exchange mechanism[90,91]. As previously noted, when an extractable compound is formed in such cases, factors affecting the stability of the complex anion in this compound play a secondary part, and factors that determine the strength of interaction of the cation and the anion are of greater significance. It has been found that thorium is extracted from sulphuric-acid solutions better by primary than by secondary amines, and better by secondary than by tertiary amines. The same behaviour is observed in the extraction of Zr, $U^{IV}$, and $Fe^{III}$, which also readily form anionic complexes in sulphate solutions[68]. This behaviour may be explained in terms of steric concepts. Steric hindrance to the approach of relatively bulky anionic sulphate complexes to monoalkylammonium cations is obviously less than to their approach to di- and tri-alkylammonium cations. To form an extractable compound the complex anion must displace the $SO_4^{2-}$ anion from the amine sulphate molecule. Since the $SO_4^{2-}$ anion is smaller than the complex sulphate anions of Th, $U^{IV}$, and Zr, the differences between primary, secondary, and tertiary amines in relation to steric hindrance to this anion are less important than for complex anions. From this it follows that the sulphate ion will be replaced by a complex sulphate ion more easily in salts of primary amines than in salts of tertiary amines. This probably explains the greater extractive power of primary amines (in comparison with secondary and tertiary amines) in the extraction of Th, Zr, and $U^{IV}$ from sulphate solutions.

The same order of extractive power of amines would obviously also be expected for the extraction of other elements from media in which they form stable anionic complexes greatly exceeding in size the anion of the amine salt which acts as extractant. When the complex anions, although predominating in the aqueous phase, are formed with greater difficulty than in the case considered (Th, Zr, $U^{IV}$), other factors — governing stabilisation of the anion and interaction of cation and anion — may be important at the same time. In view of the opposing effects of these factors, when less stable anionic complexes are formed in the aqueous phase, the differences in extractive power between primary, secondary, and tertiary amine salts may decrease in extraction by an anion-exchange mechanism, and in some cases the extractive power of amines with different numbers of alkyl groups may be practically the same[143]. In these cases it appears that the increase in steric hindrance on passing from primary to tertiary amines is probably compensated for by the increase in the stabilising action of the cation on the complex anion. When the length or volume of the alkyl chains increases, steric factors begin to play a predominating part. Thus, Sato[309,313] has shown that with cyclohexyl- and benzyl-alkylamines ($C_{12}$ alkyl) the extraction of $U^{VI}$ from sulphuric-acid solution decreases when additional alkyl chains are introduced into the amine, i.e. in the order primary > secondary > tertiary. Clearly, all the considerations mentioned above still hold good if the extraction of Th, Zr, U, and Fe sulphates proceeds by an addition mechanism, since the great volume of the complex sulphate anions formed in the extraction can probably give rise to steric hindrance in this case also.

Laskorin and his coworkers have shown[308,314] that triisooctylamine is a much weaker extractant of $V^{V}$ and $Mo^{VI}$ ions than is tri-n-octylamine. This may be explained by the greater steric hindrance to the approach of anion and cation in the case of triisooctylamine.

A more thorough investigation into the structure of amine salts could make possible a more complete elucidation of the principles of extraction by amine salts and the prediction of the relative extractive power of amines of different structure.


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# CHEMILUMINESCENCE AND THE KINETICS OF CHEMICAL REACTIONS

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## I. INTRODUCTION

Chemiluminescence — the emission of light accompanying chemical reactions — is closely connected with the kinetics and the mechanism of the reaction.

The appearance of excited states in a reaction zone is due to the occurrence of exothermic elementary acts. The measured intensity of emission is proportional to the rate of the elementary process in which energy is evolved, and hence is related to the kinetic parameters of the reaction. Investigation of the kinetics, the temperature dependence, and the spectra of the emission may give much valuable information for an understanding both of the reaction mechanism and of the actual phenomenon of chemiluminescence — of the ways in which chemical energy is transformed into radiation.

It must be emphasised that a study of chemiluminescence divorced from the mechanism of the corresponding reaction can hardly provide a fruitful approach. For example, the weakening of emission accompanying the introduction of a new component into the reaction mixture can be equally well explained by its retarding effect on the reaction velocity or by its quenching action on excited states which appear at the same rate as before. In the absence of information on the rate of the chemical reaction and of the influence of the additive on it, no choice can be made between these fundamentally different effects.

The present review surveys the relationship between the chemiluminescence and the kinetics of reactions. From the considerable number of papers on chemiluminescence, those have been selected which report either the investigation of chemiluminescence in reactions whose mechanism has been reliably established or the parallel study of a reaction by chemiluminescence and chemical kinetic methods.

Special attention has been paid to the prospects for using chemiluminescence as a method for the quantitative investigation of reaction kinetics.

The main information has been divided into three parts — (1) gas-phase reactions (hot and cold flames, reactions of atoms obtained in high concentrations from electric discharges), (2) liquid-phase reactions (oxidation of cyclic hydrazides and of acridine compounds) accompanied by bright chemiluminescence, and (3) reactions accompanied by very weak chemiluminescence, which do not differ fundamentally from the previous reactions, but comprise a wide range of both scientific and practical interest, and therefore are discussed as a separate group.

## II. CHEMILUMINESCENCE OF FLAMES

The intensity of the emission from many flames exceeds the equilibrium value corresponding to the temperature of the flame. In particular, the glow from cold and dilute flames is purely chemiluminescent. The radiation from low-temperature flames is to a greater or lesser extent chemiluminescent[1,2]. The non-equilibrium character of the radiation can be shown by comparing its absolute intensity with the intensity of the radiation from a black body having the same temperature as the flame. Thus according to Kondrat'ev[1] the intensity of the radiation from an oxygen–hydrogen flame at 10 mmHg and 1000°K exceeds the equilibrium value by a factor of $10^{12}$, while the corresponding factor for the $2CO + O_2$ flame at 100 mmHg and 1400°K is $10^{10}$.

The character of the radiation can be assessed also from measurements of the intensity distribution in the emission spectrum. The non-equilibrium character of radiation is indicated by a difference between the true temperature of the flame and the rotational temperature of individual species: in the oxygen–acetylene flame at 1 atm, for example, the true temperature is 3400°K, while the rotational temperature of hydroxyl is 5400°K, and that of $C_2$ is 4700°K.[3] Finally, departures from equilibrium can

be assessed from the characteristic quenching of luminescence with increase in the pressure of the reactants or on the introduction of inert gases. Quenching phenomena have been observed, for example, in the hydrogen and carbon monoxide flames[1].

Flame emission spectra usually comprise one or more band systems observed on a background of a continuous spectrum. The source of the energy responsible for the chemiluminescence is usually the recombination (or disproportionation) of atoms and free radicals, in which a large amount of energy, equivalent to quanta in the visible and ultraviolet regions of the spectrum, is evolved at once, in a single act. Therefore measurements of chemiluminescence in flames give information on the reactivities of atoms and free radicals, their concentrations, and their concentration distributions in the flame and in the combustion products.

The use of chemiluminescence data in the study of reaction kinetics in flames and combustion products is based on the existence of proportionality between the emission intensity $I$ and the rate $w$ of the chemical process resulting in chemiluminescence:

$$I = \eta_{ch}\omega, \quad (1)$$

where $\eta_{ch}$ is a proportionality coefficient representing the quantum yield of the radiation. In general $\eta_{ch}$ may depend on the temperature and on the composition of the mixture in which reaction is occurring. The principal cause of variation in the light yield is change in the composition of the mixture. The coefficient $\eta_{ch}$ may vary both as a result of strengthening or weakening of quenching processes and as a result of energy transfer processes, which may affect the nature of the luminescent species. The temperature variation in the light yield is usually small, and is due mainly to the temperature dependence of the probability of radiationless transitions. The kinetics can be measured by various methods based on chemiluminescence:

(a) Measurement of intensity of emission in a chemiluminescent reaction occurring in the system.

(b) Measurement of intensity of emission from an added luminescent substance. In this case chemiluminescent reactions may be altogether absent in the actual system investigated. The chemiluminescence of the added substance (activator) arises from energy transfer.

(c) Measurement of intensity of emission occurring on addition of a substance which enters into a chemiluminescent reaction with one of the components of the system. In this case, too, chemiluminescent reactions may be absent from the actual system investigated.

All these chemiluminescent methods are used in kinetic investigations of flame reactions. The latter two methods are employed especially frequently.

## 1. Chemiluminescent Reactions with Additives

The flame and the products of the combustion of hydrogen form the subject of most quantitative investigations of chemiluminescence. The reaction involves O and H atoms and the OH radical. The application of chemiluminescent methods makes it possible to measure relative and absolute concentrations of these species and their distribution in the combustion products, and to obtain rate constants for their recombination.

Concentration distributions of H atoms in the hydrogen flame and in the reaction products have been measured, for example, from the emission arising on the introduction of copper into the flame. A bright emission band due to CuH is recorded, its intensity $I_{CuH}$ at $\lambda = 4280$ Å being proportional to the concentration of H atoms[4,5]. Reid and Sugden have shown[6] that the constant $k'$ in the expression $I_{CuH} = k'[H]$ is independent of temperature. Therefore $[H]/[H]^\circ = I_{CuH}/I^\circ_{CuH}$ ($I^\circ_{CuH}$ being the intensity of emission at the concentration of H atoms chosen as standard), and relative concentrations of H atoms can be measured by $I_{CuH}$. These measurements can be converted to absolute concentrations provided that [H] is measured at one point by some absolute method. According to Sugden's data[7] the equilibrium

$$OH + H_2 \rightleftarrows H_2O + H \quad (2)$$

is rapidly established in the products of the combustion of hydrogen. This makes it possible to determine the concentration of OH radicals and their distribution in the products of the hydrogen flame from known values of [H] and the equilibrium constant of process (2). In this way the following recombination rate constants have been obtained[5]

$$H + OH + H_2O \rightarrow H_2O + H_2O \quad k_{1650} = 1.5 \times 10^{-30}\ cm^6\ s^{-1},$$
$$H + H + H_2O \rightarrow H_2 + H_2O \quad k_{1650} = 6 \times 10^{-32}\ cm^6\ s^{-1}.$$

The addition of halogens to hydrogen flames having a high fuel content results in continuous emission in the visible region, due to the reaction $H + X \rightarrow HX + h\nu$, where X is a halogen atom[8]. This emission resembles the continuum of the hydrogen flame arising in the reaction $H + OH \rightarrow H_2O + h\nu$.[9] The weak continuum emitted in the visible region when an alkali metal M is added to a hydrogen flame has an intensity proportional to [OH][M]. The continuum probably arises[10] in the reaction $M + OH \rightarrow MOH + h\nu$. In all these cases the emission intensity can be used to determine the relative concentration of H atoms and OH radicals in different parts of the flame and combustion products. These data can be used also to calculate the distribution of oxygen atoms, since the equilibrium

$$H_2 + O \rightleftarrows H + OH$$

is rapidly established in the flame.

A method suggested by Gaydon[11] has often been used recently to determine the concentration of atomic oxygen. It is based on measurement of the intensity of the yellow-green glow in the reaction.

$$NO + O \rightarrow NO_2 + h\nu. \quad (3)$$

In Gaydon's work this method was employed only qualitatively, the emission serving as an indicator of atomic oxygen. The work of Karmilova and Kondrat'ev[12], who made absolute measurements of the intensity of the yellow-green emission of $NO_2$, showed that the intensity is a quantitative measure of the concentration of atomic oxygen in the CO flame. The concentration of O atoms was close to the equilibrium values in flames having a temperature above 2600°K; at lower temperatures it exceeds the equilibrium value. The possibility of the quantitative use of reaction (3) to measure relative and absolute concentrations of atomic oxygen in flames has been confirmed by later work. Thus James and Sugden[13] have shown that the intensity of the emission from the combustion products of hydrogen to which nitric oxide has been added is proportional to [NO] and to the concentration of O atoms, the latter being calculated from the equilibrium constants.

Measurements of the absolute light yield in reaction (3) taking place in the combustion products of the hydrogen flame have been used[14] to evaluate the rate constant of reaction (3)†. The value of $2\times10^{-18}$ cm$^3$ s$^{-1}$ for the rate constant agrees well with the value obtained by Kaufman[15] using a different method.

### 2. Emission from Luminescent Additives

Emission lines due to various metal impurities can be observed in the spectra of many flames. Gaydon and Wolfhard[3] put forward the hypothesis that the excitation of metal atoms in flames is effected by the energy released by the recombination of atoms and free radicals. The number of excited impurity atoms may correspond to the temperature of the flame, but can also considerably exceed the equilibrium value. This is especially characteristic of low-temperature and highly dilute flames, in which the concentration of atoms and free radicals far exceeds the equilibrium value. Measurements of the emission intensity from a metal impurity can be used as a quantitative method for studying the kinetics of reactions involving atoms and free radicals. Thus the decay of the chemiluminescence of metallic sodium has been used[16] to measure the kinetics of the recombination of atomic hydrogen at 1072°K in the products of combustion from a mixture of $H_2 + O_2 + N_2$. The absolute concentration of H atoms was measured from the rate of their reaction with $D_2O$ or $D_2$.

In the products of combustion, hydrogen is removed by the reactions

$$H+H+M \rightarrow H_2+M, \quad (4)$$

$$H+OH+M \rightarrow H_2O+M. \quad (5)$$

If M = Na, both reactions result in the formation of excited sodium atoms emitting a resonance line. The probability of the excitation of sodium in these reactions is of the order of unity[17].

Since the concentrations of H atoms and OH radicals are balanced by the occurrence of process (2), the decrease in emission intensity can be used to measure the relative concentration of H atoms, although they immediately disappear by the two reactions (4) and (5). The time variation in the emission intensity is almost independent of the relative proportions of $N_2$, $H_2$, and $H_2O$, which are evidently equally effective as third bodies.

Analogous measurements can be made with other metals, e.g. thallium and lead, the resonance emission of which is excited in the processes[18]

$$H+H+Tl \rightarrow H_2+Tl^* \quad (\lambda=535\ m\mu m),$$
$$H+OH+Pb \rightarrow H_2O+Pb^* \quad (\lambda=405.8\ m\mu m).$$

New excitation reactions occur when halogens $X_2$ and metal vapours are introduced simultaneously into a hydrogen flame[19]

$$H+X+M \rightarrow M^*+HX \quad (X=Cl, Br).$$

In these processes the heat of reaction can be almost completely transformed into the energy of excitation of the metal atom. Thus the heat of reaction of H + Cl (102 kcal × × mole$^{-1}$)‡ is almost completely utilised for the excitation of a lead atom (excitation potential 100 kcal). Measurements of the emission of metal atoms in reactions between hydrogen and halogen atoms can also be used in kinetic investigations.

## III. REACTIONS OF NITROGEN, OXYGEN, AND HYDROGEN ATOMS

Methods analogous to those described above are used also to investigate non-flame reactions of nitrogen, oxygen, and hydrogen atoms. In this case the atoms are usually obtained in electric discharges, and their reactions are investigated in a flow apparatus from the distribution of emission intensity along the reaction tube.

### 1. Reactions of Atomic Nitrogen

It was observed in 1900 that nitrogen which has passed through an electric discharge exhibits a yellow afterglow[20], associated with the reactions[21]

$$N(^4S)+N(^4S)+M \rightarrow N_2(^5\Sigma_g^+)+M \text{—rate-determining stage},$$
$$N_2(^5\Sigma_g^+)+M \rightarrow N_2(B^3\Pi_g)+M,$$
$$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+)+h\nu \text{ — chemiluminescence}.$$

Simultaneous recording of the emission intensity and mass-spectrometric measurement of the concentration of atomic nitrogen[21] have shown that $I = \alpha[N]^2$, the coefficient $\alpha$ being proportional to the pressure of $N_2$. This shows that the luminescence arises from a termolecular recombination. Measurement of the absolute intensity of the glow has yielded an estimated rate constant for the recombination of N of $2\times10^{-33}$ cm$^6$ s$^{-1}$.[21] A more accurate value for the constant — $1.72\times10^{-32}$ cm$^6$ s$^{-1}$ — has been obtained by measuring the distribution of emission intensity along the tube through which the mixture of atomic and molecular nitrogen from the electric discharge is passed[22].

The absolute concentration of nitrogen atoms was determined by a method of "chemiluminescent titration"[23] with NO. The nitric oxide enters from a small volume through a calibrated orifice into the tube along which the jet from the discharge is passing. The very rapid reaction N + NO → $N_2$ + O takes place, and a new chemiluminescent reaction O + NO → $NO_2 + h\nu$ appears. The yellow glow of the nitrogen does not immediately vanish, but a yellow-green luminescence, associated with the reaction of atomic oxygen, appears. Since the vessel containing the nitric oxide has a small volume, the rate of escape of NO drops rapidly, and when its amount becomes insufficient and N atoms remain, a new blue-violet luminescence appears, associated with the reaction[22,24]

$$N+O+M \rightarrow NO(A^2\Sigma^+, B^2\Pi)+M,$$
$$NO(A^2\Sigma^+, B^2\Pi) \rightarrow NO+h\nu \ (\beta \text{ and } \gamma \text{ bands}).$$

At the instant of appearance of the blue-violet glow, the quantity of NO molecules which have entered is equal to the number of N atoms. The presence of NO in the vessel is measured at this point, the flow of NO is determined from a calibration curve, and in this way the concentration of nitrogen atoms is obtained. The "titration" takes a few minutes.

### 2. Reactions of Atomic Oxygen

The recombination of atomic oxygen

$$O(^3P)+O(^3P)+M \rightarrow O_2+M \quad (6)$$

† The hydroxyl concentration was determined by the method of ultraviolet absorption[1]. The concentration of O atoms was calculated from values of the equilibrium constant of the reaction $2OH \rightleftharpoons H_2O + O$.

‡ Henceforward we shall write kcal instead of "kcal mole$^{-1}$".

is not chemiluminescent. Nevertheless, the reaction velocity and the rate constant can be measured by chemiluminescent methods. If small amounts of NO are introduced into a jet containing oxygen atoms, a quite bright emission is produced, whose intensity is proportional to the concentration of atomic oxygen[25-28]. At the same time, the reaction NO + O → $NO_2$ is slow at low NO concentrations, in comparison with other reactions of O atoms, and it has hardly any effect on the concentration of the latter[23]. The nitrogen dioxide which is formed reacts very rapidly with O atoms to regenerate NO:

$$O+NO_2 \rightarrow O_2+NO. \quad (7)$$

Reaction (7) is used for the chemiluminescent "titration" of O atoms. A gradually increasing flow of $NO_2$ is admitted to the jet. As a result of the rapid reaction (7), [O] decreases, while [NO] increases. The emission intensity, which is proportional to the product [O][NO], passes through a maximum. With further increase in the flow of $NO_2$, the intensity falls rapidly. The end-point corresponds to complete disappearance of luminescence from the tube. At this point the supply of $NO_2$ is equal to the concentration of O.[29] In a variant of this method[30], which probably yields more accurate results, measurements of the intensity distribution along the tube and the application of chemiluminescent titration enable the rate constant of reaction (6) to be determined[29,30]. The technique shows promise for the quantitative investigation of other reactions of atomic oxygen. Thus the kinetics of the consumption of oxygen atoms has been examined[29] in the presence of $H_2$, $O_2$, $N_2$, Ar, $CO_2$, CO, $N_2O$, $C_6H_6$, $SO_2$, $Fe(CO)_5$, $H_2O$, $O_3$, $C_2H_4$, $Cl_2$, and $Br_2$. Results obtained by the chemiluminescent method have been discussed in detail in a recent review by Kaufman[31].

### 3. Reactions of Atomic Hydrogen

The recombination of atomic hydrogen catalysed by nitric oxide is accompanied by luminescence in the red and near infrared regions of the spectrum, due to emission by excited HNO molecules[32-34]:

$$H+NO+M \rightarrow HNO^* + M \text{ — rate-determining stage}, \quad (8)$$

$$H+HNO \rightarrow H_2+NO. \quad (9)$$

Radiation from HNO* is observed also in the rapid reaction[33]

$$H+NO_2 \rightarrow OH+NO.$$

The kinetics of the catalysed recombination has been studied[33,34] from the intensity of the red luminescence in a low-pressure (1–2 mmHg) jet. The rate constant of reaction (8) and the intensity depend substantially on the nature of the third species M, where $I \propto [H][NO]$. From the intensity distribution along the jet and calorimetric measurements of the concentration of hydrogen atoms, the rate constant of reaction (8) was found to be $1.3 \times 10^{-32}$ $cm^6$ $s^{-1}$ (with M = $H_2$).

This reaction may perhaps be used in the future as an indicator of atomic hydrogen, and employed to study reactions of the latter with various molecules, as has been done for the reactions of atomic oxygen.

## IV. INFRARED CHEMILUMINESCENCE IN THERMAL REACTIONS

The distribution of energy among the products of exothermic reactions is not the equilibrium distribution. Reference may be made, for example, to a series of results obtained by M. Polanyi and his coworkers, who investigated the reactions of alkali-metal vapours with halogens, as well as with organic and inorganic halogen compounds. The kinetics and the characteristics of the chemiluminescence in these reactions have been discussed in detail in several review articles and monographs[2,35,36]. Here we shall consider only those facts which indicate the formation in these reactions of excited species, present in vibrationally excited or metastable states. The simplest reaction — that between the vapours of sodium and a halogen $X_2$ — occurs according to the scheme

$$Na+X_2 \rightarrow NaX+X, \quad (10)$$

$$X+Na_2 \rightarrow NaX'+Na, \quad (11)$$

$$NaX'+Na \rightarrow NaX+Na^*, \quad (12)$$

$$Na^* \rightarrow Na+h\nu, \quad (13)$$

where NaX′ is an excited molecule. The main evidence for the formation of NaX′ molecules and the excitation of sodium in reaction (12) is based on an investigation of the quenching of chemiluminescence by foreign gases, which showed that the chemiluminescence was extinguished considerably more strongly than was the fluorescence of sodium. If the reaction is carried out in a flow apparatus, the zone of maximum emission intensity is displaced in the flow direction. It is interesting that in individual cases the heat of reaction is almost completely converted into excitation energy; for example, emission of the 0.589 μm (48.5 kcal) sodium resonance line is observed in the reaction $Na_2 + I \rightarrow NaI + Na$, the heat of which reaction is 49.5 kcal.

The formation of vibrationally excited molecules in a chemical process was first detected spectroscopically by McKinley et al.[37] for the reaction of hydrogen atoms with ozone $H + O_3 \rightarrow OH' + O_2$. The reaction was carried out at 0.2 mmHg in a reaction vessel comprising two coaxial tubes. A stream of ozone from the inner tube entered an atmosphere of partly dissociated hydrogen which had passed through a discharge tube. A red glow appeared at the outlet from the inner tube, produced by vibrationally excited OH radicals, whose spectrum was recorded on a photographic plate. The spectrum contained bands corresponding to transitions from vibrational levels right up to the level of quantum number 9. The energy of this highest level (75 kcal) is close to the heat of reaction (78 kcal). Vibrationally excited molecules were detected also in a large number of photochemical and thermal reactions. By the method of flash photolysis, vibrationally excited species have been obtained, for example, in the reactions[38-40] (the numerals in parentheses indicate the highest observed vibrational level)

$$O+NO_2 \rightarrow O_2\,(8)+NO, \quad Br+O_3 \rightarrow BrO\,(4)+O_2,$$
$$O+Cl_2O \rightarrow O_2\,(8)+ClO, \quad O+NH_3 \rightarrow OH\,(2)+NH_2,$$
$$O+O_3 \rightarrow O_2\,(17)+O_2, \quad O+CH_4 \rightarrow OH\,(2)+CH_3,$$
$$Cl+O_3 \rightarrow ClO\,(5?)+O_2, \quad O+HCl \rightarrow OH\,(2)+Cl.$$

The concentrations of excited species are large here, and they are identified from their absorption spectra.

A series of investigations of infrared chemiluminescence has been made by J. C. Polanyi and his coworkers[41-45], who observed from the emission spectra the formation of vibrationally excited molecules, e.g. in the reactions

$$H+NO \rightarrow HNO' \quad H+Br_2 \rightarrow HBr'+Br,$$
$$H+Cl_2 \rightarrow HCl'+Cl \quad H+NOCl \rightarrow HCl'+NO.$$

It is seen from the above equations that, in reactions of atoms with triatomic molecules, the heat of reaction is not uniformly distributed among the products. Most of the

energy — and in isolated cases the whole of it — is concentrated on the bond which is formed. Only in the reaction H + NOCl were both species NO and HCl vibrationally excited. Even in this case, however, the distribution of energy was non-uniform: the emission of the NO constituted only a few per cent of that from the HCl.[45]

All the reactions quoted in the present Section were formerly regarded as elementary. However, the formation of excited products in different vibrational states shows that this view is an oversimplification. In fact, the measured rate constant represents the sum of the rate constants of reactions leading to products which are present in various vibrational states. Therefore investigation of the energy spectrum of the resulting products is of exceptional interest for the construction of a quantitative theory of the elementary acts in chemical processes. The first work on these lines has been undertaken recently. In the H + $O_3$ reaction it has been concluded, from measurements on the distribution of OH among vibrational levels with an initial pressure of 2–5 mmHg, that the rate constants for the formation of different excited states of OH are approximately the same[46]. However, this conclusion cannot be regarded as final, and requires further verification. Thus it has been shown[44,45,47,48] for the reactions H + NOCl and H + $Cl_2$ that the distribution of HCl among vibrational levels depends significantly on the initial pressure and the partial pressure of HCl. At higher pressures (0.1–0.2 mmHg for H + $Cl_2$ and 1–2 mmHg for H + NOCl) the HCl exhibits an approximately Boltzmann distribution among vibrational levels, and the relative rate constants for the formation of HCl molecules at a given vibrational level are closely similar for the two reactions, in spite of the differences in the nature of the reactant molecules (the $Cl_2$ molecule being non-polar, while NOCl is polar) and in the heats of reaction. These results can be explained by the fact that, at higher pressures, the original distribution of energy among vibrational levels is strongly distorted by secondary processes involving the redistribution of energy.

At pressures of around 0.01 mmHg in the H + $Cl_2$ system, emission disappears from levels located above $v = 5$ (at higher pressures the level $v = 6$ was observed). In the H + NOCl system no emission is observed from the levels $v = 8$ and $v = 9$, which had been observed at higher pressures. The distribution among vibrational levels becomes markedly different from the Boltzmann distribution, and differs greatly for the two systems. Under these conditions reaction is most rapid to form HCl molecules in their lowest vibrational states; in the H + $Cl_2$ reaction, for example, the rate of formation of HCl($v = 3$) exceeds that of HCl($v = 5$) by a factor of approximately 35. The highest vibrational levels are excited at higher pressures probably as a result of the redistribution of energy.

## V. LIQUID-PHASE OXIDATIONS ACCOMPANIED BY BRIGHT CHEMILUMINESCENCE

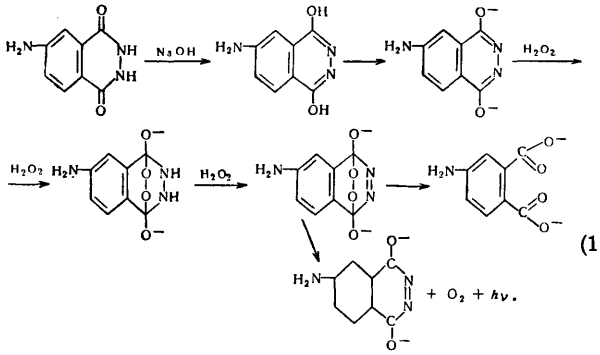
### 1. Oxidation of Cyclic Hydrazides

The chemiluminescence accompanying the oxidation of 5-amino-1,2,3,4-tetrahydro-1,4-dioxophthalazine (Luminol) with hydrogen peroxide in alkaline medium was first studied by Albrecht in 1928.[49] The luminescence was long-lived, and so intense that it could be observed with the naked eye. It has also been discovered that bright chemiluminescence accompanies oxidation of the hydrazides of benzenesulphonic[50], pyridinecarboxylic[51], aromatic, and aliphatic[52,53] acids. Several regularities have been observed in the dependence of the intensity of chemiluminescence on the structure of the hydrazides. However, many authors have based their conclusions on the results of visual observations or measurements with instruments of low sensitivity, and therefore their conclusions concerning the absence of chemiluminescence in the oxidation of a particular compound cannot be regarded as final.

Experiment has shown that several hydrazides of phthalic acids, and especially of aminophthalic acids, possess most long-lived and intense luminescence. According to Sveshnikov[54] the brightness of the emission at Luminol concentrations of $10^{-5}$–$10^{-3}$ g $cm^{-3}$ is $3 \times 10^{-7}$ to $2 \times 10^{-6}$ stilb with a layer 1 cm thick. Ordinary photometers can be used to study such reactions. Therefore the oxidation of Luminol in alkaline medium, with and without a catalyst present, has become a kind of model reaction for the study of chemiluminescence in the liquid phase. The oxidants used have been hydrogen peroxide, peroxosulphates[1], permanganate[55], $[CoCl_2(NH_3)_4]Cl$,[56] and other compounds[57]. Catalysts of various types considerably intensify the chemiluminescence[57]. Many workers have attempted to elucidate the mechanism of these reactions, by studying the effect of the nature and position of substituents in the benzene and hydrazide rings on the intensity and spectral region of the emission[58–68]. Several reaction schemes have been suggested for the oxidation of [hydrazides of] phthalic acids with hydrogen peroxide in alkaline medium, which result in the emission of radiation.

Thus Albrecht[49], Tamamushi[70], and Weber[71] assumed that the oxidation of Luminol involves the intermediate formation of a diimide and an excited dilactam form of the hydrazide. A similar hypothesis was put forward by Caen[72] for the oxidation of Rimifon (the hydrazide of isonicotinic acid). However, existence of the diimide was not confirmed experimentally.

Parker and Harris[73], and later Drew and Garwood[63,64,74], suggested that the Luminol molecule adds on a molecule of $H_2O_2$ to form a peroxide. The oxygen bridge is eliminated, and the epidioxide molecule converted into an excited Luminol molecule, which is responsible for the chemiluminescence:




(14)

Several pieces of evidence in support of this hypothesis were given[59,63]. Ojima[75] suggested a similar mechanism for the luminescence of Luminol in the presence of copper salts.

Babko and Lukovskaya[76] showed by the method of isomolar series that copper forms a 1 : 1 complex with

Luminol, and the $H_2O_2$ molecule adds on in turn in this complex, forming a new complex responsible for the emission.

Many workers have shown[63,68,73,77-80] that with variation in the $H_2O_2$ concentration the initial intensity passes through a maximum. However, different authors give different relative concentrations of Luminol and hydrogen peroxide corresponding to this maximum, covering the range 1–50 molecules of $H_2O_2$ per molecule of Luminol.

Especially detailed kinetic investigations were made by Sveshnikov[54,77-79], who used a Fabry–Gelhof photometer to study the time variation of emission intensity in the oxidation of Luminol in alkaline medium at 52°C and the effect of the $H_2O_2$ and alkali concentrations on the intensity. The time curves show that, within the limits of experimental error, the emission intensity $I$ is proportional to the Luminol concentration, while the kinetics of the variation in intensity remains unchanged when the Luminol concentration is diminished by a factor of 100. The rate of change of $I$ increases as the concentration of the hydrazide decreases. According to Sveshnikov, the chemiluminescence corresponds to some secondary reaction which is of the first order with respect to the Luminol concentration. His experimental results support the hypothesis of Drew and Garwood, and are at variance with the Albrecht–Tamamushi scheme, which requires a quadratic dependence of $I$ on the Luminol concentration.

Bernanose[81] showed that, when Luminol is oxidised with sodium hypochlorite and hydrogen peroxide, the luminescence diminishes with time according to an exponential law. Several workers, who have investigated the kinetics of the chemiluminescence of Luminol in the presence of catalysts[71,82-87], have observed the same law for the time variation of the emission. It may be surmised that the same elementary act, perhaps the unimolecular breakdown of Luminol peroxide, is responsible for the chemiluminescence in all cases.

The brightness of the chemiluminescence of Luminol depends significantly on the pH of the medium, reaching a maximum at pH 10–11. Several explanations have been suggested for this phenomenon. Some workers[66,81] consider that the pH influences an equilibrium between two forms — luminescent and non-luminescent — of Luminol. Babko and Lukovskaya[88] assume that the effect of pH is linked with the dissociation of Luminol. Erdey[89], who studied the decomposition of hydrogen peroxide in alkaline medium, showed that the ion $HOO^-$ was formed as active intermediate, the rate of decomposition of $H_2O_2$ being a maximum at pH 12. He postulated that this ion adds on to a molecule of the luminous substance to form a peroxide, whose decomposition causes the chemiluminescence (Drew and Garwood's mechanism). From this point of view the presence of an extremum in the pH dependence of the rate of decomposition of $H_2O_2$ may be one reason for the appearance of a maximum on the chemiluminescence intensity curve.

Thus, although the mechanism of the chemiluminescence of Luminol has not been finally established, Drew and Garwood's scheme (14) seems the most probable.

Besides the above mechanisms of "ionic" type, several investigators suggest "radical" mechanisms for the oxidation of Luminol with hydrogen peroxide[87,90]. These hypotheses are based on theories of the chain decomposition of hydrogen peroxide in acid medium, and also the observed[54,64,83,87,90] quenching action of inhibitors of radical reactions — quinol, Metol, cysteine, etc. — on the chemiluminescence of Luminol, which was restored as the inhibitor was consumed. These schemes do not agree with Sveshnikov's kinetic results, since they presuppose that the intensity of chemiluminescence depends on higher powers of the concentration of the luminescent substance, nor with Erdey's conclusions concerning the formation of $HOO^-$ ion in alkaline medium. Thus further kinetic and spectroscopic study of the chemiluminescent reaction of Luminol is required in order to establish the mechanism of the luminescence accompanying this process.

Although the mechanism of chemiluminescent oxidation has not yet been established, the pH dependence of the bright luminescence of Luminol is widely used in analytical chemistry. Luminol is employed to detect $H_2O_2$,[91] $CuCl_2$, $Br_2$, $KMnO_4$, $NH_3$,[92] and poison gases[53], for the quantitative determination of $H_2O_2$,[94] copper[76,88,94], and several organic compounds[94], and also as an acid–base indicator[95].

## 2. Oxidation of Lucigenin

The bright green luminescence accompanying the oxidation of alkaline *NN'*-dimethylbiacridinylium solutions with hydrogen peroxide was first investigated in detail by Gleu and Petsch[96,97] in 1935. They gave the name "lucigenin" (generating light) to the compound.

As in the case of Luminol, several hypotheses have been put forward to explain the mechanism of the luminescence of lucigenin. Only hydrogen peroxide and oxygen produce chemiluminescence in alkaline solutions of this compound, and the resulting spectrum is identical with its fluorescence spectrum.

Tamamushi and Akiyama[98,99] consider that the oxidation of lucigenin with oxygen involves formation of a diradical, 10,10'-dimethyl-9,9'-biacridinyl, which on addition of $O_2$ forms lucigenin peroxide. Under the influence of the previously formed $H_2O_2$, this peroxide is converted into a dicarbinol base, which is in an excited state and is responsible for the luminescence.

Gleu and Petsch[96] postulate a reaction scheme in which lucigenin oxide (10,10'-dimethyl-9,9'-biacridinylidene oxide) is directly responsible for the emission, while the intensity of chemiluminescence is proportional to the first power of the lucigenin concentration.

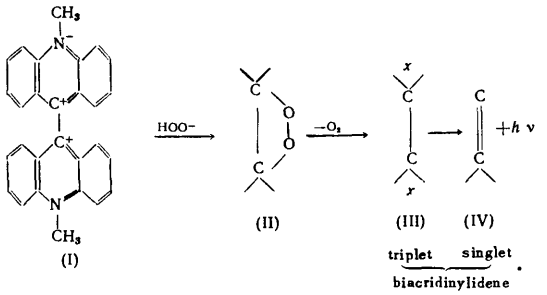
Totter et al.[100] assume that the oxidation of lucigenin involves the intermediate formation not of an oxide or a peroxide but of 10,10'-dimethyl-9,9'-biacridinylidene, followed by a monocarbinol base, which is responsible for the luminescence.

Erdey[101] considers that in alkaline medium the lucigenin molecule reacts with the $HOO^-$ ion formed on decomposition of $H_2O_2$, to yield lucigenin peroxide (similarly to the scheme of Gleu and Petsch).

Grigorovskii and Simeonov[102], having synthesised several derivatives of lucigenin, showed that lucigenin oxide and 10,10'-dimethyl-9,9'-biacridinylidene are able to emit a bright yellow-green chemiluminescence in alkaline medium under the influence of hydrogen peroxide, whereas the monocarbinol base does not emit light under these conditions.

Very interesting spectroscopic investigations were made by Karyakin[103], who studied the chemiluminescence, phosphorescence, and fluorescence spectra of lucigenin brom-

ide (I), *NN'*-dimethylbiacridinylidene oxide (II), and *NN'*-dimethylbiacridinylidene (III) (see Table). Since the chemiluminescence spectra of aqueous solutions of lucigenin and of lucigenin oxide are not identical, Karyakin considers that the oxide is not an intermediate product in the oxidation of lucigenin, and that the emission from the oxide represents an independence process. The chemiluminescence spectra are similar to the phosphorescence spectra. This implies that an excited triplet level is responsible for the chemiluminescence. Karyakin[103] and Erdey[104] suggest an emission mechanism for lucigenin comprising the stages — (1) $H_2O_2$, or most probably the $HOO^-$ ion, reacts with the starting material to form a transannular epidioxide; (2) the latter decomposes thermally with the evolution of $O_2$ and formation of the corresponding diradical (triplet) state; and (3) the diradical passes into the ground state, emitting a quantum of light:




On addition of a catalyst, lucigenin peroxide (II) decomposes to form an excited methyloxoacridine, which emits a blue glow.

In a study of the kinetics of the chemiluminescence of lucigenin and the dependence of the intensity of chemiluminescence on the concentrations of lucigenin, $H_2O_2$, and alkali[54,79], Sveshnikov showed that, whereas with Luminol the curve for the time variation in the intensity represents a complicated process, in the case of lucigenin the curves follow exactly an exponential law. The kinetic curves show that the rate of variation in chemiluminescence increases with decrease in the concentration of the substance, as in the case of Luminol. This confirms the hypothesis that both lucigenin and Luminol inhibit the decomposition of $H_2O_2$. Furthermore, Sveshnikov showed that, with lucigenin too, the dependence of the initial intensity of chemiluminescence on the concentration of the substance in the presence of large excesses of $H_2O_2$ and NaOH is not quadratic. Moreover, the strengthening of chemiluminescence with increase in lucigenin concentration is even less than was to be expected for a linear relationship[54]. Sveshnikov's results, and also those of Kroh[105] indicating that the oxidation of lucigenin is of the first order, make the Gleu and Petsch and Karyakin–Erdey scheme the most probable. Tamamushi and Akiyama's hypothesis, according to which a quadratic dependence of reaction velocity on lucigenin concentration should be observed, obviously does not correspond to reality.

Lucigenin, like Luminol, is employed in analytical chemistry for the detection of copper(II), lead, and mercury(II)[104,106,107], as a chemiluminescent indicator[108,109], etc.

TABLE. Positions of chemiluminescence and photoluminescence maxima for lucigenin bromide (I), *NN'*-dimethylbiacridinylidene oxide (II), and *NN'*-dimethylbiacridinylidene (III).

| Compound | Position of maximum | | |
|---|---|---|---|
| | chemiluminescence | fluorescence | phosphorescence |
| I | 480,515 | 480,515 | 480,515 |
| II | 550 | 505 | 548 |
| III | 525 | 515 | 523 |

## VI. SYSTEMS SHOWING WEAK CHEMILUMINESCENCE

We have discussed above reactions which are accompanied by bright chemiluminescence. The high emission intensity in these reactions is due either to a high rate of occurrence of exothermic processes or to a high yield, i.e. the efficient conversion of chemical into light energy. These conditions are not satisfied in reactions occurring at moderate temperatures (low rates) and with the formation of products which are unable to luminesce efficiently (low yields). Such reactions will therefore be accompanied not by bright but by weak chemiluminescence, even if they include stages in which the energy evolved is equivalent to quanta of visible light. Nevertheless, it is clear that there is no fundamental, qualitative difference between systems having bright and those having weak chemiluminescence, and emission may be observed in many slow "ordinary" reactions provided that a sufficiently sensitive detector is available.

The first investigations of weak chemiluminescence were made before the Second World War by Audubert and his coworkers[110,111]. With the aid of Geiger–Müller counters they detected extremely weak ultraviolet emission in many reactions, such as the neutralisation of strong acids by strong alkalis, the hydration and dehydration of quinine sulphate, several oxidation–reduction reactions — the autoxidation of bisulphite, the oxidation of organic substances by permanganate, chromic acid, bromine, and iodine, the anodic oxidation of aluminium, magnesium, silicon, etc. The number of photons emitted from 1 $cm^2$ of surface in 1 s did not exceed $10^4$ (in isolated cases $10^5$). Hence the yield, i.e. the ratio of the number of photons emitted to the number of molecules which have reacted, was of the order of $10^{-14}$–$10^{-15}$, which is extremely low. Only in the decomposition of azides was the emission sufficiently intense for its temperature coefficient and its spectrum to be determined.

A striking feature of Audubert's experiments was the huge size of the quanta emitted, the range 200–240 mμm corresponding to amounts of energy of 140–120 kcal. Nevertheless, the sum of the heat of reaction and the activation energy of the reactions investigated did not exceed 50–80 kcal. Audubert assumed that twin collisions could occur between energy-rich molecules of the products, but this hypothesis remained unproven.

At the end of the 1930s Audubert ceased to investigate chemiluminescence, and did not return to it again. One of his last papers on chemiluminescence finished with the words: "In the present state of the exceptionally unfavourable and technically difficult method it is not surprising that the number of results as yet obtained is small. But it is to be hoped that advances in the technique of photoelectric counters will make possible the widespread use of a method which has already yielded such interesting conclusions"[111]. In fact the application of highly sensitive light transducers — photomultipliers, photoresistors,

etc. — has enabled a weak emission to be detected in many chemical reactions, and its regularities to be investigated[112,113]. Luminescence in the visible region of the spectrum has been studied in — the thermal decomposition of peroxides, hydroperoxides, and azo-compounds in solution[112-115]; the thermal decomposition and oxidation in the gas phase of peroxides, hydroperoxides, alkyl iodides, alkyl nitrites, nitric acid, nitromethane[113,114], acetaldehyde[116], propionaldehyde and butyraldehyde[117], ethyl hyponitrite[118], n-hexane, and diethyl ether[117]; the electrolysis of ethanol, acetic acid, potassium acetate[113,114], sodium acetate, sodium propionate, sodium citrate, sodium tartrate, Grignard reagents, amino-acids, and several other organic substances[119]; the oxidation with oxygen of hydrocarbons and other organic compounds in solution[114,120-123]; the condensation of acid chlorides with amines and ketones, and polycondensation (production of nylon)[124,125]; the oxidative degradation of polypropylene and other polymers[126]; the oxidation of urea with hypohalites[127]; the oxidation of sodium sulphite in aqueous solution catalysed by metal salts[128]; and the oxidation of oxalyl chloride with hydrogen peroxide[129]

Thus chemiluminescence has been detected in a large number of reactions of the most varied classes and types. In view of these results, chemiluminescence must evidently be regarded as a general phenomenon, accompanying the occurrence of any reaction in which exothermic stages are involved.

## 1. Chemiluminescence in Induced Oxidations

Until recently no quantitative investigation had been made of chemiluminescence accompanying oxidation by molecular oxygen. In order to find a reaction in which excited species are formed, and compare the regularities in chemiluminescence with the kinetic regularities, a series of investigations[113,114,130,131] were based on induced oxidation as model reaction, the kinetics of which is well known[132-134]. The reaction scheme of an induced oxidation is

$$\begin{array}{l} \text{1) chain initiation (appearance of radicals R) at rate } w_i \\ \left.\begin{array}{l} \text{2) } R + O_2 \xrightarrow{k_2} RO_2 \\ \text{3) } RO_2 + RH \xrightarrow{k_3} ROOH + R \end{array}\right\} \text{chain propagation,} \\ \left.\begin{array}{l} \text{4) } R + R \rightarrow R{-}R \\ \text{5) } R + RO_2 \rightarrow ROOR \\ \text{6) } RO_2 + RO_2 \rightarrow \text{inactive products} + O_2 \end{array}\right\} \text{chain termination.} \end{array} \qquad (15)$$

where RH is the substance undergoing oxidation, ROOH the hydroperoxide, R the hydrocarbon radical, and $RO_2$ the peroxy-radical.

Examination of the energetics of reactions (1)–(6) in scheme (15) shows that only reactions (4)–(6) are sufficiently exothermic to excite luminescence in the visible region of the spectrum (the range 350–620 mμm corresponds to 80–45 kcal or 3.3–2.0 eV). At sufficiently high oxygen concentrations the radicals R are converted by reaction (2) into peroxy-radicals, and only $RO_2$ radicals recombine. Under these conditions the emission intensity $I$ is proportional to the rate of recombination $w_{rec}$:

$$I = \eta_{ch} w_{rec} = \eta_{ch} k_6 (RO_2)^2, \qquad (16)$$

where $\eta_{ch}$ is the number of photons emitted in a single act of recombination.

Under steady-state conditions the rate of destruction of radicals is equal to their rate of formation $w_i$, which is proportional to the rate of decomposition of the initiator:

$$w_i = 2 f_{cell} k_0 c, \qquad (17)$$

where $c$ is the initiator concentration, $k_0$ its decomposition rate constant, and $f_{cell}$ the probability of escape of primary radicals from the "cell", the factor 2 indicating that the decomposition of one molecule yields two radicals.

It follows from Eqns. (16) and (17) that

$$I = 2\eta_{ch} f_{cell} k_0 c.$$

If decomposition is slow, the intensity will not vary with time, and at a given temperature will be determined by the formula

$$I = 2\eta_{ch} f_{cell} c a_0 e^{-E/RT} = \text{const}\, e^{-E/RT}, \qquad (18)$$

where $a_0$ is the preexponential factor and $E$ the activation energy of decomposition.

Eqn. (18) indicates an Arrhenius temperature dependence for the intensity. This relationship is in fact well satisfied (Fig. 1), the activation energy determined experimentally from the chemiluminescence $E_{ch}$ proving to be identical with $E$, the activation energy of decomposition of the corresponding substance measured by chemical methods[112-114,135].

If the rate of decomposition of the substance at the experimental temperature is considerable, the concentration will decrease according to the exponential law $c = c_0 e^{-k_0 t}$. The emission intensity should decay according to the same law:

$$I = I_0 e^{-k_0 t} \text{ or } \log I = \log I_0 - 0.43\, k_0 t.$$

This relationship has been observed, for example, in the decomposition of the intermediate product in the ozonisation of 2,7-dimethyloctane[136] and of ethylbenzene hydroperoxide[121], as well as of peroxides formed by the exposure of solutions of deoxyribonucleic acid to X-rays[137]. The decomposition rate constants determined from chemiluminescence data coincided with those obtained by chemical methods.

The kinetics of chemiluminescence may be different in complex reactions, since the rate of the exciting process may vary in a complicated fashion in the course of the chemical change. In the decomposition of the hydroperoxide of 1,1-diphenylethane in glacial acetic acid, for example, the emission intensity increases as a sigmoid curve, passes through a maximum, and then falls[115] (Fig. 2). An investigation comprising experiments with the addition of reactant and products while the reaction is

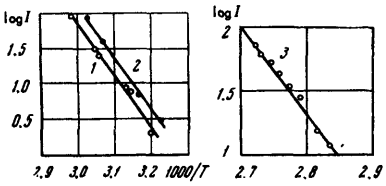



Fig. 1. Temperature dependence of the intensity of chemiluminescence in the oxidation of a series of hydrocarbons initiated by:
1) 2,7-dimethyloctane hydroperoxide; 2) tetralin hydroperoxide; 3) azoisobutyronitrile.

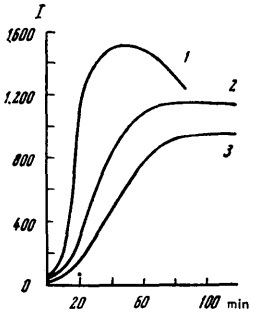


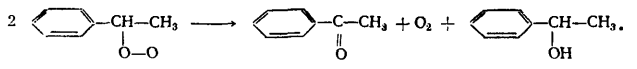

Fig. 2. Kinetic curves of chemiluminescence in the decomposition of 1,1-diphenylethane hydroperoxide in acetic acid at different temperatures and hydroperoxide concentrations: 1) 98.5° and 0.048 M; 2) 87° and 0.050 M; 3) 75.4° and 0.078 M.

progressing, dilution of the reaction mixture during the reaction, and studies of the effects of temperature and of the initial concentration of hydroperoxide has shown that the observed kinetics of chemiluminescence is governed by the formation of intermediate products. Breakdown of one of these products results in the formation of radicals, whose recombination excites the chemiluminescence[115]. Examples of the application of chemiluminescent methods to detect intermediate products in complicated reactions have been given also in papers[117,138] which are considered in other Sections of the present review.

It has been reported many times (see e.g. Ref. 139) that oxygen intensifies chemiluminescence, although it is an effective quencher of luminescence. This apparent contradiction has been eliminated by work[130] showing that oxygen exerts both stimulating and quenching effects. The stimulating action is observed at low oxygen concentrations, and is chemical in nature.

It follows from the reaction scheme (15) that, as the oxygen concentration increases, the concentration of $RO_2$ radicals also increases, as does the contribution of process (6). Hence the intensity changes, too, since the emission yield will depend on the structure of the reactant radicals and the products formed. The products of the recombination of $RO_2$ radicals are oxygen-containing compounds which luminesce in the visible or near ultraviolet region. Recombination of R radicals involves the formation of molecules which do not luminesce in the visible range. Therefore the conversion of chemical into excitation energy and the subsequent emission of light should occur far more efficiently in the former than in the latter case. This results in an intensification of the luminescence with increase in the concentration of oxygen. The stimulating effect of oxygen ceases when all the radicals have been converted into peroxy-radicals[120,130,138,140,141,159].

The disproportionation of, for example, peroxy-radicals of ethylbenzene involves the formation of 1-phenylethanol, acetophenone, and molecular oxygen[142]:



In order to identify the excited state, determinations were made of the quantum yield of the emission, the life of the excited state, and the luminescence spectra[140,143-145]. Examination of the results showed that the excited species responsible for the emission in the oxidation of ethylbenzene was acetophenone in its triplet state (one molecule of triplet acetophenone was formed in the reaction per $10^5$–$10^6$ acts of recombination). Thus the chemiluminescence represents the radiative transition of acetophenone to the ground (singlet) state; the yield of this process is 1 photon per $10^3$–$10^4$ excited molecules[140,145].

The views on the chemical mechanism of the intensification of luminescence by oxygen and on the excitation of chemiluminescence in the recombination of peroxy-radicals, formulated in Ref. 130, have subsequently been checked many times, and have been quantitatively confirmed by various methods.

## 2. Measurement of Rate of Oxidation

The marked difference in the emission yield of the recombination of $R^\cdot$ and of $RO_2^\cdot$ radicals has been used to measure the rate of induced oxidation[140,146]. In an experiment the solution was saturated with air or oxygen, and the reaction vessel closed. At this instant a gradual decrease in the concentration of dissolved oxygen in the system began. After a certain time $t_f$ a fall in emission intensity was observed, caused by the complete exhaustion of $O_2$ and replacement of $RO_2^\cdot$ by $R^\cdot$ ("oxygen fall"). With many hydrocarbons the rate of oxidation is independent of the $O_2$ concentration right down to very low values of the latter ($10^{-6}$–$10^{-5}$ M), which, incidentally, is responsible for the sharpness of the drop in emission. It may therefore be assumed that

$$w_{O_2} = \frac{d[O_2]}{dt} = \frac{[O_2]_0}{t_f}. \qquad (19)$$

and the rate of oxidation may be determined from $t_f$ and $[O_2]_0$. The reliability of this method of measuring rate of oxidation has been tested and confirmed on the oxidation of several organic substances (ethylbenzene, cumene, toluene, decalin, cyclohexane, methyl oleate, n-decane, n-heptane, and ethyl methyl ketone) initiated by the thermal decomposition of azoisobutyronitrile and dicyclohexyl peroxodicarbonate[140]. According to scheme (15), the rate of oxidation is

$$w_{O_2} = \frac{k_3}{\sqrt{k_6}}[RH]\sqrt{w_i} + \frac{1}{2}w_i. \qquad (20)$$

The higher the concentration of hydrocarbon, the higher the rate of oxidation and the shorter the time $t_f$. This is clearly evident from Fig. 3. Eqns. (19) and (20) can be used to determine the concentration of dissolved oxygen $[O_2]$ and the ratio of the elementary rate constants $k_3/\sqrt{k_6}$, provided that the rate of initiation $w_i$ is known. From the change in rate due to decomposition of the initiator and the known value of $w_i$ we can determine the decomposition rate constant of the initiator $k_0$ and its efficiency $f_{cell}$[147] with the same accuracy as by the use of other methods for measuring the rate of oxidation.

Measurement of rate of oxidation at low hydrocarbon concentrations enables us to estimate the relative efficiencies of active initiator radicals in abstracting a hydrogen atom from the hydrocarbon[147]. It is also possible to obtain some qualitative information on the reaction. In a pure inert solvent, for example, $w_i = w_{O_2} = [O_2]_0/t_f$[146,147], whence it follows that molecular oxygen is not evolved in

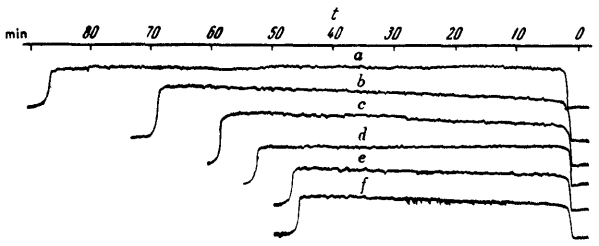



Fig. 3. "Oxygen falls" in chemiluminescence accompanying the oxidation of ethylbenzene in chlorobenzene as solvent, initiated by azoisobutyronitrile ($w_i = 1.9 \times 10^{-7}$ M $s^{-1}$), with different concentrations (M) of ethylbenzene:
*a*) 0.078; *b*) 0.234; *c*) 0.391; *d*) 0.548; *e*) 0.704; *f*) 0.781.[140,146]

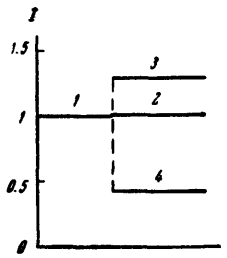



Fig. 5. Change in intensity of chemiluminescence accompanying decomposition of 1,1′-diphenylazoethane in chlorobenzene on addition of 2 vol.% of various hydrocarbons:
1) pure chlorobenzene; 2) addition of ethylbenzene; 3) diphenylmethane; 4) cyclohexene.

the recombination of active radicals of the initiator azoisobutyronitrile, whereas oxygen is always liberated in the recombination of hydrocarbon peroxy-radicals.

The kinetics of the consumption of oxygen and of the variation in emission intensity have been calculated on an M-20 electronic computer[140,148]. As can be seen from Fig. 4, the theoretical curve shows a considerable lack of symmetry: i.e. it has the same shape as the experimental curves. Comparison of theoretical and experimental curves enables the ratio $k_3/\sqrt{k_6}$ to be assessed as of the order of $10^3$ litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ $s^{-\frac{1}{2}}$ for most of the hydrocarbons investigated.

The yield and intensity of chemiluminescence differ for the recombination of peroxy-radicals of different hydrocarbons[114,145,149,150]. The effect of radical composition on emission intensity is shown in Fig. 5, which illustrates the changes in intensity accompanying the decomposition of 1,1′-diphenylazoethane $C_6H_5.CH(CH_3).N:N.CH(CH_3).C_6H_5$ in chlorobenzene on addition of various hydrocarbons[150]. Decomposition of this azo-compound in the presence of molecular oxygen yields peroxy-radicals of ethylbenzene, the luminescence arising as a result of their recombination.

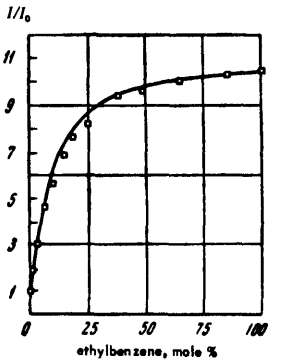



Fig. 6. Dependence of intensity of chemiluminescence on composition of mixture in the simultaneous oxidation of cumene and ethylbenzene initiated by the decomposition of azoisobutyronitrile at 60° and $w_i = 10^{-7}$ M $s^{-1}$. The points represent experimental values; the curve has been calculated.

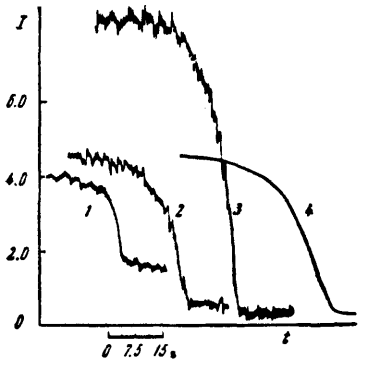



Fig. 4. Kinetic curves for the weakening of chemiluminescence, caused by replacement of peroxy-radicals by hydrocarbon radicals[140], in the oxidation, initiated by the thermal decomposition of azoisobutyronitrile (0.061 M) in benzene at 63°, of the hydrocarbons:
1) toluene; 2) ethylbenzene; 3) decalin; 4) theoretical curve.

Addition of 2% of ethylbenzene does not affect the emission intensity, since the concentration and composition of the radicals remain unchanged. Additions of other substances capable of reacting with peroxy-radicals of ethylbenzene change the intensity owing both to the appearance of a new species of radicals and new recombination reactions and to the decrease in the rate of recombination of the peroxy-radicals of ethylbenzene.

For the same reasons the intensity of luminescence in the simultaneous oxidation of two substances will depend on the composition of the mixture and the emission yields as well as on the kinetic parameters, the ratios of the rate constants for the elementary acts. Fig. 6 shows the dependence of emission intensity on the composition of a mixture of cumene and ethylbenzene undergoing oxidation. The full line represents the dependence calculated from the rate constants[151] and the measured quantum yields of chemiluminescence. The good agreement between calculated and experimental curves indicates that measurements of chemiluminescence can be used to determine the kinetic parameters of this complicated reaction[150].

### 3. Chemiluminescence in Inhibited Oxidations and the Activity of Inhibitors

The intensity of chemiluminescence in various oxidations with hydrogen peroxide and molecular oxygen has been observed to diminish on the addition of inhibitors of free-radical reactions[113,119,126,152-155]. In several cases the dependence of emission intensity on inhibitor concentration has been used to determine the concentration of the latter[122,156]. Until recently no quantitative study had been made of the relation between the activity of an inhibitor InH and its ability to diminish the intensity of luminescence. It became possible to solve this problem as a result of work establishing the mechanism of the excitation of chemiluminescence in oxidations with molecular oxygen[113,114,130]. In order to describe the process of inhibited oxidation, scheme (15) must be supplemented by the reactions[157,158]

$$\left.\begin{array}{ll} 7)\ \mathrm{InH}+\mathrm{RO}_2^{\bullet} \xrightarrow{k_7} & \mathrm{In}^{\bullet}+\text{products},\\ 8)\ \mathrm{RO}_2^{\bullet}+\mathrm{In}^{\bullet} \xrightarrow{k_8} & \\ 9)\ \mathrm{In}^{\bullet}+\mathrm{In}^{\bullet} \xrightarrow{k_9} & \end{array}\right\}\ \text{stable products.}$$

The inhibitor radical In$^{\bullet}$ which is formed is usually inactive and incapable of participating in chain propagation. Additions of an inhibitor lower the concentration of peroxy-radicals and thus retard the oxidation. Since luminescence is associated with the recombination of $RO_2^{\bullet}$ radicals, the diminution in their concentration produced by the addition of inhibitors results in a weakening of chemiluminescence. After such addition new chemiluminescent reactions do not arise, since the In$^{\bullet}$ radicals formed are relatively inactive, and the heat evolved in reactions (8) and (9) is insufficient to excite luminescence in the visible region of the spectrum. This kinetic scheme, in which the power of inhibitors to weaken emission is linked with their activity towards $RO_2^{\bullet}$ radicals, has been put forward by one of the present authors[159].

As can be seen from the scheme (15), the rate of a chain oxidation is

$$w = k_3(\mathrm{RO}_2^{\bullet})(\mathrm{RH}). \qquad (21)$$

Therefore $w/w_0 = [RO_2^{\bullet}]/[RO_2^{\bullet}]_0$, where the subscript 0 denotes the absence of inhibitor. On the other hand,

$$\frac{I}{I_0}=\frac{[\mathrm{RO}_2^{\bullet}]^2}{[\mathrm{RO}_2]_0^2},\ \text{or}\ \sqrt{\frac{I}{I_0}}=\frac{[\mathrm{RO}_2]}{[\mathrm{RO}_2]_0^2}. \qquad (22)$$

Comparison of Eqn. (21) with (22) shows that

$$\frac{w}{w_0}=\sqrt{\frac{I}{I_0}}. \qquad (23)$$

The relationship (23) has been tested and confirmed experimentally[123,160]. Its applicability shows that the weakening of chemiluminescence is caused by the diminution in the concentration of peroxy-radicals§, and that the intensity of chemiluminescence is a measure of their relative concentration. Hence it at once follows that the relative activities of inhibitors can be characterised by their concentrations at which the emission intensity decreases, e.g. is halved[161] (which corresponds to a 30% decrease in the concentration of peroxy-radicals). The reciprocal of the inhibitor concentration is then taken as a measure of the activity. In this way a series of inhibitor activities — for phenols and amines[161] — has been obtained, characterising their reactivity towards peroxy-radicals.

New chemiluminescent methods have been proposed, based on the above kinetic scheme, for determining the activity of inhibitors. The dependence of emission intensity $I$ on inhibitor concentration $[\mathrm{InH}]_0$

$$\sqrt{\frac{I}{I_0}}=1+1.1\frac{k_7}{\sqrt{k_6}}\frac{[\mathrm{InH}]_0}{\sqrt{w_i}} \qquad (24)$$

has been obtained[162] from this scheme. The kinetic parameter $k_7/\sqrt{k_6 w_i}$ is then determined from the slope of the linear plot of $\sqrt{I/I_0}$ against $[\mathrm{InH}]_0$.

The kinetic chemiluminescence curve, representing the increase in concentration of peroxy-radicals resulting from the gradual consumption of inhibitor, is S-shaped (Fig. 7), with a point of inflection at $I/I_0 = 0.55$.[162]

It has been shown[148] that in general the slope at the point of inflection on the kinetic curve of chemiluminescence $[d(I/I_0)/dt]_{max}$ should be proportional to the ratio $k_7\sqrt{w_i}/\sqrt{k_6}$ if the emission intensity varies as a result of the consumption of some substance by reaction with the radicals responsible for the luminescence. Proportionality is then maintained independently of what other elementary acts enter the reaction scheme. An actual calculation of the above scheme has enabled the proportionality coefficient to be evaluated[162]:

$$\left[\frac{d(I/I_0)}{dt}\right]_{\max}=0.22\frac{k_7}{\sqrt{k_6}}\sqrt{w_i}, \qquad (25)$$

and measurements of the maximum slope to be used to determine the parameter $k_7/\sqrt{w_i/k_6}$. By combining the relations (24) and (25) we can use chemiluminescence measurements to obtain values of the parameter $k_7/\sqrt{k_6}$, which characterises the relative activity of an inhibitor, and the rate of initiation $(w_i)_{calc}$.

Experiments on fifteen inhibitors (phenols and amines) have shown[163] satisfactory agreement with Eqn. (24). Application of Eqn. (25) revealed that the slope of the kinetic curves decreases with increase in the initial concentration of inhibitor $[\mathrm{InH}]_0$. This was explained by a decrease in activity of the inhibitor as its concentration

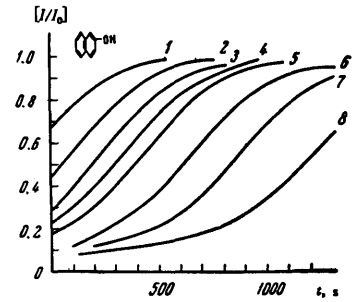



Fig. 7. Kinetic curves representing the variation in intensity of chemiluminescence accompanying the oxidation of ethylbenzene, initiated by the decomposition of azoisobutyronitrile at 60° and $w_i = 4.14 \times 10^{-7}$ M s$^{-1}$, in the presence of different initial concentrations (in $10^{-5}$ M) of 2-naphthol:
1) 0.69; 2) 1.38; 3) 2.07; 4) 2.76; 5) 3.45; 6) 5.17; 7) 6.9; 8) 9.5.

§ Many phenols are known as deactivators of excited states. Therefore the weakening of the luminescence might have been attributed *a priori* to physical quenching. The applicability of Eqn. (23) indicates that, under the experimental conditions, physical deactivation is negligible, if present at all, the chemical reaction of $RO_2^{\bullet}$ with InH being decisive.

increases. The same conclusion, on the concentration dependence of activity, was reached independently[164] from measurements of the activity of inhibitors from the rate of oxidation of styrene. The dependence of $k_7$ on $[InH]_0$ can be eliminated if data for a series of experiments with different values of $[InH]_0$ are used to extrapolate the maximum slope to $[InH]_0 \to 0$. Then simultaneous application of Eqns. (24) and (25) yields values of $k_7/\sqrt{k_6}$ and also of $(w_i)_{calc}$, the latter being practically identical with values of $w_i$ specified in the experiment[163]. This identity of the values of $w_i$ is a criterion of the correctness of the new chemiluminescent methods[163].

Experiments with a single inhibitor but in different oxidisable substances revealed a significant dependence of the ratio $k_7/\sqrt{k_6}$ on the nature of the oxidisable substance. The activity of $RO_2^\cdot$ varies comparatively little with the natue of the radical R,[151] so that values of $k_7$ should be similar for different $RO_2^\cdot$ radicals. At the same time, values of $k_6$ may differ by several orders of magnitude. If, therefore, values of $k_7/\sqrt{k_6}$ in two non-polar substances undergoing oxidation differ by a factor of more than 3–4, this is usually to be attributed to a difference in the values of $k_6$. On this reasoning it was concluded[163] that $k_6$ is considerably lower for 2,7-dimethyloctane than for ethylbenzene. This conclusion has been confirmed by direct experiments[165], in which concentrations of peroxy-radicals have been measured, by the electron spin resonance method, during the progress of liquid-phase oxidations.

Curves of the initial emission intensity and of the time of reaching the point of inflection, plotted as functions of the initial concentration of inhibitor from a series of kinetic chemiluminescence curves (Fig. 7), can be employed as calibration curves to determine inhibitor contents[122]. The sensitivity of the method depends on the value of $w_i$, and also on the activity of the inhibitor, reaching around $10^{-7}$ M. Since chemiluminescence is observed in the oxidation of various classes of substances — aldehydes, ketones, acids, alcohols, hydrocarbons, etc. — the proposed method can be used to determine inhibitor contents in practically any oxidisable substance[122].

The use of calibration curves enables us to determine with which radicals ($R^\cdot$ or $RO_2^\cdot$) a given inhibitor reacts. Experiments are carried out in which the inhibitor is subjected to the action of initiator radicals $R^\cdot$ in the absence of $O_2$ for a definite time. After this the kinetics of chemiluminescence, now in the presence of $O_2$, is recorded, and the change in concentration of inhibitor during reaction with $R^\cdot$ radicals is determined from the calibration curve. The experiments have shown, for example, that ionol does not react with $R^\cdot$ radicals[148].

### 4. Chemiluminescence in the Oxidation and Decomposition of Hydroperoxides Catalysed by Salts of Metals of Variable Valency

Chemiluminescence has been observed[115,121,166] in the oxidation of toluene, cumene, ethylbenzene, and diphenylmethane catalysed by the acetates or stearates of cobalt, manganese, and copper. The quantitative relationship between the kinetics of chemiluminescence and the kinetics of the reaction has been investigated in the oxidation of ethylbenzene in glacial acetic acid with cobalt acetate as catalyst[121,166]. Recently the kinetics of this reaction has been studied quantitatively by the usual methods[167,168]. Chemiluminescence was measured with the same specimen of catalyst under the same conditions. As a result, the kinetics of chemiluminescence could be directly compared with the reaction kinetics. The experiments showed that, in the course of the process, the emission intensity increases to a constant value independent of the catalyst concentration. Increasing the latter merely shortens the time needed to reach the steady state. Initial additions of a hydroperoxide eliminate the stage of increasing emission. The initial intensity of luminescence is proportional to the concentration of the additive. Soon after the start of the experiment the intensity reaches the same level as in the absence of an initial addition. Hence it follows that the observed kinetics of chemiluminescence is associated with the accumulation of hydroperoxide, and that the steady emission intensity corresponds to a steady state of oxidation, in which the rate of consumption of hydroperoxide is constant. The intensity of luminescence in the steady state is proportional to the rate of oxidation. As a result, intensity measurements can be used to obtain the fundamental kinetic parameters of the reaction — the dependence of rate of oxidation on the concentrations of hydrocarbon and of catalyst, and the activation energy of the reaction.

The observed regularities in chemiluminescence are explained quantitatively by the scheme representing the kinetics of the catalysed oxidation of ethylbenzene[167]. This scheme differs from that of oxidation initiated by thermal decomposition solely in the initiation reaction. In the present case formation of $R^\cdot$ or $RO_2^\cdot$ radicals at a rate $w_i$ occurs on reaction of the hydroperoxide with the catalyst:

$$ROOH + nCo(AcO)_2 \xrightarrow{k_i} \text{free radicals}.$$

When the rates of formation and consumption of hydroperoxide become equal, the maximum reaction velocity $w_{st}$ is reached, equal to the rate of initiation

$$w_{st} = k_i^2[RH]^2/k_6 = w_i.$$

The emission intensity is given by the equation

$$I_{st} = \eta_{ch}k_6[RO_2^\cdot]^2 = \eta_{ch}w_i = \eta_{ch}k_i^2[RH]^2/k_6,$$

i.e. $I_{st} \propto w_{st}$, in conformity with experiment[121].

In order to describe quantitatively the kinetics of chemiluminescence in the initial, non-stationary stage of the oxidation process, an investigation was made of the catalytic decomposition of ethylbenzene hydroperoxide by a chemiluminescent method and by analysis of the consumption of hydroperoxide[169]. Experiments were made with initial additions of hydroperoxide to a solution of the hydrocarbon in acetic acid. Fig. 8 shows that the emission intensity and the hydroperoxide concentration diminish exponentially during the course of the decomposition reactions. The straight lines have practically the same slope. This permits measurements of the kinetics of chemiluminescence to be used to determine $k_{eff}$, the effective decomposition rate constants for the hydroperoxide. Since the emission intensity is proportional to the hydroperoxide concentration, comparison of the initial intensity accompanying a definite initial addition of hydroperoxide with the steady-state intensity will yield the steady-state hydroperoxide concentration $[ROOH]_{st}$¶. It follows from the kinetic scheme that the rate of oxidation is

$$w_{O_2} = -\frac{d[O_2]}{dt} = k_{eff}[ROOH]_{st}.$$

¶ This method of determining the hydroperoxide concentration is of intrinsic interest, and can be employed to estimate traces of peroxy-compounds. Its limiting sensitivity of $5-10 \times 10^{-7}$ M considerably exceeds that of chemical methods of analysis[169].

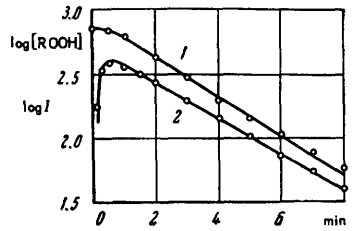



Fig. 8. Semilogarithmic anamorphoses of kinetic curves at 47° for 20% ethylbenzene (RH) in acetic acid containing 0.037 M ROOH and 0.032 M $Co(OAc)_2$: 1) decomposition of ethylbenzene hydroperoxide; 2) chemiluminescence.

To check the accuracy of chemiluminescent methods of determining $k_{eff}$ and $[ROOH]_{st}$, a comparison was made between values of $w_{O_2}$ and $k_{eff}[ROOH]_{st}$, which showed that the difference did not exceed 10–15%.[169]

Chemiluminescent methods have also enabled the mechanism of the catalysed decomposition of the hydroperoxide to be investigated[138]. The initial stage of the decomposition was observed to be accompanied by an increase in the emission intensity (Fig. 8), which was shown to be associated with the formation of an intermediate product, a cobalt(III) salt. This salt reacts with the hydroperoxide according to Eqn. (27):

$$\begin{aligned} &ROOH + Co(OAc)_2 \rightarrow RO_2^{\bullet} + Co(OH)(OAc)_2, \\ &Co(OH)(OAc)_2 + AcOH \rightarrow Co(OAc)_3 + H_2O, \end{aligned} \qquad (26)$$

$$ROOH + Co(OAc)_3 \rightarrow RO_2^{\bullet} + Co(OAc)_2 + AcOH, \qquad (27)$$

which results in an increase in the rate of decomposition and a corresponding intensification of the luminescence. From kinetic measurements on the growth and subsequent fall in the emission, the latter due to consumption of the hydroperoxide, the equilibrium concentration of the intermediate product could be determined kinetically. Calculations gave values of the order of 1% based on the concentration of the bivalent salt. Similar values for the concentration of the tervalent form of the catalyst were obtained in independent spectrophotometric experiments[170].

Chemiluminescent methods show that two different radicals are actually formed in the catalytic decomposition of the hydroperoxide[138]. When decomposition is carried out in the presence of oxygen, RO• radicals are converted into peroxy-radicals according to the scheme

$$\begin{aligned} &RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}, \\ &R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}. \end{aligned}$$

Half the peroxy-radicals are then formed from RO•, since in the steady state the reactions (26) and (27) occur at the same rate. If, when the steady state has been established, oxygen is removed from the system (by bubbling a pure inert gas through), the emission intensity drops sharply to a definite level lower than half the previous value. This result can be explained by the fact that, in the absence of oxygen, conversion of RO• into $RO_2^{\bullet}$ radicals is impossible, and that some of the $RO_2^{\bullet}$ radicals are used up by reaction with the hydrocarbon and hydrocarbon radicals. From the rate of decomposition of the hydroperoxide and the emission intensity before and after removal of oxygen, the rate of recombination of $RO_2^{\bullet}$ in the absence of oxygen can be determined. These results were used, with reactions (4) and (5) of scheme (15) taken into account, to calculate values of the parameter $k_3/\sqrt{k_6}$, which were close to those obtained by the usual kinetic methods[138].

## 5. Chemiluminescence in Low-Temperature Gas-Phase Oxidations

Little study has yet been made of chemiluminescence in the gas-phase oxidation of organic substances. Until recently, in effect, only visual observations had been made, in which the temperature range of the luminescence was determined. The emission intensity was found to increase with rise in temperature, and the range of chemiluminescence was displaced to lower temperatures with increase in concentration of the oxidisable substance[171,172]. Just as with liquid-phase reactions, the application of highly sensitive photometric instruments has made it possible to detect chemiluminescence in various reactions. In the case of reactions in which it had been known earlier, the limits to its observation could be greatly shifted towards lower temperatures.

A more detailed investigation has been made of the chemiluminescence accompanying the oxidation of acetaldehyde[116,117,173], the kinetics of which has been studied thoroughly[174,175]. Investigations were made at 100–200° and initial pressures of the reaction mixture varying from a few tenths to several hundred millimetres of mercury. Fig. 9 shows kinetic curves for the luminescence and the variation in pressure obtained in one of the experiments, as well as kinetic curves for the consumption of the reactants and the accumulation of the products of the reaction. The emission curve passes through two maxima, the first of which is sharp and the second very flat. The former

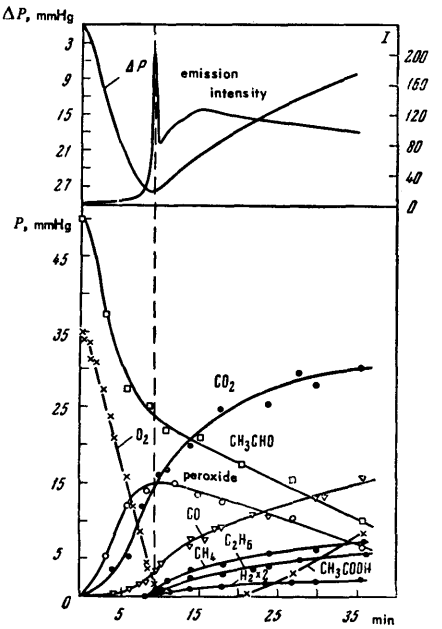



Fig. 9. Kinetic curves for intensity of chemiluminescence, pressure, consumption of reactants, and accumulation of products in the oxidation of acetaldehyde at 182°.

corresponds to a minimum on the pressure curve. This relationship is maintained however the experimental conditions are varied (by changing the temperature, pressure, and composition of the mixture, or adding a homogeneous catalyst). Oxygen quenches chemiluminescence, and the emission becomes stronger when its concentration is diminished[116]. At the instant at which the first maximum is reached, the process of oxidation with molecular oxygen terminates. This is evident both from the oxygen consumption curve and from the appearance of products ($CH_4$, $C_2H_6$, $H_2$) which could not be formed in the presence of oxygen. Thus the first luminescence maximum represents a change in the nature of the process, a transition from oxidation by molecular oxygen to oxidation by peroxy--compounds[174]. A similar sharp luminescence maximum was first observed in work on the oxidation of pentane[176], the author concluding from indirect arguments that this maximum was associated with the complete exhaustion of oxygen in the system.

Since the rate of consumption of oxygen is constant (Fig. 8), the time required to reach the first luminescence maximum can be conveniently used to determine the reaction velocity and its dependence on various parameters. It is obvious that

$$w_{O_2} = \frac{[O_2]_0}{t_{max}}.$$

With the rate of oxidation known, it is possible to obtain the principal kinetic characteristics — the activation energy, and the order with respect to the aldehyde, oxygen, and the total pressure — of the first stage of the reaction[117]. Kinetic parameters determined by the chemiluminescent method and from the fall in pressure are practically identical and agree with those determined by other methods[174,175].

It is possible to create artificially conditions under which the rate is constant, or the reaction will follow a known kinetic law. This can be achieved, for example, by carrying out a low-temperature initiated oxidation. In this case $t_{max}$ can be used as a kinetic characteristic of different reactions, since an oxygen maximum is observed in the oxidation of many substances[117]. Determinations of the dependence of $t_{max}$ on $[O_2]_0$ have enabled kinetic parameters to be evaluated[117] in the radical reaction of the oxidative decomposition of di-t-butyl peroxide and the chain oxidation of acetaldehyde:

for the reactions

$$CH_3^{\cdot} + O_2 \rightarrow CH_3OO^{\cdot} \ (k_2)$$

and

$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6 \ (k_4),$$

$k_2/\sqrt{k_4}$ = 123 litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$ at 105°;

for the reactions

$$CH_3CO^{\cdot} + O_2 \rightarrow CH_3CO_3^{\cdot} \ (k_2')$$

and

$$CH_3CO^{\cdot} + CH_3CO^{\cdot} \rightarrow (CH_3CO)_2 \ (k_4'),$$

$k_2'/\sqrt{k_4'}$ = 510 litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$ at 87°.

Determination of the chemiluminescence spectra has shown[173] that the luminescent species in the oxidation of acetaldehyde is the excited formaldehyde molecule. The presence of formaldehyde among the reaction products has been detected also by chemical analysis. From the dependence of the intensity of chemiluminescence on the concentration of oxygen, which obeys the Stern–Volmer equation, the lower limit to the life of excited formaldehyde has been found to be $\tau \geqslant 1.3$ μs.[177]

The problem of routes to the formation of excited formaldehyde has been discussed in the literature[178-182], mainly in connection with investigations on cold flames. The general view has now apparently become established that excitation occurs in reactions involving alkoxy-radicals[179-182]: e.g. in the case of methoxy-radicals

$$CH_3O^{\cdot} + CH_3O^{\cdot} \rightarrow CH_3OH + CH_2O + 76 \text{ kcal (Ref. 178)}, \quad (28)$$

$$CH_3O^{\cdot} + OH^{\cdot} \rightarrow H_2O + CH_2O + 98 \text{ kcal (Ref. 182)}, \quad (29)$$

$$CH_3O^{\cdot} + CH_3^{\cdot} \rightarrow CH_4 + CH_2O + 82 \text{ kcal}. \quad (30)$$

These heats of reaction are sufficient to excite formaldehyde (77 kcal)[183].

The formation of excited formaldehyde molecules is not a distinguishing feature of cold-flame oxidation, as has generally been assumed, for it occurs at considerably lower temperatures in slow oxidation processes. It has therefore proved possible to study the mechanism of the formation of excited formaldehyde molecules in model systems containing radicals of known composition[184]. The following sources of free radicals were used — (*a*) $CH_3^{\cdot}$ radicals from di-t-butyl peroxide $(CH_3)_3C.O.O.C(CH_3)_3$; (*b*) $CH_3O^{\cdot}$ radicals from[185] methyl nitrate $CH_3ONO_2$, methyl nitrite $CH_3ONO$, and dimethyl peroxide $CH_3OOCH_3$; and (*c*) $CH_3O^{\cdot}$ and $HO^{\cdot}$ from[185] methyl hydroperoxide $CH_3OOH$.

Luminescence was absent from the decomposition of methyl nitrate, methyl nitrite, dimethyl peroxide, and also a mixture of dimethyl and di-t-butyl peroxides, which enabled reactions (28) and (30) to be eliminated. The luminescence of formaldehyde was observed on decomposition of the hydroperoxide. The emission was sharply increased by additions of dimethyl peroxide, which itself decomposes without luminescence. The observed intensification of the emission is readily explained by an increase in the concentration of $CH_3O^{\cdot}$ radicals. Hence it follows that the excited formaldehyde is formed in reaction (29). An advantage of this process compared with (28) and (30) is its large heat of reaction.

Since there is no difficulty in introducing $CH_3O^{\cdot}$ radicals into a chemical system (by adding dimethyl peroxide, hyponitrites, etc.), the luminescence of formaldehyde may provide a convenient indicator for the detection of hydroxy--radicals. It is obvious that, conversely, hydroxyl may be an indicator of methoxyl (perhaps of alkoxyl) radicals[184].

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The results discussed in the present paper demonstrate the great possibilities and prospects for the application of chemiluminescent methods in the quantitative investigation of the kinetics and mechanism of various chemical processes. Recently the range of application of chemiluminescent methods of investigation has been greatly extended by the discovery of new chemiluminescent reactions. Chemiluminescent methods have been suggested for controlling technological chemical processes[186]. This in considerable measure stimulates interest both in the phenomenon itself and in the use of chemiluminescence to study the kinetics and the mechanism of chemical reactions.

## NOTE ADDED IN PROOF

New results have recently been published on the luminescence of Luminol and lucigenin[187-189].


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# THE PARTITION CHROMATOGRAPHY OF LIPIDS

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## I. INTRODUCTION

Lipids of natural origin are usually mixtures of aliphatic compounds of different *classes*, characterised by a definite number of polar functional groups, COOH, OH, $NH_2$, etc. The structural differences between lipids within a given class are determined entirely by two parameters — the number of methylene groups and the number and position of double bonds. A set of lipids in which one of the parameters is constant while the other changes monotonically forms a *homologous series*. Each class may contain several such series. Their detailed analysis is of considerable theoretical and practical importance.

A mixture of lipids is separated into individual classes by adsorption chromatography; separation of the classes into homologous series and separation within the series generally does not take place in this case, since the differences in polarity among lipids within a class are small compared with the changes in polarity due to the functional groups. Even these relatively slight differences, however, are quite sufficient for the separation of lipids within classes and homologous series by the method of *partition chromatography*†.

Partition chromatography, discovered in 1941 by Martin and Synge [1], was applied in the field of lipids only in 1948, in work by Ramsey and Patterson [2] and Boldingh [3]. In the last 17 years, several hundred scientific papers and a large number of reviews [4-19] have been devoted to the partition chromatography of lipids.

The subject of the present review is the use of various types of partition chromatography in the analysis of natural

† This term, which is now firmly established, cannot be regarded as appropriate, since the mass is partitioned between solid, liquid, or gaseous phases in *any* chromatographic separation. Here and subsequently we shall have in mind *a system of two immiscible liquid phases*, one mobile and one stationary.

lipids. The theoretical principles of the method and the characteristic features of the apparatus used are not examined in detail: this information can be found in textbooks [9,17]. Little reference is made to studies on the chromatography of aliphatic compounds with short chains (up to $C_8$), steroids, and other isoprene derivatives, or to the extremely large number of papers in which established chromatographic methods have been applied without any fundamental modification. The present review covers the most important work on the partition chromatography of lipids published before 1st March 1964.

## II. CHROMATOGRAPHY WITH A POLAR STATIONARY PHASE

Following the historical order, we shall examine first of all systems in which the stationary phase is more polar than the solvent passing through, although at the present time these forms of chromatography are used in the field of lipids much less frequently than are reversed-phase systems (see Section III).

### 1. Column Chromatography

Column chromatography has been used for the purification, separation, and identification of aliphatic acids and other lipids.

Columns of cellulose powder have been used to purify phospholipids from peptides and amino-acids. The lipids were eluted with a mixture of chloroform, butanol, and water [20], chloroform, ethanol, and water (80 : 20 : 2.5) [21], or chloroform and methanol [22]. In the chloroform–methanol system, the phospholipids left the column in the sequence — phosphatidic acids, Φ-choline (Φ = phosphatidyl), sphyngomyelin, Φ-aminoethanol, Φ-serine, and Φ-inositol [23]. Phospholipids have also been separated by means of acetone at -18°. [24] A mixture of methanol, hexane, water, and acetic acid (30 : 50 : 5 : 1) has been used for the fractionation of the hydroxamate derivatives of the "even" $C_{14-22}$ saturated and $C_{18}$ unsaturated acids. The hydroxamates were detected by their reaction with $Fe^{3+}$ and identified from their melting points. The retention time increased with increase in polarity; derivatives with the same polarity were not separated. An advantage of the hydroxamates over the original acids is their greater solubility in the stationary phase [25].

In 1948, Ramsey and Patterson [2] proposed the use of silica gel as carrier for the partition chromatography of aliphatic acids. This method was standardised with $^{14}C$ acids [26,27] and has been used repeatedly for the separation of lipids [28–33]. For partition chromatography the silica gel was suspended in the lower phase of the system [2,29,30,33], and the column was filled under pressure [29–31,33]. The specimen (3.3–3.8 mg of lipids per g of carrier) [30,33,34] was dissolved in the upper phase and introduced into the column. The solvent (upper phase) was passed at a rate of 0.6–1.2 ml $min^{-1}$. [29,30] The acids were separated in the systems: furfuryl alcohol–2-aminopyridine (1 : 1)/hexane [2], 0.25 *N* $NH_4OH$ in methanol/isooctane [29], 0.2 *N* $NH_4OH$ in a mixture of 2-methoxyethanol and water (9 : 1)/hexane [30], and 0.3 *N* NaOH in methanol/cyclohexane [34]; thus the aliphatic acids moved along the column as the salts of organic or inorganic cations. Hydroxy-acids have been separated by means of the systems: 0.1 *N* $NH_4OH$ in 95% methanol/petroleum ether [35] or methanol–hexane–acetone (2 : 10 : 1); [36] and dicarboxylic acids formed by the oxidative splitting of lipids have been separated using the systems: 0.2 *N* $NH_4OH$ in a mixture of 2-methoxyethanol and water (9 : 1)/mixture of hexane and dibutyl ether (1 : 1), [30] 1 M Na citrate (pH 5.4)/chloroform–butanol [37] or methanol–water–hexane–acetone (7.7 : 1.9 : 77 : 34). [33] The products obtained by the oxidation of triglycerides with a permanganate–periodate mixture were separated in the 90% ethanol/petroleum ether system [38]. Neutral derivatives of the acids have been fractionated in the systems: nitromethane/petroleum ether [31,39] or 2-phenoxyethanol/heptane [32]. The time required for the analysis on columns of silicic acid was 20 h. [30] For the quantitative determination, the individual fractions of the eluate were titrated with 0.05 *N* NaOH using phenolphthalein [2,33] or Phenol Red [30] as indicator. The silica gel can be impregnated with indicator before the separation; in this case the acids migrate in the form of coloured bands [29,30]. Derivatives of aliphatic acids form coloured zones on the column in the absence of indicators [31,32,39]. The eluate contained 95–105% of the original lipids [2,29,30,33].

The lipids leave the column in order of increasing polarity. The even saturated $C_{10-22}$ mono- and di-basic acids are readily separated [2,29,30,34,37]; a difference of one $CH_2$ group is sufficient for separation of the $C_{6-10}$ dicarboxylic acids [33]. Ricinoleic and dihydroxy stearic acids are separated from one another and from other acids [35,36]. The products of the oxidation of glycerides have been separated into fractions SSS + SSA and SAA + AAA, where S and A are the acyl groups of saturated acids and azelaic acid [38]. In the series of *p*-phenylazophenacyl esters of $C_{2-18}$ saturated acids [32] and the 2,4-dinitrophenylhydrazones of these esters [31], homologues differing by one $CH_2$ group were separated completely. The homologous series formed by the 2,4-dinitrophenylhydrazones of the $C_{2-18}$ aliphatic aldehydes was fractionated by Ramsey's method using columns [39]. In agreement with Martin's fundamental equation [1] for partition chromatography, the logarithm of the retention volume $V_R$ for these compounds in the column was found to depend linearly on chain length. This relationship was used for the identification of lipids [28,29,40].

The new method of *crystallisation chromatography* in a column has been used for the separation of the triglycerides of saturated acids. A brass column was filled with steel wool and sand. The temperature in the lower part of the column was 20 deg lower than that in the upper part; the central portion was kept at a constant temperature. The mixture of glycerides was introduced into the upper part, and the column was filled with acetone; hexane or carbon tetrachloride was then supplied at the rate of 1–2.8 ml $min^{-1}$. The high-melting components were retained in the column in the form of crystals of the stable $\beta'$ form. The MyrMyrMyr glyceride left the column first, followed by the PalPalPal and StStSt glycerides‡. The eutectic mixture of PalStPal and StPalPal glycerides was not separated [41].

### 2. Paper Chromatography

In early work, *aliphatic acids* of decreasing polarity were eluted from the point of application with aqueous methanol or acetone; by selection of a suitable solvent, the mixture of acids was partly separated into two or even three

‡ Myr, Pal, and St represent the myristoyl, palmitoyl, and stearoyl radicals.

components[42-50]. The triglycerides[44] and polymerised lipids[44,45,47] remained at the starting point. The salts of aliphatic acids were separated from the other lipids by means of water[42]. Petroleum ether, ether, and dichloro--ethylene were used for the separation of mixtures of di-, tetra-, and hexa-bromostearic acids respectively[51]. Di-, tetra-, and hexa-hydroxystearic acids, obtained by the permanganate oxidation of unsaturated $C_{18}$ acids, were separated in the butanol–ethanol–water–conc. $NH_4OH$ (75 : 15 : 8 : 2) system[52]. Aliphatic acids containing conjugated bonds were treated with maleic anhydride vapour before separation; the products of the diene synthesis remained at the start, and the unsubstituted acids moved in the solvent front with 75–99% methanol[45,46]. Mono- and di-basic $C_{2-12}$ acids (products of the oxidation of lipids) can be separated in 1 *N* $NH_4OH$ in 78% ethanol[53]. This separation is more frequently carried out by chromatography of the hydroxamates in water-saturated butanol or phenol; the hydroxamates are detected with $Fe^{3+}$.[54-58].

The lipids from skin, blood serum, and spinal fluid, and also triglycerides from vegetable oils, have been separated into several fractions in 99% methanol[59,60], a mixture of methanol with acetone[61], or a mixture of diisobutyl ketone, acetic acid, and water (8 : 5 : 1).[62] Phospholipids[7,11,17] were separated by means of a mixture of chloroform, methanol, and water (32 : 8 : 1),[63] a mixture of acetone with methanol followed by water-saturated phenol[64], aqueous ethanol[65], a mixture of lutidine with methanol (3 : 2),[66] and (with the use of aminoethylcellulose anion-exchange paper) a mixture of diisobutyl ketone, acetic acid, and water (8 : 5 : 1).[67] The efficiency of separation on untreated paper is usually low. A mixture of Φ-choline and sphyngomyelin has been separated from a mixture of Φ-aminoethanol and Φ-serine[63]. The compounds Φ-choline, Φ-serine, and Φ-aminoethanol have been separated by successive treatment with two solvent systems[64]. Saturated and unsaturated Φ-choline and lyso-Φ-choline have been separated in a one-dimensional system[65]. Acetylation of the $NH_2$ groups of Φ-aminoethanol leads to its complete separation from Φ-choline and sphyngomyelin[66]. A more effective separation was observed on anion-exchange paper; the $R_f$ values at 4° were — Φ-inositol 0.29, sulpholipid 0.30, Φ-glycerol 0.42, digalactolipid 0.49, Φ-aminoethanol 0.58, Φ-choline 0.61, galactolipid 0.68, and triglycerides 0.98.[67]

Aliphatic acids and other lipids are sometimes separated with a non-aqueous polar phase. The monobasic $C_{4-14}$ unsaturated acids (10–100 mg) have been separated on paper impregnated with potash alum, a mixture of carbon tetrachloride, methanol, and conc. $NH_4OH$ (81 : 18 : 1) being used[68]. The same acids, in the form of their 2,4-dinitrobenzyl esters, were separated with dimethylformamide in a mixture of cyclohexane and hydrocarbons of b.p. 190–220°.[69] Glycerol and the mono- and di-glycerides of stearic acid have been separated in the system n-butanol–acetic acid–water (4 : 1 : 5)/formaldehyde[70]. The $R_f$ value was always proportional to the chain length.

Phospholipids have been separated on paper with formaldehyde, the solvent being a mixture of butanol, acetic acid, and water (4 : 1 : 5), or by a two-dimensional system with the same mixture and a neutral solvent, tetrahydrofuran–diisobutyl ketone–water (45 : 5 : 6).[71-73] In the acid solvent the lipids were arranged in the order (from the front) triglycerides, Φ-aminoethanol + Φ-choline, lyso-Φ-choline, Φ-serine, Φ-inositol, lyso-Φ-inositol, and glycolipid[71]; in the neutral system, sphyngomyelin, Φ-choline, Φ-aminoethanol, polyglycero phosphatide and cerebroside, and also lyso-Φ-choline and lyso-Φ-aminoethanol, were separated[72,73].

Lipids are detected by the usual reactions (see Section III4E); thus phospholipids give colour reactions with molybdophosphoric acid, stannous chloride, ninhydrin, Schiff's reagent, permanganate, iodine, or Nile Blue[64,71]. For neutron-activation analysis, the dry chromatograms were irradiated in an aluminium container with slow neutrons ($5 \times 10^{11}$ neutrons $cm^{-2}$ $s^{-1}$) for 15 h. The strip was kept for 1 week until the short-lived isotopes had decayed completely, after which the strip was exposed with X-ray film, or the radioactivity of the zones was measured with a Geiger counter. The minimum detectable quantity of lipids ($z$) amounted to 0.05 μg P $cm^{-2}$.[74,75]

## III. REVERSED-PHASE CHROMATOGRAPHY

### 1. General Features of Reversed-Phase Chromatography

We have so far examined the chromatography of lipids in ordinary partition systems where the stationary phase is the more polar. For effective separation by partition chromatography, however, the stationary phase should be a substance in which the components to be analysed have a higher solubility; during the chromatographic process these compounds are slowly eluted by a larger volume of the mobile phase, in which they are less soluble. Since lipids containing > 10 C atoms are sparingly soluble in water but have a high solubility in non-polar substances, it is better to carry out the separation of lipids with systems in which the stationary phase is less polar than the mobile phase, so that the lipids are distributed on the chromatogram in the opposite order to that given above (see Section II), so-called reversed-phase systems. This term reflects the historical development of chromatography, since systems with the "normal" relationship of polarities for the individual phases were developed before reversed--phase chromatography (see Section I), which was first used by Boldingh in 1948 to separate the methyl esters of aliphatic acids[3], and was later developed by Howard and Martin[76], Kaufmann[7], Inoue[56], Schlenk[14], Gunstone[77], Buchanan[78], and others.

The solubility of lipids in non-polar phases is determined by the interaction between the aliphatic chains of the lipids and the solvent resulting from van der Waals forces, which increase with increasing chain length and decrease under the influence of double bonds. The chain is shortened to the minimum extent by *trans* double bonds, whose influence on the van der Waals forces is not so marked as that of *cis* bonds, which reduce considerably the effective length of the molecule; this makes it possible to separate geometric isomers (see Section III4D). The appearance of a double bond in the chain leads to an appreciable increase in the solubility of lipids in the polar phase, as a result of the occurrence of dipole interactions.

The main rule in reversed-phase chromatography is that within a given class the appearance of a double bond in the aliphatic chain of a lipid (at a sufficient distance from the ends of the chain) and shortening of the chain by two $CH_2$ groups usually increase the chromatographic mobility to equal extents. This relationship makes it possible to predict the relative mobility of lipids from their composition, on the basis of the polarity constant $K = 100 - m + 2e$, where $m$ is the number of carbon atoms and $e$ the number of double bonds: lipids with equal values of $K$ are not

separated from one another in reversed-phase systems. Deviations from this rule are rarely observed (see Sections III3 and III4F).

It may be assumed that lipids of equal polarity have equal values for the distribution coefficient $\alpha$. For the experimental determination of $\alpha$ for aliphatic acids in the aqueous acetone/paraffin oil system, 2 mg of the acid was dissolved in 0.5 ml of the non-polar phase, the solution mixed with 0.5 g of carrier (kieselguhr), and 5 ml of aqueous acetone added. The system was brought to equilibrium at 35° and centrifuged, and 2 ml specimens of the upper phase were titrated with $A$ ml of 0.001 $N$ potassium hydroxide in methanol. The residue was treated with 5 ml of 95% acetone, which eluted completely the acid from the non-polar phase, and 2 ml specimens were titrated with $P$ ml of alkali. The value of $\alpha$ (the ratio of the concentrations of acid in mobile and stationary phases) was calculated from the formula $\alpha = AV/(6P - A)$, where $V$ is the volume of the non-polar phase. The percentage accuracy $T$ of the determination, found from the equation $T = 100NE(2A + 3P)/W$, where $N$ is the normality of the alkali, $W$ the weight of acid, and $E$ the equivalent of the acid, usually amounted to 100 ± 5%. The values of $\log_{10} 100\alpha$ for different aliphatic acids, plotted against the concentration of acetone in the solvent, gave a family of parallel straight lines; these straight lines coincided for acids of equal polarity. The optimum conditions for separation were achieved at a solvent concentration at which $\alpha$ for the given acid was 0.16 and its value for the next higher homologue was 0.08. [79]

The following symbols were introduced for the mathematical description of the reversed-phase system for the separation of palmitic and stearic acids: $\alpha'$ is the distribution coefficient of the acids under the conditions of the chromatographic separation; $p$ the number of theoretical plates in the column; $a$ the number of the eluate fraction, where each fraction has a volume equal to the volume of the mobile phase in a theoretical plate; $E_a$ the fraction of dissolved substance present in the eluate $a$; $V_m$ the volume of mobile phase in the column; $v$ the volume of each eluate in the experiment; $f$ the number of the experimental eluate fraction containing the greatest quantity of dissolved substance, counted from the moment when the solvent front leaves the column; $E'_{max}$ the fraction of dissolved substance in eluate $f$; $c = V_m/v$ is the volume of mobile phase in the column, expressed as the number of eluate fractions in the experiment; and $A_\epsilon\{x\}$ is the area of the normal error curve for the argument $\{x\}$.

A column containing $p$ plates was considered. On the assumption that each plate behaves like a separating funnel in countercurrent distribution, the quantity of dissolved substance $T_{n,r}$ with distribution coefficient $\alpha$ in the $r$th plate after $n$ transfers was determined from the formula for countercurrent distribution:

$$T_{n,r} = \frac{n!}{r!\,(n-r)!} \times \left(\frac{1}{\alpha+1}\right)^n \times \alpha^r. \qquad (1)$$

After $p$ transfers the solvent front reaches the last $p$th plate, after which a known quantity of dissolved substance $E_{a+1}$ leaves the column with the eluate:

$$E_{a+1} = \frac{(p+a)!}{p!\,a!} \times \frac{(\alpha')^{p+1}}{(\alpha'+1)^{p+a+1}} = \frac{p+a}{a(\alpha'+1)} \times E_a. \qquad (2)$$

The fraction of dissolved substance in the eluate reaches a maximum when $\alpha' = p/a$. The ratio $a/p$ is equivalent to the total volume of eluate necessary for the attainment of the maximum, expressed in volumes of the mobile phase of the column:

$$1/\alpha' = a/p = fv/V_m. \qquad (3)$$

Eqn. (3) and data on the position and height of each peak on the experimental elution curve obtained with 67% acetone as solvent were used to calculate the actual distribution coefficient $\alpha'$ for palmitic (0.50) and stearic (0.22) acids. Division of $\alpha'$ by the ratio of the liquid phases in the column (2.5) gave the true distribution coefficients $\alpha$ as 0.20 and 0.09 respectively in good agreement with the experimental values of 0.16 and 0.08.

From Eqns. (2) and (3) we can obtain the equation

$$p = 2\pi(1+\alpha') \times \left(\frac{E'_{max} \cdot V_m}{\alpha' \cdot v}\right)^2 = 2\pi f\,(f+c)\,(E'_{max})^2, \qquad (4)$$

which makes it possible to calculate the number of plates $p$ for each acid from the position and height of the eluate maximum on the elution curve. For palmitic and stearic acids, the values of $p$ were 70 and 114 respectively. The calculated values of $\alpha'$ and $p$ were substituted in Eqn. (2), and used to construct the theoretical elution curve; this showed satisfactory agreement with the curve obtained experimentally.

The percentage contamination of each peak by the substance corresponding to the neighbouring peak $\eta$ was determined from the equation to the normal error curve

$$\eta = 100\left(0.5 - A_\epsilon\left\{\frac{\sqrt{p}(\sqrt{B}-\sqrt{A})}{\sqrt{AB}}\right\}\right),$$

where $A = 1 + 1/\alpha'_A$ and $B = 1 + 1/\alpha'_B$. Thus to obtain fractions of the required purity ($\eta \geqslant 0.2\%$) in the separation of an acid having $\alpha' = 0.50$ from another acid, in a reversed-phase system with an efficiency $p = 100$, the value of $\alpha'$ for the latter acid should not exceed 0.23. It can be seen that the system used by the authors cited [79] ensures almost complete separation of palmitic ($\alpha' = 0.50$) and stearic ($\alpha' = 0.22$) acids.

Mathematical treatment of a reversed-phase chromatographic system makes it possible to select the optimum conditions of solvent composition and column efficiency for the separation of a lipid mixture.

## 2. Column Chromatography

A. Preparation of columns. In 1950, Howard and Martin [76] proposed the use of hydrophobic Celite treated with dimethyldichlorosilane vapour as stationary-phase carrier. The Celite was mixed with neutralised (with alumina) paraffin oil [77] (1:0.8 by weight [14,80], 1:1, [76,81], or 1:1.4 [77]), suspended in the mobile phase, and transferred to the column. The paraffin oil can be replaced by silicone oil (b.p. 195–230° at 0.25 mmHg) [14,81] or acetylated castor oil [77], isooctane [82], heptane [83,84], or cyclohexane [85].

Rubber powder swollen in benzene [86], petroleum ether [35,87,88], or acetone [89] has been used simultaneously as carrier and non-polar phase. Soya-bean oil polymerised with $S_2Cl_2$ ("factice") has properties similar to those of rubber [90]; separation using factice is no less effective than that using Celite and paraffin oil [84]. Polyethylene powder swollen in acetone [91,92] or polyethylene on Celite [93] can be used for a separation not merely 3–8 times in succession, as in the case of the phases given above, but for an unlimited period. Use has also been made of cellulose impregnated with paraffin oil [94] and of nylon fibres, on

which 2–6 μg of acids were separated by means of a mixture of acetone, ethanol, and water and detected with Bromocresol Green[95].

B. Production of chromatogram. A specimen containing 1–10 mg of each component for columns of diameter 1–2 cm [76,77,84,93,96] or 150–250 mg of the mixture for broader columns [14,97] is introduced in the form of a solution in the mobile [76,93] or stationary [14,84,96] phase, depending on the solubility of the lipids. The volume of the solution should correspond to one theoretical plate [84]. The rate of flow of the mobile phase may vary over the range (ml $h^{-1}$) 4–20, [85,91,93] 35–60, [76,84,90,98] 120–180, [14,99] and up to 300, [83] the efficiency of the column being slightly higher at lower rate of flow. The temperature of the separation should be kept constant. Unsaturated acids are usually separated at 10°, [96,98] mixtures of acids on rubber and polyethylene columns at 20–25°, [86,92] and columns containing paraffin oil are kept at 35°. [14,76,80,99] The eluate is collected in an automatic collector [87], and the concentration of lipids in the fractions is determined gravimetrically [35,85] or by titration with 0.01 *N* potassium hydroxide in methanol using Bromothymol Blue as indicator [76,77,80,82,92,96,99]. In other cases two volumes of water are added to the eluate, and nephelometer readings $S$ and $S_1$ for the specimen and a standard are determined. In the range 2–20 μg, the relationship between $\log_{10}(S/S_1)$ and the mass of the lipids was linear [14,81,100]. The concentration of glycerides was determined colorimetrically with hydroxylamine and $Fe^{3+}$. [84] A differential refractometer has been used for the continuous recording of lipids at the column outlet; the area of the peaks on the chromatogram was not proportional to the mass [90]. Between 97% and 103% of the original lipids was detected in the eluate [35,77,80,82,89–91]. The purity of the specimens isolated reached 99–100%. [14,83]

Aqueous solutions of acetone, saturated with the non-polar phase, are commonly used as solvents for the separation of lipids. The following acetone concentrations (%) have been used for the elution of saturated acids — $C_6$ 30, $C_8$ 40, $C_{10}$ 50, $C_{12}$ 53, $C_{14}$ 58–60, $C_{16}$ 65–67, $C_{18}$ 70–73, $C_{20}$ 75–78, $C_{22}$ 80–83, and $C_{24}$ 85–90. [14,76,77,80,89,91,96] A mixture of acetone, heptane, and water (5 : 1 : 0.629) has been used as solvent for the separation of triglycerides from coconut oil [84], and 95% acetone for that of glycerides from linseed oil [90]. Increase in the concentration of water increases $V_R$ and the efficiency of the column [76,84]. Acids and their derivatives have also been separated by means of a mixture of methanol with acetone (3 : 1), [86] 65–100% methanol [82,98], 40–70% ethanol [93], a mixture of acetonitrile with methanol (17 : 3), [83] and a mixture of acetic and formic acids with water (2 : 2 : 1). [94] Acids and their methyl esters have been separated in the acetonitrile–water (3 : 1) system [14,81]. The use of aqueous ethanol for the fractionation of 2-mono- and 1,2-di-glycerides led to their conversion to the stable 1-mono- and 1,3-di-isomers; in aqueous acetone no migration of the acyl groups was observed [85].

C. Separation of the lipids. Saturated normal aliphatic acids differing by one $CH_2$ group are readily separated and leave the column in order of decreasing values of the constant $K$. [14,76,77,80–82,86,87,91] The value of $V_R$ for lactobacillic acid (11,12-methyleneoctadecanoic acid) coincides with that for stearic acid [87]. Unsaturated acids are separated from one another, but not from saturated acids having the same value of $K$. [8,77,83,87,99]

For the quantitative analysis of a mixture, a specimen of acids is hydrogenated in the presence of 5–20% Pd on carbon for 24 h; [77,97,101] the hydrogenation products (saturated acids) are readily separated on a column [8,102–104]. Another specimen of the acids is cleaved at the double bonds by means of 5% permanganate [99,104], hydroxylated with peroxyformic acid [87,105], or subjected to ozonolysis in methyl acetate at -40° for 5 min. [77] The results of the simultaneous determination of the original acids and the products of their hydrogenation and oxidation make it possible to establish fairly precisely the composition of a given mixture [77]. Thus oleic and petroselinic acids are not separated in a reversed-phase system, but the pelargonic and lauric acids produced by their oxidation are readily separated in this system [99].

Hydroxy-, epoxy-, and keto-acids, because of their high polarity, leave well away from ordinary acids, and are separated both in unchanged form [76,86–88,99] and as their acetates on columns containing acetylated castor oil [35,77]. The value of $V_R$ for hydroxystearic acid coincided with that for lauric acid [35,77]. The chlorophenacyl esters [93] and fluorides of aliphatic acids [94] were separated in the same way as the unsubstituted acids. Columns containing paraffin oil were used to separate mono-, di-, and tri-glycerides [85] and also triglycerides differing by four $CH_2$ groups or by two double bonds; glycerides differing by two $CH_2$ groups or by one double bond were not separated completely [84]. Methyl esters, cholesterol esters, and triglycerides were separated on a factice column into fractions having identical values of $K$; the values of $\log V_R$ were found to vary linearly with the number of carbon atoms in these compounds [90].

### 3. Chromatography on Glass Plates

Chromatography on a thin layer of adsorbent attached to a glass plate has now been widely adopted as a method for the separation of lipids by adsorption. At the same time plates carrying silicic acid are being used in the chromatography of lipids on an ever increasing scale as carriers of a non-polar phase.

For the *reversed-phase* separation, activated plates were treated with 10–15% undecane in petroleum ether [106–108], 10% dodecane in hexane [109], or 5% tetradecane [107,108,110–115], 0.5% [116,117] or 10% [118–120] paraffin oil, or 5% silicone oil [110,121] in ether. Heavy oils cannot be removed from the plate by heating [110]. The separation of lipids and the detection of the individual zones are carried out by the methods generally used in thin-layer chromatography [122].

The results of partition chromatography on plates in general do not differ from those obtained in other forms of reversed-phase chromatography; the possibility of working on the ultramicro-scale, however, makes it possible in a number of cases to achieve higher rates and efficiencies of separation. Plates are often used for two-dimensional chromatography: the lipids are separated in one direction into classes without the application of a non-polar phase, after which part of the plate is impregnated with hydrocarbons and the lipids of each class are separated into fractions of different polarity [106,109].

The $C_{10-18}$ aliphatic acids (0.5–20 μg) have been separated with a mixture of acetic acid and acetonitrile (1 : 1) [107,108] or 85% acetic acid [119] in 1 h. For the separation of acids having equal values of $K$, 0.5% bromine was added to the polar phase: the transformation of the unsaturated acids led to a marked increase in their mobility [108,112]. Lipids having the same polarity can also be separated by *hydrogenation*:

the acids on the plate are sprayed with a 1–2% palladium suspension, hydrogenated with $H_2$ in a desiccator, washed with 5% HCl, and separated by means of undecane [108,112,119]. The saturated $C_{18-34}$ acids have been separated in the propan-2-ol–ethanol–acetic acid–water (8:3:4:1.3)/tetradecane system at 42°, and determined quantitatively with Cu acetate (see Section III4E*a*)[114]. The $C_{13-25}$ 2-methyl--4-keto-acids and $C_{12-22}$ hydroxy-acids have been separated by the use of 80% acetic acid [111]. The solvents used for the $C_{12-34}$ aliphatic alcohols have been 85% acetic acid and 90% acetone [114,115].

Methyl esters have been separated in acetic acid–acetonitrile–water (2:14:5) [121] and acetone–acetonitrile (7:10) [109] mixtures. Saturated and unsaturated esters of equal polarity were separated at 4–6° (see Section III4D) or in the presence of peracetic acid (Section III4F). [121] Methyl and ethyl esters with different numbers of double bonds have been separated on a non-impregnated plate carrying silicic acid, by fourfold treatment with a mixture of petroleum ether and benzene (4:1); the plate was then impregnated with paraffin oil, and fractions differing in the number of carbon atoms were separated. The methyl esters were separated from the ethyl esters of the same acids [119]. An analogous method was used to separate cholesterol esters; ethyl methyl ketone–acetonitrile (7:3) [118,119] and acetic acid–chloroform (80:15) [116,117] were used as solvents.

Triglycerides have been separated by means of an acetone–acetonitrile (4:1) mixture [107,119] and acetic acid [117]; in 35–100 min, linseed oil was separated into nine fractions and soya-bean oil into six fractions. In most cases no separation of triglycerides of equal polarity took place. The mobilities of glycerides with the same values for $K$ are not always identical, however [110]. Repeated treatment of plates with a single solvent, with drying after each treatment, leads to the separation of 1–2 μg of components of equal polarity. Thus the following glycerides are separated — LenLenLen from LauLauLau, LolLolLol from MyrMyrMyr, OlOlLol from MyrOlOl, OlOlLol from PalPalLol, OlOlOl from PalOlOl, OlOlOl from PalPalPal, PalPalOl from PalPalPal, etc. §. Threefold treatment made it possible to separate a mixture of OlOlOl, PalOlOl, PalPalOl, and PalPalPal glycerides, and also to separate the glycerides of oleic acid from the corresponding glycerides of elaidic acid. In this case linseed oil is separated into not 9 but 15 fractions, soya-bean oil into 13 fractions, ground-nut oil into 12 fractions, etc. [113]. Thus the double bond of the triglycerides is compensated for not by exactly two $CH_2$ groups, as in the previous case, but by approximately 2.4 groups; the $Rf$ value for the more unsaturated component increases with increase in the difference in the number of double bonds in lipids of equal polarity. Decrease in the molecular weight of the stationary phase, an unfavourable ratio between the components of the specimen, and increase in the weight of the specimen lead to a decrease in the efficiency of separation of the glycerides [123]. A solution of 0.5% of bromine in a mixture of propionic acid and acetonitrile (3:2) is suitable for the separation of triglycerides of equal polarity; the hydrogenation method described above is also used [108,112].

§ Lau, Ol, Lol, and Len represent the acyl radicals of lauric, oleic, linoleic, and linolenic acids.

## 4. Paper Chromatography

A. Preparation of paper and application of stationary phase. Suitable grades of chromatographic paper for the separation are those exhibiting sufficient strength during washing in water [17]. These requirements are satisfied by the following papers: Whatman No. 1 [15,124–128], No. 3 [17,129], and No. 4 [124,130]; Schleicher and Schüll No. 595 [3,15], No. 598 [131], No. 2040*b* [132,133], No. 2043*b* [7,17,123,134,135], and No. 2043*b* Mgl [136,137]; Toyo No. 2 [138,139]; and Macherey Nagel No. 214 [134]. "B" or "M" paper from Leningrad Factory No. 2 [140–145] or No. 69 "Goznak" [146,147] have also been used; these grades are less satisfactory than those listed above [144]. The paper was purified by washing with 0.5–10% hydrochloric acid [144,148], 3% nitric acid [142], 20% formic acid [147], 95% acetic acid [127], aqueous acetone [149], ethanol [148], ether [127,146,148], or benzene [150], washed with water, dried at 90–120°, [125,128,130,135,144] and kept over ignited calcium chloride [136,150].

In early work, attempts were made to convert cellulose into its ethers in order to give the paper hydrophobic properties. To obtain the octadecyloxymethyl ether the paper was treated with 0.5% octadecyloxymethylpyridinium chloride in toluene at 90° for 3 h. [151] The hydroxamates of acids have been separated on paper acetylated with acetic anhydride in benzene at 70° [152,153] or palmitoylated in the same way [105]. Cellulose esters have not been widely used in chromatography, since hydrophobic paper is more readily prepared by impregnating ordinary paper with high-boiling lipophilic substances.

For the separation of the $C_{10-20}$ aliphatic acids, the paper is usually impregnated with undecane saturated with the mobile phase [134,139,154–163], pressed out with filter paper under a load of 4 kg for 10–30 min, and kept in air for 10 min. [137,140,144,150,156] The optimum undecane content is 100–250 mg $g^{-1}$. [133,136,150,164] After the separation, the concentration of undecane in the front is double its original value, and the concentration at the point of application falls almost to zero. The flow of undecane can be decreased by decreasing its original concentration, by using hydrophobic paper as carrier, and by keeping the chromatograms horizontal during the separation. The rate of movement of the mobile phase increases appreciably if the initial section of the strip is not impregnated [159]. Undecane can be removed from the paper at 80–95°.

With decrease in polarity of the lipids to be separated, it is generally necessary to use stationary phases of higher molecular weight and lower polarity. As a result of the lower solubility of these substances in the mobile phase, the efficiency of separation and the limiting weight of the specimen increase; removal of the phase before application of the colour tests for lipids becomes impossible, however. Saturated and unsaturated acids and methyl esters have been separated using 10% tetradecane in petroleum ether [135], 5–10% liquid paraffin in benzene, ether, or carbon tetrachloride [141,142,145–147,165,166], or a 10% mixture of liquid paraffin and paraffin oil in benzene [141,145]. Saturated acids from $C_{20}$ upwards, and also triglycerides, have been separated on paper impregnated with 5–15% paraffin oil ($d$ = 0.885–0.890) in benzene, ether, and petroleum ether [127–131,148,149,167–174]. The paper is usually impregnated by drawing the strip through the solution or by ascending and horizontal suction [147,170,171,175]. The non-polar phase corresponds to 10–15% on the weight of the paper [165].

Paper impregnated with 10–30% rubber latex, after swelling in acetone, can be used to separate acids and methyl esters

in methanol–acetone (1 : 1) and 80% methanol–isooctane systems[3,168]. A mixture of 0.5% rubber and 30% naphthalene in benzene (4 : 1) has also been used[176]. Tetralin and decalin have been used to separate the 2,4-dinitrophenylhydrazones of *p*-bromophenacyl esters ("bromazones"), the 2,4-dinitrophenylhydrazones, acetol-, and acetoxymercurimethoxy-derivatives of unsaturated methyl esters, glycerides, and phospholipids[138,163,177-184], and also aliphatic acids[185].

Vegetable oils have been used for impregnation only in early work[124,186,187]; the efficiency of hydrocarbon phases is exceeded only by that of castor oil in the separation of hydroxystearic acids[126].

Among organosilicon compounds, use is made of silicone oil (1–5% Rodorsil 240, Dow Corning 200, Tip-2 in cyclohexane or ether), which is sparingly soluble in mobile phases[49,125,139,143].

The concentration of stationary phase in the system determines the duration of the experiment: at an undecane concentration of 150 mg $g^{-1}$, analysis of the acids takes 1–2 h, and at 600–700 mg $g^{-1}$ movement of the polar phase ceases[188]. If the concentration of this phase is 0.1%, the saturated acids up to $C_{26}$ can be separated without heating the chamber[189]. The differences in the $R_f$ values ($\Delta R_f$) increase with decrease in the concentration of the phase, so that the reversed-phase system is a true partition system, in which there is no adsorption[16,188]. To obtain reproducible $R_f$ values, the concentration of the phase should be uniform along the length of the strip[5].

B. Production of chromatogram. If the concentration of individual lipids in the mixture is low, they must be isolated by preparative methods before separation. Higher $C_{20-36}$ acids have been concentrated from wax by crystallisation with urea[141]. Polyunsaturated acids from fish oils have been fractionated as the Li salts[190]. Aliphatic acids from wood have been separated from resin acids by chromatography[191]. On paper impregnated with potassium hydroxide, alcohols moved with the toluene front and acids remained at the point of application[192].

A sample containing 10–100 μg of each component[7,78,141,170,174,176] or 100–500 μg of a mixture of lipids[15,126-128,134,147,161,167,193] in solution in chloroform[15,78,126], alcohol[127,167,170], ether[128], acetone[146,147], or benzene[16,179,193] is applied to a starting line at a distance of 2–6 cm from the edge[78,126,147] in the form of bands[147,193] or spots[126]. To prevent crystallisation, saturated $C_{20-30}$ acids should be kept at 80–90° before the separation[15]. Unsaturated acids with conjugated bonds should be applied immediately after isolation, to avoid polymerisation[194]. The common unsaturated acids are also decomposed on paper in the absence of solvent[125].

The strip is treated in the vapour of the mobile phase[126,137,155,195] and developed by descending[78,126,128,140,164,179], ascending[141,144,146,167,176,184,196], horizontal[7,188,197], or circular[160,161,163,173,198] methods; the last method can be used for the preparative separation of lipids (more than 10 mg)[172]. The mobile phase usually moves a distance of 20–35 cm from the point of application. The efficiency of the separation increases if the upper part of the strip is wedge-shaped, as described by Matthias[17,132,199]. Ascending chromatography in test-tubes is used for the rapid analysis of acids[137].

C. Mobile phases. The mobile phase should have high polarity and low volatility, it should readily dissolve the lipids of the specimen, and its miscibility with the non-polar phase should be low. With increase in the polarity of the phase, $\Delta R_f$ increases and the solubility of the lipids decreases. If, however, the quantity of water is decreased, the duration and efficiency of separation are reduced. The mobile phases unavoidably contain the stationary phase of the system (80–90% saturation).

Acetic acid is almost always present in the mobile phase. The 90% acetic acid/undecane system separates the $C_{16-18}$ saturated and unsaturated acids[15,16,137,140,144,156-158,161,163,193], cyclopentenyl aliphatic acids[200], and aliphatic alcohols[192]. Sometimes 90% acetic acid is used with paraffin oil[126,173] and liquid paraffin[146]. The 95–100% acetic acid is used for the $C_{20-34}$ saturated acids[15,126,127,129,160,174,201,202] and polyunsaturated glycerides[132,172,198], and 50–75% acetic acid is used for the $C_{10-14}$ unsaturated acids and $C_{10-18}$ hydroxy-, epoxy-, and keto-acids[15,126,127,140,157,168,202], the thiocyanato-derivatives of the acids[203], monoglycerides[143], and oximes of $C_{8-18}$ aldehydes[204]. If the specimen contains $C_{10-24}$ aliphatic acids, separation with an acetic acid concentration gradient from 50% to 90% is used; the concentration $Ct$ at time $t$ is calculated from the formula $C_t = C_0 e^{-vt/V}$, where $C_0$ is the original concentration of acid, $V$ the volume of the mixing chamber, and $v$ the rate of supply of acid to the chamber[15,170]. The use of formic acid for the separation of aliphatic acids — 98% acetic acid–85% formic acid–water (30 : 10 : 1)[141,142,145,147,166] or 85% acetic acid–88% formic acid (1 : 1)[205] — increases the efficiency of separation and makes the zones more compact. Systems containing acetonitrile or acetone dissolve lipids readily, increase the rate of separation and $\Delta R_f$, and withstand temperatures up to 45°.[7,15,188] Acetic acid–acetonitrile (5 : 7)[190], acetone–acetic acid–water (8 : 2 : 1)[7,16,133,188], acetone–acetic acid (3 : 1)[165], or 85% acetone–90% acetic acid (3 : 2)[164] mixtures are used for acids; acetone–acetonitrile (4 : 1)[131,150,172] and acetone–methanol (9 : 1[128,172] or 3 : 1[130]) mixtures are used for triglycerides; and acetic acid–acetonitrile (3 : 1)[196,204,206] is used for the acetoxymercurimethoxy-derivatives of the allyl esters of saturated acids and the allylurethanes of higher alcohols, and also for the oximes of diesters of dihydroxyacetone. Aqueous 80–98% solutions of acetone have been used to separate mono- and tri-glycerides[134] and aliphatic acids[126,207].

Systems containing methanol — methanol–acetic acid (30 : 1), 90% methanol–acetic acid (30 : 1)[179], methanol–acetic acid (5 : 1)[139,163,178,182], 90% methanol–acetic acid (5 : 1)[178,181,183], and 70% methanol–acetic acid (3 : 2)[184] — have been used for the separation of "bromazones" and the acetoxymercurimethoxy-derivatives of unsaturated lipids and phospholipids. Saturated $C_{20-36}$ acids have been separated in the systems methyl acetate–acetic acid–water (5 : 20 : 2)[139,162], 99.5% propan-2-ol–96% ethanol–acetic acid–water (8 : 2.5 : 4 : 1.25)[135], and methanol–acetic acid–water (5 : 4 : 1)[16]. Aqueous 75–95% methanol[167,176,177] and ethanol[124,186], 55–65% propan-2-ol[156], and propan-2-ol–methanol–water (11 : 5 : 4)[208] are hardly ever used at the present time for the separation of acids, because of the low values of $\Delta R_f$ and the "mutual dissolution" taking place when zones with low lipid concentration are absorbed by larger neighbouring zones[193]. Mixtures of methanol with chloroform (1 : 3)[205] or with tetrahydrofuran and carbon tetrachloride[125] and an acetic acid–chloroform mixture (16 : 3)[209] have been used for the separation of triglycerides.

The 2,4-dinitrophenylhydrazones of $C_{8-18}$ aldehydes have been separated in the dimethylformamide–formamide (5 : 2)/hydrocarbons of b.p. 150–180° system, and their acetoxymercurimethoxy-derivatives have been separated in the same system with tetralin[7,210,211].

D. Temperature of separation. Mutual saturation of the phases and chromatographic separation are usually carried out at 20 ± 2°. Increase in temperature increases $R_f$ and the rate of separation, but leads to flow of the non-polar phase [16]. Cooling to 17° stops the separation of saturated acids, whose solubilities (in g per 100 g of acetic acid) have the following values at 20° and 30° respectively — $C_{10}$ 567 and 8230, $C_{12}$ 81.8 and 297, $C_{14}$ 10.2 and 51.1, $C_{16}$ 2.14 and 8.11, and $C_{18}$ 0.12 and 1.68. [159,188]

The decrease in solubility with temperature is used for the separation of saturated and unsaturated acids of equal polarity. The saturated acids can be precipitated before separation from petroleum ether at -20°. [163,212] In the acetone–undecane system, the following saturated acids remain at the point of application — $C_{18}$ and above at -20°, $C_{16}$ and above at -30°, $C_{14}$ and above at -38°, and $C_{12}$ and above at -50° — the acids which move at a given temperature being separated from one another [188]. After application of the acids, the strip was kept at -30° and then developed for 20 h in the systems (1) acetone–propionic acid–water (4 : 3 : 0.5)/undecane at -30°, or (2) 85% acetic acid–85% formic acid–water (10 : 10 : 1)/silicone oil at -10°. The saturated acids from $C_{14}$ did not move [15,125,188]. In two-dimensional chromatography, system (2) was used in the first direction, and 93% acetic acid at 20° in the second direction [213]. In the separation of *cis*- and *trans*-isomers, system (1) eluted oleic acid, while elaidic acid remained at the point of application [18,214].

To increase the solubility of the saturated acids, the temperature in the chamber has to be raised to 30° for the $C_{20-26}$ acids [7,15,125,127,188,205], to 45–55° for the $C_{24-28}$ acids [139,145,149,173], and to 55–85° for the $C_{26-34}$ acids [129,135,141,174].

E. Detection and quantitative determination of lipids. Coloured lipids, for example the "bromazones" of aliphatic acids, can be determined quantitatively at once by photometric methods [181]. Most lipids of the aliphatic series are colourless, however. These are detected and determined quantitatively by means of the colour reactions given by the carboxyl, hydroxyl, and other groups, double bonds, or the aliphatic chain itself.

(*a*) *Reactions of the carboxy-group.* Aliphatic acids and other acidic lipids are most readily detected by a non-specific test with an indicator [7]: 0.2–0.4% Bromothymol Blue in alcohol, pH 8–8.3, [151,168,176] Bromophenol Blue [134,215,216] or Bromocresol Green [177], 0.05% Cresol Red and cresolphthalein in 0.8% NaOH, [198,217] Malachite Green [185], Nile Blue [158,217], thymolphthalein, and Phenol Red [217,218]. With Pyrogallol Red, $z$ = 15 μg. [219] The colour produced by the acids disappears rapidly. The results obtained by titrating the acids with 0.005 *N* NaOH using Bromothymol Blue as indicator after their extraction from the paper agreed with the results of the thiocyanatometric determination [134,215].

Hydroxamic acids have been detected with acidic 1.5–2% $FeCl_3$ in a mixture of ethanol and butanol (1 : 4) in the form of purple zones [152,153]. The sensitivity of this reaction is lower than that of the reaction with indicators [178]. The methyl esters of aliphatic acids, obtained with $^{14}C$-diazomethane, were determined quantitatively by scanning a radio autograph of the chromatogram on an MF-4 microphotometer [165,220].

Aliphatic acids are usually determined as the heavy-metal salts [7]. To obtain the Co salts, the strip was held in $NH_3$ vapour, immersed for 1 h in 0.03–2.5% $^{59}Co$ acetate at pH 5.8–6.0, containing 2–3 μc $^{60}Co$ $ml^{-1}$, treated with ammonium sulphide to develop the colour, and measured on a Geiger counter with an accuracy of 2.5%. [221,222] The $^{59}Co$ salts alone are not suitable [43].

Basic copper(II) acetate is used more frequently than other salts [7]. The strip is immersed in a mixture of saturated copper acetate and water (1 : 49) for 20 min, and washed with water acidified with acetic acid to reveal the pale green zones due to the acids [186]. Potassium cyanoferrate(II) (1–1.5%) is used to obtain the dark brown colour of copper cyanoferrate(II) ($z$ = 5 μg). [155,156,158,167] If this solution is acidified, the salts are converted into the free aliphatic acids. Thus the reaction with copper acetate and potassium cyanoferrate(II) can be carried out repeatedly, to increase the sensitivity [188]. Under the influence of 5% ferric chloride, copper cyanoferrate(II) gives blue zones of $FeCu[Fe(CN)_6]$. [146]

In the reaction of copper salts, treated with ammonia vapour [133], with a basic 0.03% alcoholic dithiooxamide (rubeanic acid) solution, $z$ = 0.1 μg Cu. [126,223,224] By repeated development of the colour, the $C_{30-36}$ acids from wax, which can be separated only in very small quantities, have been detected [224]. The same reaction is given by aldoximes and ketoximes [204].

Copper salts can be detected from the liberation of oxygen and foaming with hydrogen peroxide and $NH_4OH$ ($z$ = 5–10 μg). [225] When Cu acetate solution moves along the paper, the aliphatic-acid zone brings about distortion of the front [59]. The colour of the copper salts of aliphatic acids is intensified by 0.5% Rhodamine B [43,49] and aniline–ethanol (1 : 1). [137]

The stoichiometric reaction leading to formation of the copper salts of acids from $C_{12}$ upwards is often used for quantitative determinations. For an approximate estimate, measurements are made of the area of the spot $T'$, and the quantity of acid $C'$ is calculated from the formula $T' = k \log C' + b$, where for oleic acid $k$ = 182 and $b$ = 166, and for linoleic acid $k$ = 134 and $b$ = 189. [193] The ratio of the zones is usually determined quantitatively with a photoelectric densitometer. The coloured chromatograms or their photographs are drawn past the 1 mm slit of the photoelement, and the light absorption is recorded. The area of the peaks on the curve is proportional to the molar concentration of the acids [144,146,155,223]. To obtain a uniformly low light-absorption background, it is necessary to purify the paper (see Section III4A) and to remove as far as possible the stationary phase, acetic acid (without heating), and the copper salt solution, whose pH should not exceed 5. [53,126,204,226] If the non-polar phase cannot be removed from the paper, acids with low values for $K$ are not converted completely into the copper salts, and a correction must be introduced into the calculation [126]. When the light absorption between the peaks does not return to zero, the area for each component is found by means of supplementary lines [126,227]. Beer's law is obeyed over the range 1–60 μg of the acids [126,228]. The accuracy of the determination of acids whose concentration exceeded 2% [7] reached ±3%. [228]

Polarographic and colorimetric methods have proved that the reaction is stoichiometric. Copper ions were eluted with 0.06–1 *N* $H_2SO_4$. A linear relationship between the height of the step on the polarogram and the quantity of copper was observed for 1–7 μg copper $ml^{-1}$. [227,229,230] In the colorimetric estimation with 0.1 M tetraethylthiuram

disulphide [231] or 0.001% dithizone [232], Beer's law was obeyed over the range 10–30 μg ml$^{-1}$. The accuracy of both methods was ±5%. [230,231]

Silver salts were obtained in 1% ammoniacal silver nitrate within 5–30 min; excess of the salt was washed out, and the Ag was fixed with dilute HCl. [186] For the $C_{20-34}$ acids, the solution was heated to 55–85°. [129,174,186] The silver salts were coloured by heating to 140–150° for 10 min [129,194] or by treating with ammonium sulphide [167,186], sodium sulphide [147], hydrogen sulphide [156], phenylhydrazine [43], and 0.03–0.5% *p*-diethylaminobenzylidenerhodanine [43,174,233]. The accuracy of the densitometric determination of the $C_{16-18}$ acids on an MF-4 apparatus with a supplementary projecting lens was adequate [147]; photographs of chromatograms of the $C_{24-34}$ acids were scanned on an MF-2 apparatus with unsatisfactory results [174]. After the paper had been ashed, the accuracy of the determination of 0.2–2 μmole of silver with dithizone was ±5%. [233] Aliphatic acids can also be determined radiometrically with $^{110}$Ag. [234]

The mercury salts (0.1% $Hg^{2+}$ acetate in 0.5% acetic acid for 15 min) were more stable to hydrolysis by water than were the copper salts, and the paper background was lighter. The salts were coloured with 0.2% 1,5-diphenylcarbazone [78,173], the colour was eluted with methanol and toluene (1 : 1), and measurements were made at 530 mμm. [15,173] The radiometric determination was carried out with $^{203}$Hg. [234]

The lead salts (1–3% lead acetate, pH 5.3–5.7, 20–40°) were coloured with hydrogen sulphide, 1.5% ammonium sulphide, or a solution of 2 g of sodium sulphide, 100 g of ammonium nitrate, and 30 ml of hydrogen peroxide per litre ($z$ = 0.05 μg of acid). 2-Hydroxy-acids are not detected by means of lead [139,164,168]. After extraction from the paper with 10% nitric acid, the lead was determined with dithizone at 520 mμm. Satisfactory accuracy in the measurements was achieved by thorough purification of the paper, reagents, and the quartz vessel from traces of heavy metals [142]. The reaction of the acids with bismuth nitrate (at 70–80°) and ammonium sulphide gave values of $z$ equal to those for reactions with the lead salts [127,141,148].

(*b*) *Reactions of the hydroxy-group.* The vicinal OH groups of monoglycerides and polyhydroxystearic acids have been detected by Schiff's reaction with 1% periodate, sulphur dioxide, and pararosaniline ($z$ = = 10–20 μg) [70], or with a solution containing 35% borax, 0.8% potassium iodide, 0.9% boric acid, and 3% starch (the lipids gave white spots on a blue background) [52]. For radiometric determination, mono- and di-glycerides were acetylated with $(^{14}CH_3CO)_2O$. [220]

(*c*) *Reactions of the double bond.* Unsaturated lipids are detected by oxidation or replacement of the double bonds. On oxidation in 0.1–1% alkaline permanganate, unsaturated lipids after 1.5–5 min give brown spots of manganese dioxide [48,132,139,141,166]; acid permanganate gives white spots on a pink background [7]. Densitometric measurement of the colour produced by the action of alkaline permanganate has been carried out in reflected light; the concentration of aliphatic acids, glycerides, and sterol esters was determined from the height [209] or the area of the peaks with an accuracy of 3–5%. [166] Unsaturated acids were oxidised with sodium periodate and 1% potassium permanganate, and scanned on a microphotometer [235].

In the ozonisation, the band was treated with sodium hydrogen sulphite, then with oxone for 20–60 min, and finally with Schiff reagent [208,236].

Unsaturated lipids on a moist strip without hydrocarbons or with silicone oil give brown or yellow spots in iodine vapour at different pH values [125,132,150,220]. The colour was scanned with a blue filter [205]. The iodine reacting with the double bonds was detected with 0.5–1% starch in the form of blue spots on a light background ($z$ = 3–4 μg) [127,128] or with 0.2 *N* silver nitrate and the photographic developer Eukobrom [237]. Bromine and thiocyanogen may be partly liberated from the double bonds in ammonia vapour: $Br^-$ was detected with Phenol Red and chloramine ($z$ = 0.1 μg) [238], and $CNS^-$ with $Fe^{3+}$ salts [203]. The vapour and solutions of $^{131}$IBr have been used for the radiometric microdetermination of the mass and iodine number of lipids [222,234,239,240].

Mercury(II) acetate in methanol is also used for the replacement of double bonds in *salts and esters* of aliphatic acids [7,15,229]:

$$-CH{=}CH- \xrightarrow{Hg(OCOCH_3)_2,\ CH_3OH} -CH(OCH_3)-CH(HgOCOCH_3)- .$$

The acetoxymercurimethoxy-derivatives of the esters are synthesised before separation [178,184,196]; the derivatives of the salts are prepared on the paper in 2% mercury(II) acetate containing 1% acetic acid only after the separation [241]. The combined mercury is detected with 0.1–0.2% alcoholic 1,5-diphenylcarbazone and ammonia vapour [78,196]; hydrogen sulphide colours mercury after its displacement from the derivatives by hydrogen chloride vapour ($z$ = 1 μg of linolenate) [184,188]. Colorimetric determination with 1,5-diphenylcarbazone [178] or dithizone [196], polarography [229], and densitometry [184,196] are used for the quantitative determination. Kaufmann used the acetoxymercurimethoxy-derivatives to determine saturated and unsaturated acids having equal values of $K$, for example palmitic and oleic acids. Parallel chromatograms were coloured with copper or mercury acetate. Since the carboxy-group is equivalent to one-half of a copper or mercury atom, and the double bond to one mercury atom, the value of $y$ (the percentage concentration of the saturated acid) was calculated from the formulae

$$y = [(2e + 1 - x)/2e] \times 100;\ x = F_{Hg}^{corr}/F_{Cu};\ F_{Hg}^{corr} = F_{Hg}(F_{Cu}^{stand}/F_{Hg}^{stand}),$$

where $e$ is the number of double bonds in the unsaturated acid which is not separated from a given saturated acid, $F_{Cu}$ and $F_{Hg}$ are the areas of the peaks for a non-separating mixture of the saturated and unsaturated acids, obtained by scanning chromatograms coloured with copper and mercury salts respectively, and $F_{Cu}^{stand}$ and $F_{Hg}^{stand}$ are the areas for the standard (stearic acid) [241].

Osmium tetroxide vapour detects 5 μg of oleic and 2.5 μg of linoleic acids as grey spots on a light background [7,161].

(*d*) *Reactions of the aliphatic chain.* A number of methods for the detection of lipids are based on the selective adsorption of lipophilic dyes and other substances from aqueous–alcoholic solutions or on the formation of inclusion compounds [11]. Of the fluorescent dyes, use is generally made of 0.05% Rhodamine B, [7] which detects mono-, di-, and tri-glycerides and aliphatic alcohols as white spots, which exhibit blue fluorescence, on a pink background ($z$ = 2 μg) [7,134,192]. Under the influence of permanganate, the colour of the spots changes to yellow [130]. The colour of Rhodamine is intensified by Nile Blue, quinine, Acridine Orange, etc. [43,61,242]. Rhodamine B has been used for the approximate determination of monoglycerides from the area of the spot [134,215]. Protoporphyrin detects phospholipids, acids, and glycerides as fluorescent red spots on a light background ($z$ = 1 μg) [243].

The complexes of lipids with fat-soluble dyes, readily detectable in visible light, are formed only after the

removal of hydrocarbons from the paper [158,167]. Sudan IV, [3] Oil Red O, [62] and other dyes have been tested; the best was found to be Sudan Black B, [150] which detects the esters of polyhydric alcohols and stearins, but which, unlike Rhodamine, does not colour the esters of monohydric alcohols [244]. Unsaturated lipids combine with Sudan more readily than do saturated lipids; in direct light the colour changes to pinkish brown [245]. Solutions of fat dyes in 50% diacetin have been used for the densitometric determination of glycerides; the accuracy of the measurements was improved by impregnating the strip with paraffin oil, 1-bromonaphthalene, and an emulsifying agent [246]. Because of their surface-active properties, lipids can be detected from the change in the hydrophilic nature of separate sections of the strip after the separation. On paper carrying paraffin oil, the esters of aliphatic acids and sucrose and triglycerides gave transparent spots in water and potassium hydroxide solution respectively [132,247]. Triglycerides can be hydrolysed on paper with 10–20% potassium hydroxide at 95°, and then detected by means of copper salts. On complete hydrolysis, no colour is produced by Sudan [131,150,248,249].

$\alpha$-Cyclodextrin, combined with lipids by inclusion reactions, is not coloured by iodine vapour and gives white spots on a blue ground. Di- and tri-glycerides, which do not form inclusion compounds, must be hydrolysed beforehand on the paper by means of pancreatin [125,220]. The inclusion reaction has been used for the densitometric determination of triglycerides and methyl esters [205].

F. Separation of lipids. Homologues differing by a $CH_2$ group and, in series of equal chain length, homologues differing by a free or substituted double or triple bond, hydroxy- or keto-group, etc., are separated in a reversed-phase system. *Homologous series* which have now been separated include the normal saturated $C_{10-36}$ aliphatic acids, even and odd [78,127,141,201], mono-, di-, tri-, and poly-unsaturated $C_{11-28}$ acids [126,141,157,190], mono-, and di-acetylenic acids [126], cyclopentenyl unsaturated acids [200], $C_{14-24}$ normal saturated 2-hydroxy-acids [127], $C_{30}$ mycolic acids [169], saturated and unsaturated hydroxy-, dihydroxy-, and keto-acids [126,158,177,202], $C_{14-26}$ saturated 2-methyl-4-oxo-acids [222], di-, tetra-, and hexa-bromo-derivatives of stearic acid [158], adducts of maleic anhydride with acids containing conjugated double bonds [216], the 2,4-dinitrophenylhydrazones of $C_{2-22}$ normal saturated acids, even and odd [178], the "bromazones" of $C_{2-26}$ normal saturated and unsaturated acids, aldehydes, and ketones, and their acetoxymercurimethoxy-derivatives [139,178,182], the acetoxymercurimethoxy-derivatives of unsaturated acids [179] and the allyl esters of $C_{20-30}$ saturated acids [196], $C_{10-18}$ saturated and unsaturated alcohols [192] and their allylurethanes [206], the acetoxymercurimethoxy-derivatives of the allylurethanes of $C_{10-30}$ saturated and unsaturated alcohols [206], the 2,4-dinitrophenylhydrazones of $C_{8-18}$ saturated and unsaturated aldehydes and their acetoxymercurimethoxy-derivatives [210], the oximes of $C_{8-18}$ esters of dihydroxyacetone and higher aldoximes [204], the esters of saturated and unsaturated acids with mono- and poly-hydric aliphatic and aromatic alcohols [244], mono-, di-, and tri-glycerides of the same or different acids [125,134,162,205,208], the triglycerides, of synthetic [125,132,144,162,183,205] and natural origin, containing residues of $C_{8-24}$ saturated and unsaturated acids [128,130-132,134,150,162,183], and also the acetoxymercurimethoxy-derivatives of the glycerides [183].

Tuberculostearic and nonadecanoic acids have equal $R_f$ values, so that chain branching does not influence mobility [126,200]. If the double bond is sufficiently far from the ends of the chain, the polarity rule applies (see Section III1). A double bond next to a carboxy-group, however, does not alter $R_f$ values: thus octadec-2-enoic and stearic acids are not separated [126]. Mobilities are the same for cycloalkene and alkene double bonds [200], isolated and conjugated double bonds [126], and double bonds in the *cis*- and *trans*-positions [126,157]. Replacement of a double bond in a chain by a triple bond increases the $R_f$ value [126,157]. The polarity of the OH group is greater than that of the CO group, so that 12-hydroxy- and 12-oxo-stearic acids are separated from one another [126]. In a series of hydroxy- and keto-acids, the chromatographic mobility decreases as the functional group approaches the carboxy-group [158,202].

The acetoxymercurimethoxy-derivatives of Φ-cholines have been separated into five fractions of different acid composition, the degree of unsaturation of the acyls increasing with increase in the $R_f$ value [182]. Soya-bean Φ-cholines have been hydrogenated and hydrolysed on paper in a study of the acid composition [250].

If members of different homologues series have the same values for $K$ and the same $R_f$ values, separation of these lipids requires either elimination of the unsaturated components or displacement of the polarity equilibrium in the mixture by saturation of the double bonds with hydrophilic or hydrophobic substituents. Before the chromatographic separation, the aliphatic acids were separated into saturated and unsaturated acids by the early method of Twichell and Bertram [7,155], by crystallisation of the copper salts from ethanol [186], or by crystallisation of the acids from 55% acetonitrile [251]. The unsaturated components were detected and determined by parallel separation of the original lipids and the lipids oxidised by 1% alkaline permanganate [126,141]. For complete decomposition of the unsaturated acids during the separation, use was made at 37° of the mobile phase acetic acid–formic acid–hydrogen peroxide (9 : 1 : 1 or 6 : 1 : 1), containing peroxyformic acid; the saturated acids were not oxidised in this phase [78].

On hydroxylation with permanganate or addition of thiocyanato-groups to the double bonds, the $R_f$ values for the acids increased, and on halogenation with iodine bromide the $R_f$ values decreased [252,253]. The mobility of unsaturated acids increased after bromoacetoxylation and bromomethoxylation with *N*-bromosuccinimide and also after formation of the acetoxymercurimethoxy-derivatives of the "bromazones" of these acids. The diastereoisomers of the bromoacetoxy- and bromomethoxy-derivatives of polyunsaturated acids each form two zones on the chromatograms [136,139,254]. Aliphatic acids with equal $R_f$ values have been separated by *hydrogenation* of the double bonds, with the formation of corresponding saturated acids of lower polarity [15,125]. In some cases the acids were separated before and after hydrogenation in the presence of palladium oxide on barium sulphate in ethanol [197], or of platinum oxide by Adams' method in acetic acid [126]. If the lipids contain palmitoleic acid, the complete mixture of acids is not hydrogenated, but only the fraction containing the palmitoleic, myristic, and linoleic acids; the hydrogenation products are subjected to further separation [191,224,255]. In other cases the hydrogenation was carried out directly on the paper (see Section III3), after which the hydrogenated and non-hydrogenated mixtures were separated [256-259]. For the determination of linolenic and $\alpha$-elaeostearic acids, which have identical $R_f$ values, adducts of elaeostearic acid with maleic anhydride are prepared in the presence of iodine, and the mixture of acids is hydrogenated and subjected to further separation [260,261]. Carbonyl groups in lipids are

reduced with a solution of sodium hydroborate in tetrahydrofuran[262]. For the determination of acids of equal polarity, use has also been made of low-temperature chromatography (see Section III4D) and the reaction of the double bonds with mercury salts (Section III4E*a*).

Thus the polarity rule introduces considerable difficulties in the analysis of lipids. On the other hand, the identification of complex mixtures, e.g. of triglycerides, where a fraction of given polarity may contain six, seven, or more components, is sometimes greatly facilitated, since lipids of known structure are correlated with a given chromatographic zone on the basis of a strict relationship.

Reversed-phase systems are seldom used for the fractionation of lipid mixtures into classes: the differences in polarity are so great that separation in any one system becomes impossible (see Section I). Moreover, lipids from different classes, with different values for $K$, often have the same $Rf$ values. Thus octadec-*cis*-9-en-1-ol is not separated from myristic acid, and diglycerides are superimposed on the stearic acid zone[192,208]. The concept of a "universal" polarity constant $K_{univ}$ has been introduced to compare classes on the basis of their absolute polarity. A standard of reference is provided by the homologous series of esters of monohydric alcohols and even normal aliphatic acids: for these the values of $K$ and $K_{univ}$ coincide. For lipids of another homologous series, $K_{univ}$ is equal to the value of $K$ for the substance of the reference system which has the same $Rf$ value as this lipid. The increment $i$, i.e. the difference between $K_{univ}$ and $K$ for a given lipid, is constant for a given series. The additive value of $i$ depends on the number of $CH_2$, COOH, and OH groups, double or ester bonds, the position of the functional groups, and other factors. The value of $i$ is 14 for triglycerides, 12 for the esters of unsaturated acids, 10 for 2-hydroxy--acids, 2 for the esters of aromatic alcohols, etc. This absolute polarity scale is extremely useful for the identification of lipids according to their classification in a specific homologous series[202,244].

It can be seen that the mobility of lipids during separation depends on their composition. The relationship between the $Rf$ value in different systems and the parameters of the molecule have been described by *empirical equations*: $Rf = 1.42 + (-0.062)m$; $Rf = 1.671 - 0.1326m + 0.0028m^2$; and $Rf = 1.50 - 0.0625m$ for saturated aliphatic acids, or $Rf = 1.42 - (-0.062)(m-2)$ and $Rf = 1.57 - 0.06m$ for unsaturated acids[124,133,195]. The dependence of the $Rf$ values on $m$ for aliphatic acids or their *p*-phenylazophenacyl esters was linear[32,201]. This relationship was not observed for triglycerides[150]. The $Rf$ values for $C_{18}$ unsaturated acids was found to be a linear function of the number of double bonds in the chain[134].

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The methods of partition chromatography are now being widely used for the separation of lipids of natural origin. The various methods are not all equivalent, however.

Column chromatography with a polar stationary phase is used for the analysis of an individual homologous series of aliphatic compounds or their polar derivatives; more modern methods are necessary for the separation of mixtures of several series of lipids. The analysis of lipids on paper with a polar stationary phase has now been largely replaced by other forms of chromatography, which give much more effective separations. Of considerable practical interest is the application of this procedure to the analysis of the oxidation products of lipids and the separation of phospholipids; ion-exchange paper or paper impregnated with hydrophilic organic phases such as formaldehyde or formamide must be used.

Of much wider application are reversed-phase systems, which are used in column chromatography for the preparative separation of lipids, in particular of lipids with oxygen--containing functional groups in the chain. This method does not require complicated and expensive equipment, and makes it possible to obtain several grammes of pure specimen in sufficiently high yield under mild conditions. This form of chromatography is less suitable for analytical separations, since it requires several centigrammes of material and the actual operations are fairly tedious[8].

Reversed-phase chromatography on glass plates is now being used on an ever increasing scale for analytical separations. In combination with the highly effective methods of thin-layer chromatography, in particular with separation on silica gel impregnated with silver nitrate, lipids of a given class can be characterised from the values of $m$ and $e$ on a single plate. The possibilities for the preparative separation and quantitative determination of lipids are apparently more restricted in this case, although work of this nature has recently been reported[123].

Reversed-phase chromatography on paper continues to occupy a leading position among partition-chromatographic methods for the study of lipids. By changing the compositions of the stationary and mobile phases, the temperature, the duration of the experiment, and other factors, the optimum separation conditions for a specific mixture of lipids are rapidly found. The time required for the separation (several hours) and the sensitivity of the detection of the lipids (fractions of a microgramme) approach in a number of cases of paper chromatography, those characteristic of thin-layer and gas–liquid chromatography. An extensive range of qualitative reactions which can be carried out directly on the paper is available for the identification of lipids. The analytical separation is readily combined with densitometric quantitative determination and radiographic measurement of the activity of individual zones.

The simplicity and reproducibility of the separation are two of the most important advantages of paper chromatography: the analysis can be carried out without great expenditure of labour or money, in any laboratory equipped with the minimum of apparatus and reagents. The method is not only very convenient for the rapid estimation of the composition of individual fractions of the eluate from a chromatographic column, but can also be used by itself in preparative work for the isolation of lipids in quantities of 1–50 mg.

Thus reversed-phase partition chromatography on paper is entirely suitable for the analysis of classes and homologous series of lipids of simple composition. For the identification of multicomponent natural mixtures of lipids and the identification of individual compounds, this method must be combined with adsorption and gas–liquid chromatography, spectroscopy, and other modern methods for the analysis of lipids.

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# THE CHROMATOGRAPHY OF BIOPOLYMERS ON CALCIUM PHOSPHATE GELS

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## I. INTRODUCTION

An important factor determining the success of a chromatographic separation is the choice of a suitable adsorbents. Progress in this field in recent years has led to the appearance of two main types or groups of adsorbent[1], which are now widely used for the chromatography of the most varied biopolymers.

One of these groups — calcium phosphate sorbents or gels — consists of molecular adsorbents. The other group consists of various ion exchangers, based chiefly on cellulose[2].

Both groups of adsorbent have an extensive, well hydrated surface, but the adsorption of biopolymers on these materials takes place in different ways. The principles of the action of these adsorbents also differ[3] and their chromatographic selectivity with respect to biopolymers is probably not the same[1]. Both groups of adsorbents are now widely used for the chromatography of the most varied biopolymers.

A number of reviews have been published[4-6] on ion exchangers based on cellulose. No reviews have been published on the use of calcium phosphate gels for the chromatography of biopolymers.

The aim in the present review has been to collect and summarise available published data on the chromatography of biopolymers on calcium phosphate sorbents.

## II. METHODS OF PREPARATION AND CHARACTERISTICS OF CALCIUM PHOSPHATE SORBENTS

Until recently, only tricalcium phosphate $Ca_3(PO_4)_2$ and calcium hydrogen phosphate or brushite $CaHPO_4.2H_2O$ were generally employed in chromatographic practice. In recent years, a particular form of calcium phosphate — hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ — has begun to be used extensively in the chromatography of proteins. Tricalcium phosphate was at one time used fairly extensively as an adsorbent for the chromatography of proteins. Mention may be made, for example, of the isolation and purification of catalase by the use of tricalcium phosphate[8,9].

Tricalcium phosphate is now seldom used for the chromatography of proteins in column experiments. We shall therefore not deal further with this type of calcium phosphate, except to point out that $Ca_3(PO_4)_2$ usually contains a considerable quantity of hydroxyapatite[10]. This is due to the fact that the primary product formed in the preparation of tricalcium phosphate is pseudoapatite[11], which is subsequently converted into one modification of tricalcium phosphate and partly into hydroxyapatite[12].

A second example of a calcium phosphate gel, which is still used in the chromatography of proteins, in calcium hydrogen phosphate or brushite. The structure of brushite obtained by mixing solutions of $CaCl_2$ and $Na_2HPO_4$ depends to a marked extent on the pH. Formation of the precipitate usually takes place at pH 6.3–6.5. At the same time, it is known[10] that at pH 6.2 and above, calcium hydrogen phosphate may undergo slow hydrolysis into another form of calcium phosphate with the structure of hydroxyapatite.

Since the chromatography of proteins and other biopolymers is usually carried out in the approximate pH range 6.8–7.2 (i.e. above pH 6.2), the experimenter is in fact concerned with the unstable changing structure of an adsorbent containing a considerable proportion of hydroxyapatite.

In this respect, an undeniable advantage is shown by another calcium phosphate gel, which is now widely used in the column chromatography of biopolymers, namely hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$. This material has a high stability over a wide pH range.

The modern chromatography of biopolymers on calcium phosphate columns may be taken as dating from 1956, when Tiselius, after a number of preliminary experiments[13-16], published a method for the preparation of hydroxyapatite suitable for the chromatography of proteins[10]. In this

method, 0.5 M solutions of $CaCl_2$ and $Na_2HPO_4$ are run at the same rate into a vessel with constant stirring; after decantation, the resulting precipitate of brushite ($CaHPO_4$) is washed with distilled water and boiled with 40% NaOH solution for 1 h. The precipitate is then washed repeatedly with a series of phosphate buffer solutions of different molarities. In this method the operation of boiling the $CaHPO_4$ precipitate with alkali is extremely important, since at this stage the calcium hydrogen phosphate is hydrolysed to a new form of calcium phosphate — hydroxyapatite.

The acidic precipitate of brushite, which usually forms large crystals, is converted, during this operation in alkaline medium, into fine crystals of hydroxyapatite suitable for the chromatography of proteins. X-Ray diffraction study of the resulting adsorbent[10] showed it to be hydroxyapatite, but the molar Ca/P ratio was found to be 1.53 instead of the usual value of 1.67 for hydroxyapatite[10]. This is apparently due to the ability of sodium or phosphate ions to enter the crystal lattice of the adsorbent in different proportions.

Hydroxyapatite prepared by Tiselius' method is now widely used in the chromatography of proteins. The actual preparation of the adsorbent, however, involves a large number of operations and is very time-consuming. To obtain a satisfactory rate of flow it is usually necessary to apply external pressure. A recent paper[17] reports that, to obtain hydroxyapatite by Tiselius' method with a satisfactory rate of flow from the column, it is necessary to prevent the deposition of highly dispersed material after the adsorbent has been washed with water. The need for extremely thorough stirring of the precipitates when the adsorbent is boiled has also been reported[17].

Somewhat later, in 1959, Main and his coworkers proposed a new method for the preparation of hydroxyapatite[18] with properties similar to those of hydroxyapatite prepared by Tiselius' method. In this case the precipitate obtained after mixing solutions of $CaCl_2$ and a sodium phosphate buffer of pH 6.7 is boiled in concentrated $NH_4OH$ solution. The precipitate is converted into hydroxyapatite during this operation. X-Ray diffraction study of the resulting adsorbent[18] showed it to consist of pure hydroxyapatite with Ca/P = 1.53. The hydroxyapatite obtained by this method, however, sorbs proteins comparatively weakly[17]. Main et al.[18] used this adsorbent chiefly for the chromatography of nucleic acids.

Anacker and Stoy[19] recently proposed another method for the preparation of hydroxyapatite suitable for the chromatography of proteins. In this method, 1.5 M $K_2HPO_4$ and 1.4 M $CaCl_2$ solutions are added with constant stirring to 0.1 M $CaH_4(PO_4)_2$ solution. The precipitate obtained in this way is converted into hydroxyapatite in 0.05 M NaOH at 40° over a period of several days. The resulting precipitate consists of pure hydroxyapatite.

Comparison of the adsorptive properties for proteins exhibited by hydroxyapatites prepared in different ways shows that the adsorbents prepared by the methods of Tiselius[10] and Anacker[19] give similar adsorption curves. Hydroxyapatite prepared by Main's method[18], however, gives a curve which differs sharply from them. The ability of this hydroxyapatite to sorb proteins is much lower.

Thus although hydroxyapatites obtained by different methods have the same chemical composition, their abilities to adsorb proteins are different. There is also a significant difference in the rates of flow of liquid through columns filled with calcium phosphate gels prepared by different methods. For the adsorbent prepared by Tiselius' method[10] the rate of flow through a standard column may reach an average of 20–22 ml $h^{-1}$ with the application of external pressure. For the hydroxyapatite prepared by Main's method[18] the average is given as 25–30 ml $h^{-1}$ without pressure, whereas for columns filled with hydroxyapatite prepared by Anacker's method[19] the rate of flow reaches 200 ml $h^{-1}$ without the application of pressure.

These differences in the adsorptive power of hydroxyapatites prepared by different methods indicate that the magnitude of the adsorption of proteins on calcium phosphate gels depends not only on the chemical nature of the adsorbents (the chemical formula is the same for all three hydroxyapatites) but also on the physical non-uniformity of the adsorbent surface.

In general, the magnitude of the adsorption of a solute is determined both by the adsorption on unit area of the adsorbent–solution interface and also by the specific surface of unit mass of the adsorbent, accessible to the solute molecules[20]. In the comparison of the magnitude of the adsorption on different adsorbents of unknown specific surface, the factor responsible for differences in the adsorption is always unknown. In some cases the difference may be due to a difference in the specific surfaces of the adsorbents[20].

Hydroxyapatites prepared by different methods give precipitates with different degrees of dispersion. These probably have different specific surfaces, and the surface is apparently characterised by different degrees of physical non-uniformity. This is possibly responsible for the difference in the adsorptive power for proteins.

All this points to the need for careful standardisation of methods for the preparation of calcium phosphate sorbents, in order to obtain reproducible results in the chromatography of biopolymers on columns.

## III. METHODS OF ELUTION AND CHARACTERISTIC FEATURES OF THE CHROMATOGRAPHY OF BIOPOLYMERS ON CALCIUM PHOSPHATE COLUMNS

### 1. Methods of Elution

Phosphate buffer solutions of different concentrations are now used almost exclusively as eluants in the chromatography of biopolymers on calcium phosphate. The sorption of proteins on columns is usually carried out at low concentrations of phosphate buffer solution, and elution at higher concentrations of the same buffer, most frequently at the same pH value. Change in pH in chromatography on calcium phosphate sorbents has an extremely small influence on the experimental results compared with change in the buffer concentration[10].

Two main method are now used for the elution of biopolymers from calcium phosphate — gradient elution (gradual increase in the concentration of phosphate buffer added to the solution) and stepwise elution (the increase in the concentration of phosphate in the column is carried out in separate stages).

Under certain conditions, gradient elution usually makes it possible to detect all the components of the mixture being studied. When this method is used, however, the mutual

influence of the proteins[10] often leads to considerable overlap of adjacent fractions on calcium phosphate sorbents, and in a number of cases, even when the solution being studied contains several protein components, only one greatly elongated protein zone is obtained at the column outlet. The homogeneity of a material of this type is determined by a further chromatographic separation.

Usually in such cases it is possible to isolate the individual components of the mixture being studied. One such example is given in a paper by Tiselius[10] on the chromatography of $\gamma$-globulin from human serum on hydroxyapatite.

In stepwise elution there is always a danger that the components leaving the column may be of complex composition: proteins of different character may be present in individual fractions. On the other hand, proteins with a broad elution range may give more than one component for a given protein on leaving the column, particularly if the elution is carried out at buffer concentrations differing little from one another. The appearance of these spurious components and the conditions for their formation in the chromatography of proteins on calcium phosphate columns have been discussed in detail[3].

In most cases the chief method used to assess the results obtained in the chromatography of biopolymers on calcium phosphate is further chromatography of the products. Where the biopolymers have in fact been separated into their components, the latter are always eluted from the column in the subsequent chromatographic experiment by the same buffer solution concentrations as in the original chromatographic experiment. At the present time, the chromatography of a test material on calcium phosphate columns is usually carried out by both methods of elution, which to a certain extent supplement one another. In the examination of the material obtained, it is of course desirable to use other methods for the study of protein components in addition to further chromatographic separations.

What is the mechanism of the elution of protein polymers from calcium phosphate columns? Hardly any special study has been made of this problem. Nevertheless, on the basis of work carried out chiefly by Tiselius and his coworkers[10,16], the mechanism can now be assumed to involve replacement of the proteins by phosphate ions. The ability of calcium phosphate to take part in extensive exchange with calcium and phosphate ions from the surrounding medium has been demonstrated directly[21] using the radioactive isotopes $^{32}P$ and $^{45}Ca$. This tendency is particularly marked with phosphate ions. These ions can effectively replace ions from calcium phosphate not only in the hydrate layer but also in the interior of the crystal lattice of the adsorbent[21].

Burley and Cook[22], using a different experimental technique, showed directly that the presence of phosphate groups in proteins essentially determines the behaviour of the latter during chromatography on calcium phosphate columns. Thus egg-yolk $\alpha$- and $\beta$-lipovitellins, which have different phosphate contents, show different behaviour on elution from hydroxyapatite. $\beta$-Lipovitellin leaves the column at a phosphate buffer concentration of 0.6 M, and $\alpha$-lipovitellin only at a concentration of 2.0 M. After treatment of $\alpha$-lipovitellin with phosphatase (removal of some of the phosphate groups), however, this protein shows behaviour similar to that of $\beta$-lipovitellin and is eluted from the column with 0.6 M phosphate buffer. There is need for further studies in this direction in order to elucidate all the details of the mechanism of the elution of proteins from calcium phosphate columns.

## 2. Characteristic Features of the Chromatography of Biopolymers on Calcium Phosphate Columns

In the chromatography of proteins on calcium phosphate adsorbents, the electrostatic bonds between protein and adsorbent play an important part. Hydrogen bonds and van der Waals forces are also significant[1,7]. Since a large number of bonds are formed between the protein and the adsorbent, their simultaneous dissociation during desorption of the protein is unlikely[1]. Under certain conditions, therefore, there is a danger that reversible partial denaturation of the protein will take place with a possible change in various structures (tertiary and quaternary) in the protein molecule[23].

Moreover, the non-simultaneous dissociation of the large number of bonds of different types between the proteins being chromatographed and the surface of the adsorbent may create a complex picture, whose interpretation is as yet impossible, and may lead to internal interaction between the proteins as they move downwards through the column during the chromatographic process.

The effects of internal interaction and the mutual influence of proteins play an important part in chromatography on calcium phosphate columns[10].

Chromatographic studies are usually carried out with various protein mixtures in order to isolate a definite protein from other proteins present in the mixture. Chromatography is often the final stage in the purification or one of the operations preceding purification. Thus the "ballast" proteins present in the experimental mixture may be present in various proportions relative to the protein to be isolated.

Recent work on the chromatography of proteins on columns has shown that the affinity of a protein for a sorbent often depends on the nature of the other proteins present in the solution[10]. A protein with a high sorptive affinity usually displaces another protein with a lower affinity for the sorbent; mutual replacement of the proteins takes place on the column. The mutual replacement of proteins on calcium phosphate was first utilised by Polis and Shmukler[24] for the purification of milk peroxidase. The following factors play an important part in the mutual replacement of proteins on calcium phosphate columns, the first being the affinity of the proteins for the sorbent. It is important that the difference in the affinities for the sorbent, shown by the displacing protein and the protein being displaced from the column, should be considerable. Satisfactory results can be obtained by the mutual replacement of proteins only if the condition is satisfied. Other important factors are the quantity of replacing protein added to the column, and the concentration of the buffer solution in which the replacing protein is dissolved. All these factors have been examined in detail by Boman[25].

In addition to the replacement of proteins during chromatography on calcium phosphate columns, other effects due to the mutual influence of the proteins may be produced. It has been noted[10] that in many cases a protein (usually strongly sorbed on columns) in the presence of another protein (with a lower sorbability) itself shows a reduced sorbability during chromatography on columns.

The mutual influence of proteins evidently plays an important part in chromatography on calcium phosphate columns and may influence significantly the results of chromatographic experiments. It is thus important to understand and make allowance for all the factors influencing the chromatography of proteins and to extend our knowledge in this field, where, up to the present, a purely empirical approach to the selection of optimum conditions for the chromatography of biopolymers has been adopted.

## IV. THE USE OF CALCIUM PHOSPHATE GELS FOR THE CHROMATOGRAPHY OF ENZYME PROTEINS

In recent years, the methods of adsorption chromatography have been widely used in preparative biochemistry, particularly for the purification and isolation of the most varied enzyme proteins. Almost all work on the fractionation of enzymes now involves the use of chromatography. Chromatography is often the chief method leading to successful results in the isolation of enzyme proteins.

It is not our aim to cover completely all the literature on the use of calcium phosphate sorbents for the chromatography of enzymes, and we shall restrict ourselves chiefly to work carried out in the last ten years. It is during this period that particularly extensive use has been made of adsorption chromatography on columns in work on enzyme proteins. Thus French workers[26,27] have recently described the isolation, purification, and study of hog pancreas lipase. This work was carried out with chromatographic columns containing various adsorbents — tricalcium phosphate, brushite, hydroxyapatite, and ion-exchange cellulose. In chromatography on calcium phosphate sorbents, the chromatogram of the eluted enzyme shows one peak, irrespective of the method of elution; several active enzyme fractions were obtained on ion-exchange cellulose. The appearance of a large number of lipase components during chromatography on ion-exchange cellulose was attributed to artefacts[27]. This work is of methodological interest, since different adsorbents were used for the chromatographic study of the same material, and for pancreas lipase calcium phosphate appears to have a definite advantage over ion-exchange cellulose.

Choline esterase from human blood serum has been obtained by chromatography on hydroxyapatite[28]. In this work, the ion-exchange resin Dowex-2 was also used for the chromatographic study of the enzyme, and hydroxyapatite showed considerable advantages over ion-exchange resins. Among the enzymes which split ester linkages, enzymes hydrolysing esters of phosphoric acid have been studied by chromatography on calcium phosphate gels — phosphomonoesterase from human red blood corpuscles[29], and alkaline phosphatase from hog kidneys[30] — the chromatographic separation giving in the latter case several fractions exhibiting enzymatic activity. The question of their nature remains open. Esterase from hog liver has been separated from "ballast" proteins and obtained in the pure state by means of hydroxyapatite columns[31]. The behaviour of the purified liver esterase on hydroxyapatite columns showed that the enzyme can be separated into two or three fractions having similar specific activities[32]. Analysis of these fractions showed that their appearance is due not to differences in their primary structure but apparently to partial association of the molecules of this enzyme[32,33]. This example in particular shows the importance of making an all-round study of the products of the chromatographic separation. Chromatography on calcium phosphate gels has also been used for the study of other enzymes — amylase from wheat flour[34] and phenolase[35], where several fractions exhibiting cresolase activity were obtained. The presence of several active fractions was shown for nicotinamidase[36] by chromatography on hydroxyapatite. In this case the fractions obtained were examined in an ultracentrifuge and also by further chromatographic experiments. It was concluded that the existence of these fractions was due to an artefact produced as a result of autolysis in the early stages of isolation of the enzyme. Among the group of enzymes bringing about transfer reactions — transferases — various dehydrogenases have been subjected to chromatography on calcium phosphate sorbents[37-45]. Among the oxidases, chromatography on calcium phosphate gels has been used successfully for the isolation of monoaminooxidases from cow's blood[46]. In this case, several active enzyme fractions with similar specific activities were obtained. Another enzyme from this group — the aminooxidase from cow's blood — has recently been studied by chromatography on a column of hydroxyapatite[47]. In this case, a combination of column methods with different adsorbents — calcium phosphate and ion-exchange cellulose — was used. The advantages of hydroxyapatite over cellulose for this enzyme were noted.

Among the transaminases, enzymes which bring about the transfer of an amino-group, tyrosine–oxoglutarate–transaminase[48] and alanine–oxoglutamate–transaminase[49] have been examined by chromatography on calcium phosphate gels. In both cases, several active enzyme fractions showing different chromatographic behaviour were detected, but unfortunately they were not investigated further. Other enzymes which have been examined by chromatography on calcium phosphate gels include bacterial polynucleotide phosphorylase[50], trans-ketolase from hog liver[51], transferase from rabbit liver[52], etc. An interesting attempt has been made to use chromatography on a column of hydroxyapatite for the separation of brain enzymes[53]. Some separation of the enzyme peaks was achieved, although a more complete separation of the latter might apparently be achieved by further chromatographic experiments. This work is of interest since it is the first attempt to use chromatography on calcium phosphate for the isolation and fractionation of enzymes from brain tissue.

The above examples show that the chromatography of enzymes on calcium phosphate columns often gives several fractions exhibiting the same enzymatic activity. The same phenomenon is observed in the chromatography of enzymes on ion-exchange cellulose[7]. The question of the chromatographic heterogeneity of enzyme proteins on their elution from columns undoubtedly deserves attention. The results of chromatographic experiments on columns cannot always be interpreted unambiguously, and the reason for the appearance of enzyme fractions with different chromatographic behaviour, but the same activity, is often obscure.

Recent work on the column chromatography of biopolymers has shown that, in addition to the difficulties introduced into the interpretation of the experimental results by the actual elution technique (see Section III for more details), there are a number of other factors, not related to the method of elution, which make difficult an unambiguous explanation of the experimental data. These may be responsible for the appearance of a number of protein fractions with the same (or different) enzymic activity.

We give below examples of such cases and an assessment of the factors responsible for the appearance of a large number of components in protein polymers during chromatography of the latter on calcium phosphate columns. Thus in the chromatography of phycocyanin and phycoerythrin on hydroxyapatite, chromatographically different fractions of these proteins may appear as a result of association–dissociation effects[10].

In the case of ribonuclease from hog pancreas[54], the appearance of chromatographic heterogeneity in the enzyme was due to the removal of polyanions combined with the protein.

Changes produced by various factors in the secondary, tertiary, or quaternary structure of a protein may also be responsible for the appearance of a number of components when the protein is subjected to chromatographic study[23,55].

In other cases, the appearance of a number of components may be due to differences in the age of the material being studied[56]. The nature of the chromatographic curve may sometimes be influenced by spontaneous hydrolysis of the protein material being studied[57]. A difference in the quantity of phosphate groups in the protein can also apparently lead to the appearance of a number of components on elution from calcium phosphate columns[17]. Finally, the existence of individual active forms of the same protein may correspond to its true state. This has recently been shown in work on the chromatography of various proteins on different adsorbents[48,58-60].

Thus the above details show that a variety of factors may be responsible for the appearance of a number of components in the same protein during chromatography on columns. In all such cases, a special study of the protein fractions by different independent methods is desirable in order to evaluate the results obtained. These supplementary data will make it possible in each individual case to establish the reasons for the appearance of a number of components in the proteins being studied. It must apparently be assumed that there are a number of factors leading to the appearance of heterogeneity in protein polymers during column chromatography.

## V. THE CHROMATOGRAPHY OF SERUM PROTEINS AND OTHER PROTEINS ON CALCIUM PHOSPHATE

In recent years there has been a considerable increase in the number of papers devoted to the chromatography of plasma and serum proteins on calcium phosphate gels.

The chromatography of the proteins of normal human serum on hydroxyapatite columns was studied in detail by Hjerten[3]. The protein components were found to leave the column in a definite order. It is of interest to compare the behaviour of serum proteins on hydroxyapatite columns with the behaviour of the same proteins during chromatography on ion-exchange cellulose. Work by Sober et al.[61] revealed the distribution of the components of human serum during chromatography on diethylaminoethyl cellulose.

Table 1 illustrates the behaviour of serum proteins during chromatography on hydroxyapatite and on diethylaminoethylcellulose columns. The order in which the serum proteins leave the column is different for hydroxyapatite and diethylaminoethylcellulose (Table 1). On elution from hydroxyapatite, $\alpha_1$-globulin and albumin appear first, and $\gamma$- and $\beta$-globulins appear last; whereas on

TABLE 1.

| Adsorbent | Components of serum proteins eluted from column | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5* |
| Hydroxyapatite | $\alpha_1$** | Al*** | $\alpha_2$** | $\gamma$** | $\beta$** |
| Diethylaminoethylcellulose | $\gamma$** | $\beta$** | $\alpha_1$** | Al*** | $\alpha_2$** |

* The figures give the order in which the proteins leave the column.
** Globulin.
*** Albumin.

diethylaminoethylcellulose columns, $\gamma$-globulin and $\beta$-globulin appear first, and albumin and $\alpha_2$-globulin appear last. On elution from columns of ion-exchange cellulose, proteins having higher isoelectric points appear before proteins with lower isoelectric points; whereas on elution from hydroxyapatite, this dependence on the isoelectric points of the proteins is not observed.

From this it follows that the principles of the separation of proteins on calcium phosphate gels and on ion exchangers based on cellulose are different, that the chromatography of proteins is different for these materials, and that these groups of sorbents cannot replace one another[3].

A number of workers have studied the behaviour of individual serum protein components during chromatography on calcium phosphate columns. The albumins of human serum[3,34], ox serum[10,62,63], and horse serum[17] have been studied by chromatographic methods.

Table 2 summarises data on the chromatography, on hydroxyapatite columns, of serum albumins from different sources. Albumins of different origin, on chromatography on hydroxyapatite, give three components which are always eluted from the columns at definite phosphate buffer concentrations (Table 2). The slight difference in the percentage ratio of components eluted can apparently be attributed to a difference in the purity of the original albumin specimens and to differences in the methods used to prepare the hydroxyapatites.

An interesting feature is that the chromatography of human serum albumin on ion-exchange cellulose[61] also

TABLE 2*.

| Albumin from serum | Phosphate buffer used for elution, M | | | Ref. |
|---|---|---|---|---|
| | 0.07 | 0.11 | 0.40 | |
| Ox | 50 | 30 | 20 | 10 |
| Ox | 50 | 37 | 13 | 62 |
| Ox | 67 | 25 | 8 | 63 |
| Horse | 67 | 21 | 12 | 17 |
| Human | 50 | 30 | 20 | 3 |
| Human | 62 | 28 | 10 | 34 |

* The figures give the percentage of protein eluted from the columns.

gives not less than three different components. The reason for the appearance of chromatographic heterogeneity in serum albumin is not completely clear.

Various workers have studied the behaviour of other serum proteins — $\alpha$-globulin[3,65], $\beta$-globulin[3], and $\gamma$-globulin[3,10] — on calcium phosphate columns. In chromatography on hydroxyapatite columns, $\gamma$-globulin usually gave three components, whose real existence was confirmed by further chromatographic study[10]. Columns of hydroxyapatite have been used to separate an electrophoretically rapid component of $\gamma$-globulin from a component of lower mobility[3]. A scheme has been proposed for the isolation of $\gamma$-globulin directly from serum by means of hydroxyapatite columns[3,64].

A number of papers have been devoted to the chromatography of ceruloplasmin on calcium phosphate columns[3,66-68]. This protein has been shown to be chromatographically heterogeneous[68]. The behaviour of fibrinogen from human plasma has been studied on calcium phosphate columns[69,70]. An interesting feature is that the chromatography of fibrinogen was found to be more satisfactory at room temperature than at +4°.[69]

Thus the behaviour of proteins both from whole serum and from its individual components has been studied in some detail on calcium phosphate columns, and a number of components have been shown to be heterogeneous.

Chromatography on calcium phosphate columns has been applied successfully not only to serum proteins but also to other proteins, such as milk albumin[71], egg albumin[10,17], milk proteins[72,73], egg proteins[74], saliva proteins[75], and soya-bean proteins[76,77]. Calcium phosphate gels have also been used for the chromatography of acid mucopolysaccharides (hyaluronic acid and chondroitin sulphuric acid[78]).

It has been found that acidic mucopolysaccharides are sorbed satisfactorily only by calcium phosphate precipitated under definite conditions at pH 9.2, whereas hydroxyapatite prepared by Tiselius' method[10] sorbs these proteins very weakly. This shows again the importance of standardising methods for preparing calcium phosphate sorbents and the possibility of variation in the properties of the latter.

Finally, a number of papers have been devoted to the use of calcium phosphate gels for the chromatography of hormones — insulin[79], lactogenic hormone from sheep hypophysis[80], the luteinising hormone from hypophysis[81], the follicle-stimulating hormone from hog hypophysis[82], and the hormone which stimulates the formation of sheep plasma erythrocytes[83].

These papers show that it is possible to separate and isolate various hormone proteins by means of calcium phosphate columns. In the case of insulin[79] and the luteinising hormone from sheep hypophysis[81], chromatography has shown the existence of several fractions exhibiting hormone activity. Chromatography on calcium phosphate has also been used to isolate and purify certain protein toxins[84,85].

## VI. THE CHROMATOGRAPHY OF NUCLEIC ACIDS AND VIRUSES ON CALCIUM PHOSPHATE GELS

Calcium phosphate gels have been used only fairly recently for the chromatography of nucleic acids. One of the first papers in this field is that by Semenza[86], who used hydroxyapatite for the chromatography of DNA from calf thymus. An interesting feature is that DNA is sorbed on hydroxyapatite much more strongly than are ordinary proteins. The chromatography of DNA from calf thymus on calcium phosphate columns has also been carried out by other workers[87].

The DNA eluted from the column appears a single sharp peak[86], in contrast to the results obtained, for example, on ECTEOLA cellulose[88], where considerable heterogeneity of the DNA was observed.

According to modern ideas, DNA from cells have very high molecular weights, and are apparently not divided into subunits, but form continuous polynucleotide chains[89]. In the chromatography of these structures, there is, of course, a real danger of fragmentation and disaggregation of the DNA molecules. It is not impossible that the appreciable heterogeneity of DNA of a given type, observed in chromatography on ECTEOLA cellulose, is due to breakdown of a single DNA molecule[90]. In this respect, calcium phosphate gels apparently have an advantage, since chromatography on the latter usually gives only one peak (or a maximum of two or three) for DNA.[87] Calcium phosphate gels have been used by other workers[18,91] for the chromatography of DNA.

It has recently been shown that chromatography on calcium phosphate columns can be used for the successful separation of mixtures of DNA and RNA.[92,93] A mixture of DNA from calf thymus and RNA from tobacco mosaic virus can be separated[92] in a single operation on a calcium phosphate column.

A good separation of mixtures of DNA and RNA isolated from *Salmonella typhimurium* bacteria has also been achieved[93]. Two peaks are obtained for RNA and one peak for DNA at the column outlet. This work shows the great importance of chromatographic methods using calcium phosphate columns for the separation of complex biological mixtures such as those formed by the nucleic acids. Fairly good separation of the nucleic acids is achieved.

Interesting work has been done on the chromatography of deoxyribonucleotides isolated from the spleen of normal mice and of mice subjected beforehand to radiation[94]: a considerable difference was observed in the elution profiles for the deoxyribonucleoproteins from the irradiated and normal animals. This work indicates new possibilities for the use of calcium phosphate columns and their ability to reflect structural differences between normal and pathological cell deoxyribonucleoproteins. Chromatography on calcium phosphate columns has been carried out not only with DNA but also with RNA from different sources, high-molecular RNA from the cells of Ehrlich's ascites tumour[95], RNA from rabbit liver[96], and soluble RNA from rat liver[97] and from *Escherichia coli* microbial corpuscles[98].

This last paper[98] reported chromatography on hydroxyapatite columns to separate, in one operation, soluble RNA specific to the amino-acids valine and phenylalanine. Development of work in this direction is of considerable interest for the preparation of different types of soluble RNA specific to individual amino-acids.

Noteworthy papers have recently appeared on the chromatography of virus RNA on calcium phosphate gels — RNA obtained from Krebs' ascites tumour cells infected with encephalomyocarditis virus[99], virus RNA isolated

from foot and mouth disease virus[100], and RNA from tobacco mosaic virus[92,101] – and in some of this work[99,100], the RNA was eluted from the column in several peaks. It should be noted, however, that calcium phosphate gels have as yet been comparatively little used for the isolation and characterisation of nucleic acids; nevertheless these sorbents are extremely effective for the chromatographic study of both RNA and DNA obtained from the most varied sources.

The use of adsorption column methods for the chromatography of viruses has been carried out successfully only in recent years. Chromatographic studies on calcium phosphate columns have been carried out for the viruses of influenza[102,103], herpes[104], encephalomyocarditis[105], and encephalitis[106,107], arbor viruses[108], adenoviruses[109], measles virus[110], and also plant viruses[101,111]. The use of column-chromatographic methods in the study of macromolecules such as virus molecules, which have a very high molecular weight and complex structure, presented considerable difficulties, but suitable techniques and adsorbents have been found, which make it possible to isolate virus nucleoproteins from a complex mixture of substances by column chromatography.

Experiments with individual viruses[100] have shown that the medium in which the virus to be tested is cultivated is of importance in chromatography. For example, the chromatographic behaviour of herpes virus depended on whether the virus had been grown in a cell culture or in a chick embryo cavity. Preliminary treatment of the test material with sodium ethylenediaminetetraacetate was also important[100].

Interesting work with arbor viruses[108] has shown that chromatography on calcium phosphate columns may be a convenient and simple method for preparing stable haemagglutinin and complement-fixing antigens, both for the diagnosis of these viruses and for the detailed study of their physicochemical properties.

With adenoviruses, for example, chromatography on calcium phosphate gels can be used for rapid determination of the virus type, using type-specific sera[109], and for the isolation of three different components of adenoviruses, giving the complement-fixing reaction[109]. This last feature has also been shown in the chromatography of adenoviruses on diethylaminoethylcellulose[112].

Finally, mention may be made of the chromatography of coliphages on calcium phosphate columns[113]. An interesting feature is that the ability of calcium phosphate gels to adsorb virus nucleoproteins is much more marked than that for bacteriophages[113].

## VII. THE FURTHER DEVELOPMENT AND FUTURE PROSPECTS OF THE CHROMATOGRAPHY OF BIOPOLYMERS ON CALCIUM PHOSPHATE

In recent years a number of papers have pointed out new possibilities for using calcium phosphate gels in the chromatography of biopolymers. It has been shown[10,99,114] that chromatography on calcium phosphate columns can probably differentiate biopolymer molecules according to molecular weight. Protein molecules of small dimensions are eluted from a column by a lower phosphate buffer concentration than are molecules of high molecular weight. Thus chromatography on calcium phosphate columns can be used for the approximate estimation of the molecular dimensions and weight of protein materials to be studied by chromatographic methods.

Interesting papers on the use of calcium phosphate sorbents[10,22] point out that chromatography on calcium phosphate columns can be used successfully to detect and observe the phenomenon of the association–dissociation of protein polymers in cases where these processes take place in a pH range the same as (or adjacent to) that in which the chromatographic process is carried out.

Calcium phosphate sorbents have also been applied in a completely different field[115,116]. It has been shown that chromatography on calcium phosphate can be used to follow the changes in the protein components of blood serum in certain illnesses. Thus the presence, in the patient's blood, of different fractions of the protein ceruloplasmin alters the chromatographic curve[115] and indicates different stages of the pathological process. Chromatography on calcium phosphate columns apparently provides a sufficiently sensitive and flexible method of study and can probably be widely used for the detection of various pathological changes in blood proteins in certain illnesses.

Calcium phosphate gels have found a very interesting application in the study of serological reactions[117,118]. It has been shown possible to study the reaction of an antigen with an antibody directly on the columns. Finally, recent work has revealed a new property of calcium phosphate gels, namely their ability to adsorb certain elements[119] and heavy-metal ions[120] from the surrounding medium.

A recent interesting discovery is related to the behaviour of calcium phosphate gels in the transfer of the calcium phosphate residues of nucleosides to the surface of these gels[121]. This transphosphorylation process may take place over wide ranges of temperature and of pH. It is apparently of definite importance in the chromatography of compounds containing free phosphate groups, which may take part in this reaction.

The above review of the chromatography of biopolymers on calcium phosphate gels shows the various fields of study in which columns of calcium phosphate gels may be used. Further study of the properties of these gels, extension of the range of their application, and detailed investigation of the mechanism of the chromatography of biopolymers on calcium phosphate columns are desirable.


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# REACTIONS OF ACETALS WITH UNSATURATED ETHERS

L. S. Povarov

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## I. INTRODUCTION

Acetals are a broad and readily available class of organic compounds, but for a long time they found no significant application in organic synthesis. The only synthetic reaction in which the acetal group was used was that between acetals and organomagnesium compounds discovered by Chichibabin[1]. But this reaction, occurring under severe conditions, at temperatures above 100°, did not find wide use. The main use of acetals was connected with the need to protect carbonyl groups, for example, in the synthesis of steroids[2]. Characteristically, acetals formed as intermediates in the industrial syntheses of alcohols from carbon monoxide and hydrogen are considered to be undesirable products and find only limited application[3].

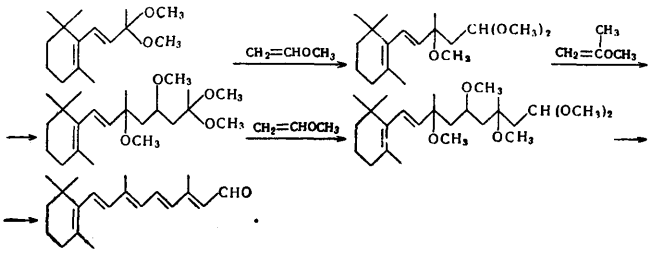
The position changed only after Müller-Cunradi and Pieroh's discovery[4], in 1939, of the reaction of acetals

with alkyl vinyl ethers under the influence of boron trifluoride. Ten years later Hoaglin and Hirsh[5], by defining the mechanism of the reaction, showed that it could be used for obtaining unsaturated aldehydes. After this, the reaction was intensively developed by the chemists of many countries and several patents and research works devoted to this reaction have appeared.

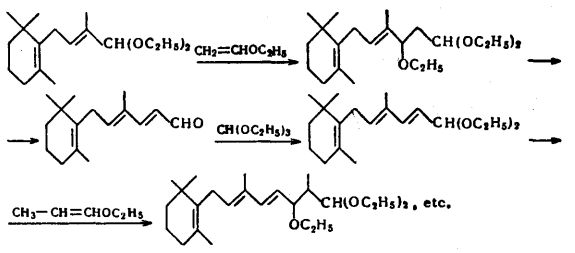
The preparation of unsaturated aldehydes by the reaction of acetals with alkyl vinyl ethers is brought about thus:

$$R{-}CH(OR')_2 + CH_2{=}CHOR' \longrightarrow R{-}(CH{-}CH_2)_n{-}CH(OR')_2 \longrightarrow R{-}(CH{=}CH)_n{-}CHO.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OR'$$

This method of synthesising polyene compounds was considered extremely promising and even one of the first patents, taken out by Copenhaver[6], contained the idea of using it to obtain Vitamin A. The essence of the proposed method was the successive condensation of $\beta$-ionone dimethyl acetal with methyl vinyl ether and isopropenyl methyl ether:



However, it is now clear that this scheme for obtaining vitamin A, which is masterly in its simplicity, is impracticable in that form and is evidently purely theoretical. Although there are others, the most unreal aspect of this scheme was the preparation of the initial acetal of $\beta$-ionone by the method described in the patent. It was only recently (1963) that Mikhailov and Povarov[7] obtained $\beta$-ionone acetal and described its properties and reaction with ethyl vinyl ether. In 1956 Isler[8] used a similar scheme to construct the $\beta$-carotene polyene chain, the starting point being not $\beta$-ionone acetal, but the acetal of the so-called $C_{14}$ aldehyde obtained from $\beta$-ionone; the route was rather complex:



Isler and coworkers[9-13], and also Inhoffen and Erdmann[14] used the same route to synthesise lycopene, zeaxanthin, cryptoxanthin, and several other carotenoids and intermediates. Mikhailov and Povarov used the reaction of acetals with alkyl vinyl ethers to synthesise difficultly accessible arylated polyene hydrocarbons[15-17].

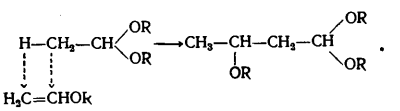
The success in the synthesis of polyene compounds encouraged the rapid increase in investigations in this direction and a further widening of the field of application of the new reaction. It was found that an extremely wide range of acetals and unsaturated ethers could be used in the reaction, and also some other unsaturated compounds with an activated double bond. For example, aliphatic or alicyclic saturated or unsaturated acetals, aromatic or heterocyclic acetals, cyclic acetals, ketals, ortho esters, etc. can be used as the acetal component. Alkyl vinyl ethers, unsaturated ethers which are substituted in the 1- or 2-positions, $\alpha\beta$-unsaturated sulphides, $\alpha\beta$-unsaturated cyclic ethers, alkoxydienes, ketens, ethoxyacetylenes, etc. can be used as the ether component. Zinc chloride, iron(III) chloride, aluminium chloride, etc. can be used instead of boron trifluoride as the catalyst.

All these facts show that the reaction of acetals with unsaturated compounds has great prospects for future development.

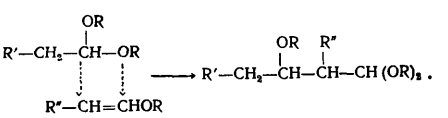
The progress achieved in investigating the reaction has already been partly surveyed in several reviews[18-20]; but there have been many new papers since then, some of which are of great interest. Furthermore it is now necessary to consider in greater detail the special features of the reaction mechanism in the light of the latest results and to generalise the information on the reactivity of acetals and ethers in this reaction. The present article is devoted to these questions.

## II. MECHANISM OF THE REACTION

Müller-Cunradi and Pieroh[4], on discovering the reaction of acetals with alkyl vinyl ethers, considered that the condensation proceeds through the mobile hydrogen of the acetal by the scheme:



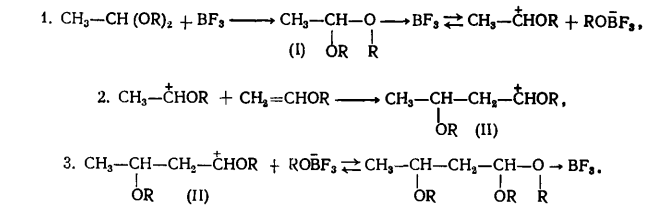
This seemed natural by analogy to some extent with the aldol condensation. However, in later work Hoaglin and Hirsh[5] found the error in this explanation without much difficulty, by performing the reaction with substituted acetals and substituted alkyl vinyl ethers. It transpired that the products are formed in accordance with another reaction scheme:



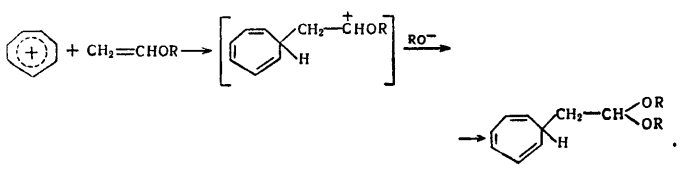
This mechanism was completely new to organic chemistry and there was no known analogy to it. Before long it received confirmation from the results of an investigation of the reactions of benzaldehyde dialkyl acetals with alkyl vinyl ethers[21,22]. In these reactions there were high yields of addition products whose formation under these circumstances was possible only by the second scheme.

Hoaglin and Hirsh[5] proposed the following scheme for the reaction mechanism with participation of the boron

trifluoride catalyst, and this was accepted subsequently by other investigators:



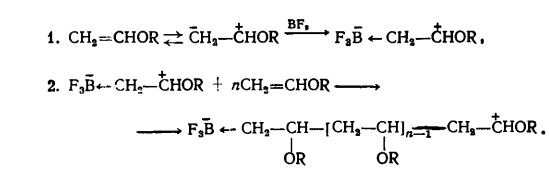
Vol'pin and coworkers[23] specially investigated the problem of the probability of a carbonium ion arising in a side reaction. For this purpose they studied the reaction of the stable tropylium ion with ethyl vinyl ether. It appeared that tropylium salts readily react with various vinyl ethers, and that the tropylium cation always attacks only the $CH_2$ group of the vinyl ether, to form a cycloheptatrienylacetaldehyde acetal:



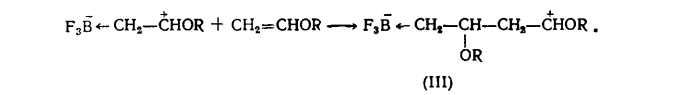
These results confirm the course of the reaction through the formation of a carbonium ion.

In simple vinyl ethers, when there is an alkoxy-group at the double bond not only is there an inherent negative induction effect but there is also a positive mesomeric effect due to the conjugation of the lone pair of electrons of the oxygen atom with the $\pi$ electrons of the double bond. The actions of these effects on the $\pi$ electrons are opposite but the mesomeric effect predominates in this instance, and as a result the electron density at the $\beta$ carbon atom is increased and consequently this atom acquires enhanced nucleophilic properties. Such a picture also holds with the analogues of simple vinyl ethers, such as cyclic unsaturated ethers of the dihydrofuran and dihydropyran type, alkoxydienes, $\alpha\beta$-unsaturated sulphides, and ketens. This can explain the high reactivity of these compounds towards electrophilic reagents, and particularly the carbonium ion produced by the action of boron trifluoride on acetals in accordance with the scheme given above, and the absence of this behaviour with unsaturated compounds having an electron-acceptor substituent at the double bond.

It is noteworthy that Hoaglin and Hirsh's ionic mechanism[5] for the reaction of acetals with vinyl ethers is reminiscent of the mechanism of cationic polymerisation, characteristic for the simple vinyl ethers[24]:

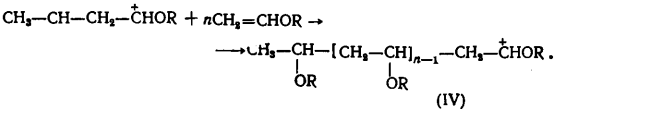


Evidently during the polymerisation a cation (III) analogous to cation (II) is produced:



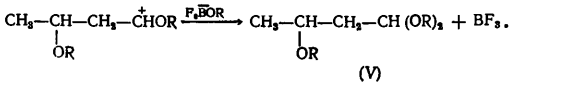
(III)

However, unlike cation (III), to which there is further addition of the vinyl ether during the polymerisation, the fate of cation (II) in the reaction of acetals with vinyl ethers can be different: in the presence of an excess of a vinyl ether it can serve as the initial link in a cationic polymerisation (first boundary case):



(IV)

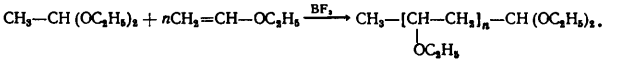
In the presence of a large excess of acetal, cation (II) is stabilised by addition of an alkoxy-group (another boundary case):



(V)

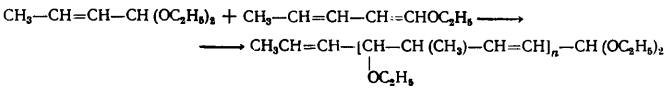
In real intermediate cases, a mixture of reaction products is formed, containing both (V) and (IV) with various values of $n$. For example, Hoaglin and Hirsh[5] obtained a curve (see Figure) for the dependence of the yield of the primary condensation product (a 1,1,3-trialkoxybutane) on the ratio of the initial acetal and vinyl ether.

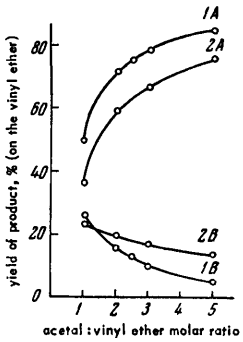
Makin and Sudakova[25] investigated the distribution of the addition products at different ratios of the initial reagents in the reaction:



Their results are in Table 1.

There are similar results for the reactions of unsaturated acetals with alkoxydienes, for example, for the reaction of crotonaldehyde diethyl acetal with 1-ethoxypenta-1,3-diene[26] (see Table 2):






Dependence of the yields of condensation products on the acetal : vinyl ether ratio: 1A) 1,1,3-trimethoxybutane; 2A) 1,1,3-triethoxybutane; 1B) 1,1,3,5-tetramethoxyhexane; 2B) 1,1,3,5-tetraethoxyhexane.

TABLE 1. Distribution of the addition products as a function of the reagent ratio.

$CH_3-[CH(OC_2H_5)-CH_2]_n-CH(OC_2H_5)_2$

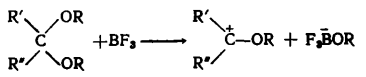
| Acetal : ether molar ratio | Yield of addition products, % | | | | | |
|---|---|---|---|---|---|---|
| | $n=1$ | $n=2$ | $n=3$ | $n=4$ | higher | total yield |
| 2 | 63 | 14.9 | 3.6 | 1.6 | — | 83.2 |
| 0.75 | 26.5 | 38.6 | 11.3 | 5.5 | 4.5 | 86.0 |
| 0.5 | 16.5 | 19.0 | 31.0 | 12.8 | 6.5 | 85.8 |
| 0.2 | 3.9 | 8 | 11.1 | 22.0 | 17.8 | 62.7 |

TABLE 2. Distribution of the addition products as a function of the ratio of initial reagents.

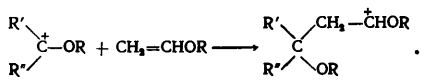
$CH_3CH=CH-[CH(OC_2H_5)-CH(CH_3)-CH=CH]_n-CH(OC_2H_5)_2$

| Ethoxydiene : acetal molar ratio | Yield of addition products, % | | | | |
|---|---|---|---|---|---|
| | $n=1$ | $n=2$ | $n=3$ | $n=4$ | total yield |
| 1:2 | 48 | 30 | 12 | 3 | 93 |
| 2:3 | 28 | 41 | 16.5 | 5 | 90.5 |
| 1:1 | 27 | 12 | 37 | 8.5 | 84.5 |
| 2:1 | 9.5 | 6 | 26.5 | 26.5 | 68 |

Hence the reaction of acetals with unsaturated ethers behaves as a reaction which is regulated by ionic telomerisation[27], in which the proportions of the products depend on the ratio of the initial reagents: the acetal (telogen) and the unsaturated ether (taxogen). However, the analogy with telomerisation reactions is not always observed. In the instances considered above, the addition of a molecule of the unsaturated compound to the type (I) cation led to the formation of a type (II) cation, differing little in reactivity from the initial cation (I). Moreover, it is obvious that the nature of the products formed will depend on the relation between the reactivities of cations (I) and (II) as well as on the ratio of the reagents. When the reactivity of cation (I) is extremely low in comparison with cation (II) then the reaction product will be a polymer. This occurs, for example, with certain acetals of ketones, the reaction being:

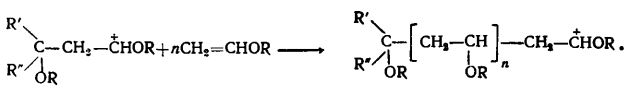


(VI)



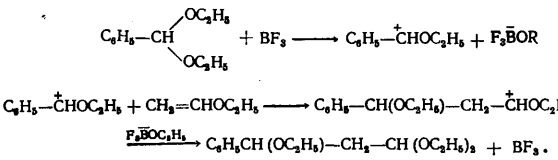
(VII)

The cation (VII) formed is much more reactive than cation (VI) and hence the further addition of the unsaturated ether is to (VII) (the first boundary case):

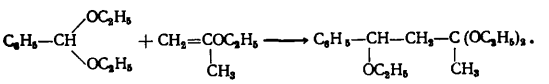


Thus, Mikhailov and Povarov[28] observed that in the reaction of the acetal of 4-ethoxy-6-methylhept-5-en-2--one with ethyl vinyl ether the primary reaction product — an acetal of 3,5-diethoxy-3,7-dimethyloct-6-enal (an acetal of diethoxycitronellal) — was formed in only insignificant quantities even when there was a large excess of the original acetal. Obviously the moderate yield of the product obtained on condensing an acetal of 6-methylhept-5--en-2-one with ethyl vinyl ether[29] was for the same reason.

When the reactivity of the initial type (I) cation is much higher than that of the newly formed type (II) cation (the opposite case to the previous one), a primary addition product of type (V) will be formed almost exclusively. An example of this is the condensation of benzaldehyde diethyl acetal with ethyl vinyl ether[22]. Even at a 1 : 1 ratio of the original reagents the primary condensation product (1,1,3-triethoxy-3-phenylpropane) is obtained in $>70\%$ yield, that is, the reaction proceeds mainly according to the scheme:



Another example is the condensation of a benzaldehyde acetal with ethyl isopropenyl ether[17]. Here the yield is still greater (81%) since the primary product formed — 1,3,3-triethoxy-1-phenylbutane — is even less reactive in subsequent condensations.



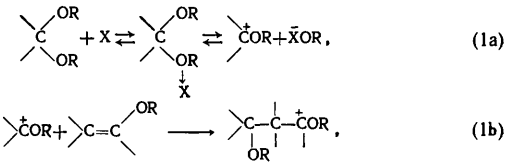
The reaction of acetals with $\beta$-bromovinyl ethers[30] and ketens[31] is also of this type, the products formed being incapable of further condensation. These reactions are considered in detail below.

Hence in these instances there is no analogy with telomerisations. In addition to the above factors the nature of the catalyst employed greatly affects the course of the reaction.

## III. EFFECT OF CATALYSTS

Lewis acids and metal chlorides are used as catalysts of the reaction; they include boron trifluoride[5], zinc chloride[8], iron(III) chloride[32-34], and also aluminium chloride, titanium(IV) chloride, and tin(IV) chloride[35], etc. The ether addition compounds of boron trifluoride and zinc chloride are most frequently employed, the latter in the form of solutions in ether, ethyl acetate, or acetic acid. Of the catalysts mentioned, boron trifluoride is the most effective, but its use is limited by its vigorous reaction with the initial acetals. For example, the acetals of the $\alpha\beta$-unsaturated series (in particular terpenes) undergo resinification in the presence of boron trifluoride. A milder catalyst in this sense is zinc chloride, particularly its solutions in ether and ethyl acetate. But it is not just a matter of the reactive nature of the catalyst with respect to the acetals.

As already mentioned, the reaction of the acetals with unsaturated ethers is connected with the dissociation of the acetals:



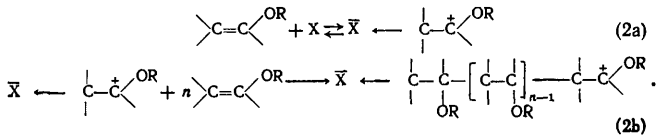
(1a)



(1b)

where X is the catalyst.

On the other hand the catalyst can cause direct cationic polymerisation of the unsaturated ether:



(2a)

(2b)

Usually the two reactions occur simultaneously but it is obvious that for the preferential occurrence of condensation by reaction (1b) it is necessary for dissociation by scheme (1a) to proceed more rapidly than the formation of the cation by scheme (2a), leading to polymerisation by Eqn. (2b). It is also evident that the ratio between the rates of reactions (1a) and (2a) will depend on the catalyst X. This can explain the fact that when ethyl isopropenyl ether reacts with an acetal of benzaldehyde in the presence of boron trifluoride the ether is polymerised according to Eqn. (2b) but in the presence of zinc chloride an addition product is formed according to Eqn. (1b) in high yield[17]. Consequently, with boron trifluoride ionisation according to scheme (2a) predominates, but with zinc chloride dissocation proceeds according to scheme (1a).

Other examples can be mentioned where the correct choice of catalyst was the deciding factor for successfully effecting the condensation. For example, 1-alkoxydienes condense with acetals almost exclusively in the presence of zinc chloride[28,36,37]. However, some acetals have not been condensed with unsaturated ethers, despite the use of a variety of catalysts. This demonstrates the low reactivity of acetals, for which their structure is responsible.

## IV. EFFECT OF ACETAL STRUCTURE

The reactivity of acetals has not been determined directly but it can be judged from how they participate in reactions with various types of unsaturated ethers. In polymerisations by scheme (2b) 1-substituted alkyl vinyl ethers are more reactive than the unsubstituted ethers[38,39]. 1-Alkoxydienes are still more reactive[40]. Hence from their tendency to polymerise, unsaturated ethers can be arranged in a series: vinyl ethers unsubstituted in the 1-position < 1-substituted vinyl ethers < 1-alkoxydienes. The tendency to ionisation by scheme (2a) will increase in the same sequence. Saturated acetals readily react with alkyl vinyl ethers unsubstituted in the 1-position according to scheme (1), but in their reaction with ethyl isopropenyl ether (ethyl 1-methylvinyl ether) and 1-alkoxydienes the polymerisation of the unsaturated ethers by scheme (2) predominate. Aromatic acetals react by scheme (1) with alkyl vinyl ethers, whether substituted or unsubstituted in the 1-position, but do not give addition products with 1-alkoxydienes. Finally, $\alpha\beta$-unsaturated acetals readily give addition products with all three types of unsaturated ethers. Consequently, here dissociation by scheme (1a) takes place most readily and predominates over ionisation by scheme (2a) with any of the unsaturated ethers mentioned. On this basis these types of acetals can be arranged in the following sequence of reactivity: saturated acetals < < aromatic acetals < $\alpha\beta$-unsaturated acetals. Moreover, this order agrees with the tendency of these acetals to hydrolyse. Table 3 shows the equilibrium constants determined by Hartung and Adkins[41] for the formation of acetals (the back reaction to hydrolysis). The decrease in $K$ corresponds to an increase in the tendency to hydrolysis. For acetals such as that of bromoacetaldehyde $K$ is high and this corresponds to the complete inability of this acetal to react even with ethyl vinyl ether by scheme (1). As a result of this reaction only a polymer by scheme (2) is formed. On the $\alpha\beta$-unsaturated acetals only acrolein acetal has an equilibrium constant higher than the aromatic benzaldehyde acetal. This suggests that acrolein acetel will be less able to condense with unsubstituted ethers, but there are no experimental results on this.

TABLE 3. Equilibrium constants for the reaction:

$$RCHO + 2\,ROH \rightleftarrows RCH(OR')_2 + H_2O$$

| R | $K$ | $-RT \ln K$ | R | $K$ | $-RT \ln K$ |
|---|---|---|---|---|---|
| $HClH_2N-CH_2-$ | 0.1340 | 119±200 | iso-$C_3H_7-$ | 0.0355 | 1980±30 |
| $BrCH_2-$ | 0.1121 | 1130±200 | $ClCH_2-CH_2-$ | 0.0294 | 2090±200 |
| $N\equiv C-CH_2-$ | 0.1070 | 1320±200 | $HOCH_2-$ | 0.0202 | 2300±200 |
| $C_6H_{13}-$ | 0.0970 | 1380±30 | $CH_2=CH-$ | 0.00455 | 3270±30 |
| $C_2H_5-$ | 0.0782 | 1510±30 | $C_6H_5-$ | 0.00163 | 3810±30 |
| $HClNH=CH-$ | 0.0770 | 1520±200 | $C_6H_5-CH=CH-$ | 0.00089 | 4160±30 |
| $CH_3-$ | 0.0744 | 1540±30 | $CH_3-CH=CH-$ | 0.00063 | 4360±30 |
| $C_3H_7-$ | 0.0691 | 1580±30 | | | |

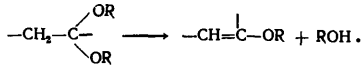
TABLE 4. Rate of hydrolysis of the acetals $R_1R_2C(OC_2H_5)_2$ in 49.6% dioxan + 50.4% water mixture at 25°.

| $R_1$ | $R_2$ | $k_2$ | $R_1$ | $R_2$ | $k_2$ |
|---|---|---|---|---|---|
| $CH_3$ | H | 0.248 | $ClCH_2$ | $CH_3$ | $8.60\times10^{-3}$ |
| $HOCH_2$ | H | $8.47\times10^{-4}$ | $C_2H_5OCH_2$ | H | $8.62\times10^{-4}$ |
| $C_6H_5$ | H | 0.267 | $C_6H_5CH_2$ | $CH_3$ | 8.45×10 |
| $C_6H_5CH_2$ | H | $8.70\times10^{-3}$ | $C_6H_5OCH_2$ | $CH_3$ | 0.350 |
| $ClCH_2$ | H | $1.03\times10^{-5}$ | $HOCH_2$ | $CH_3$ | 1.16×10 |
| H | H | $4.13\times10^{-5}$ | $CH_3COOCH_2$ | $CH_3$ | 0.228 |
| $CH_3$ | $CH_3$ | $7.52\times10^{2}$ | $BrCH_2$ | $CH_3$ | 0.138 |
| neo-$C_5H_{11}$ | $CH_3$ | $9.20\times10^{2}$ | $C_6H_5$ | H | 7.07 |
| $C_2H_5$ | $CH_3$ | $7.20\times10^{2}$ | $CH_3CH=CH$ | H | $2.98\times10^{2}$ |
| $C_6H_5CH=CH$ | H | $1.52\times10^{2}$ | | | |

## V. EFFECT OF TEMPERATURE

The possibility of influencing the course of the reaction with unsaturated ethers by changing the temperature is very restricted. Usually the reactions are performed within the limits 5–50°. On raising the temperature the reaction rate increases, but there is also a decrease in the stability of acetals sensitive to acids, both the initial acetals and those formed in the reaction. On heating, even in the

presence of insignificant amounts of acidic reagents, acetals readily decompose into unsaturated ethers and alcohols[28]:



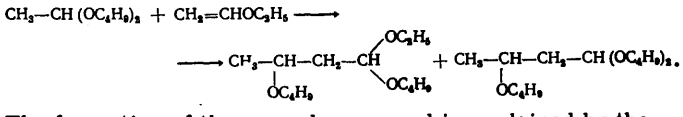
This determines the upper temperature limit of the reaction.

In many instances the reaction proceeds with evolution of heat and the reaction mixture must be cooled to avoid overheating. Occasionally, when the acetals are stable the reactants can be heated to 130–140°.[43] With highly reactive and acid-sensitive unsaturated compounds, such as 1-alkoxydienes and keten, the reaction takes place at reduced temperatures, in the last instance at -80°.[31]

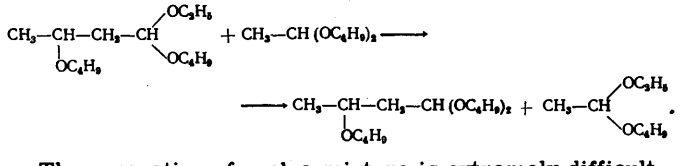
## VI. MIGRATION OF ALKOXY-RADICALS

Alkoxy-radicals in acetals exhibit great mobility and are able to migrate in the presence of acid catalysts[44,45]. This phenomenon also occurs in the reaction of acetals with unsaturated ethers under the influence of Lewis acids.

Hoaglin and Hirsh[5] showed that when an acetal and a vinyl ether have different alkoxy-groups the reaction results in the formation of a mixture containing products of the exchange of alkoxy-groups. For example, 1,3-dibutoxy-1-ethoxybutane and 1,1,3-tributoxybutane were isolated from the products of the reaction of 1,1-dibutoxyethane and ethyl vinyl ether:

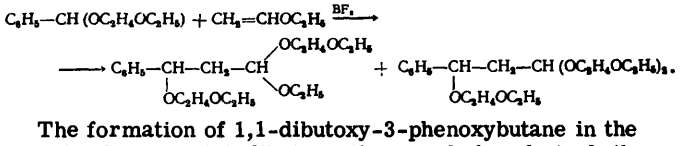


The formation of the second compound is explained by the reaction:

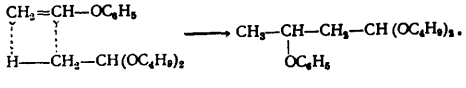


The separation of such a mixture is extremely difficult, therefore to obtain an addition product of known structure it is necessary to start with an acetal and an unsaturated ether with the same alkoxy-groups.

Povarov and Mikhailov[46] observed the migration of alkoxy-groups in studying the reaction of benzaldehyde bis-ethoxyethyl acetal with ethyl vinyl ether. They also obtained a mixture of products:

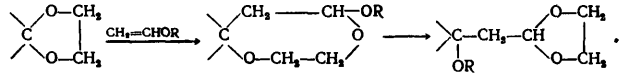


The formation of 1,1-dibutoxy-3-phenoxybutane in the reaction between 1,1-dibutoxyethane and phenyl vinyl ether, studied by Shostakovskii and Bogdanov[43], was evidently due to the migration of the phenoxy-group. The presence of this product in the reaction mixture led to authors to conclude that there was another mechanism for the reaction of acetals with phenyl vinyl ether:

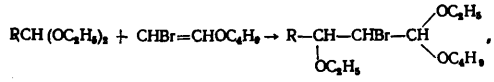


However, the formation of this product is undoubtedly due to the redistribution of the butoxy- and phenoxy-groups, particularly as the reaction is carried out at 120°.

Mikhailov and Povarov[47] showed that in the reaction of cyclic acetals with alkyl vinyl ethers the primary condensation product undergoes rearrangement, which can be explained by the intramolecular migration of alkoxy-groups:



The reaction of acetals with alkyl 2-bromovinyl ethers is another matter[30]. The course of this reaction is quite analogous to that for the alkyl vinyl ethers but there are several peculiarities. The condensation products are 2-bromoacetals in which the alkoxy-groups are only slightly mobile. The result is the absence of migration of alkoxy-groups, which was established by the example of the condensation of benzaldehyde diethyl acetal and 1,1-diethoxyethane with 2-bromovinyl butyl ether. Only the normal addition products were isolated; products of the migration of alkoxy-groups were not observed:

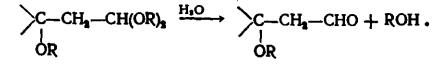


where R = $CH_3$ or $C_6H_5$.

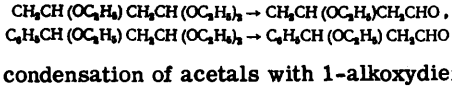
Another peculiarity of the reaction was the absence of products of secondary condensation with the unsaturated ether, also the result of the deactivating action of bromine in the 1-position on the mobility of alkoxy-groups.

## VII. HYDROLYSIS AND ELIMINATION OF ALCOHOL FROM ALKOXYACETALS

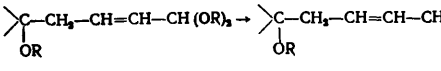
Usually the condensation products of acetals and unsaturated ethers — alkoxyacetals — are not used directly, but are hydrolysed to liberate aldehydes or ketones:



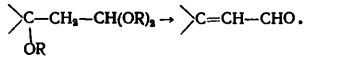
3-Alkoxyacetals are similar to saturated acetals as regards hydrolysis; they are hydrolysed by heating with aqueous acid. For example, 3-ethoxybutanal[5] and 3-ethoxy-3-phenylpropanal[22] were thus obtained:



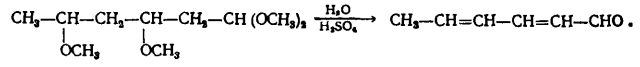
In the condensation of acetals with 1-alkoxydienes, $\alpha\beta$-unsaturated acetals are formed, which are readily hydrolysed in the presence of mineral acids in the cold[37]:



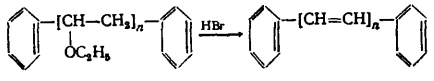
Often the hydrolysis of acetals is accompanied by the elimination of an alcohol with the aim of making unsaturated carbonyl compounds:



This is done in various ways. For example, hexa-2,4-dienal was obtained from 1,1,3,5-tetramethoxyhexane by boiling with 5% sulphuric acid[5]:

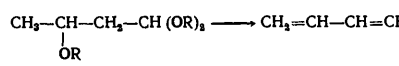


Usually under such conditions the reaction is accompanied by marked resinification, and therefore milder reagents and conditions are used, for example, heating with acetic acid in the presence of sodium acetate[8], heating with a dilute solution of phosphoric acid in dioxan[8], heating with a dilute solution of *p*-toluenesulphonic acid in toluene[37]. As Mikhailov and Povarov found[15-17], the best method of eliminating an alcohol from the diphenylpolyalkoxyalkanes, obtained as the products of the condensation of benzaldehyde acetals with vinyl ethers, consists of boiling with alcoholic hydrogen bromide:



where $n$ = 2, 3, 4, or 5.

Sometimes an alcohol is eliminated from alkoxyacetals in an anhydrous medium without hydrolysis. For example, 1-alkoxydienes are obtained from 1,1,3-trialkoxyalkanes in this way:



Mikhailov and Povarov[28] developed a liquid-phase method of carrying out this reaction under the action of *p*-toluenesulphonic acid in quinoline. Others have also employed this method[48].

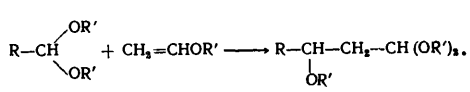
The earlier known method of vapour-phase splitting of 1,1,3-alkoxybutanes[40,49,50] were perfected by Nazarov and his coworkers[51] and used for the synthesis of several 1-alkoxydienes. Makin and Sudakova[52] employed it to make 1-ethoxyhexatriene and 1-ethoxyoctatetraene. The possibility of eliminating an alcohol from alkoxyaldehydes with aluminium oxide has also been demonstrated[53].

The above general rules for the reaction of acetals with unsaturated ethers do not exhaust the special features inherent in the reactions of various classes, which will be considered in the following Sections.

## VIII. REACTIONS OF ACETALS OF VARIOUS CLASSES

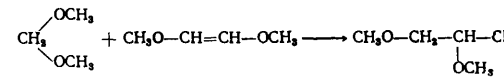
### 1. Reactions of Aliphatic Saturated Acetals

Aliphatic saturated acetals, in reacting with unsaturated ethers, form primary addition products in rather high yields (60–70%) when the reaction is carried out with a large (three- to five-fold) excess of the acetal[5]:

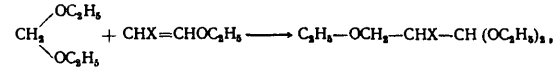


The 3-ethoxyacetals thus formed are also rather highly reactive in comparison with the initial acetals and, as they accumulate, compete with them for the molecules of vinyl ether, giving secondary addition products. When there is an excess of the vinyl ether, high-molecular-weight telomers are formed[33].

The simplest acetal, formaldehyde dimethyl acetal (methylal), was shown by Shostakovskii and coworkers[54] to react with 1,2-dimethoxyethylene, giving 1,1,2,3-tetramethoxypropane in 50% yield:

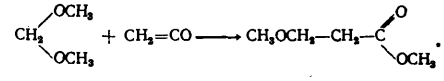


Formaldehyde diethyl acetal (ethylal) condensed with ethyl 2-chloro- and ethyl 2-bromo-vinyl ethers[55], addition products being obtained in high yields in each instance:



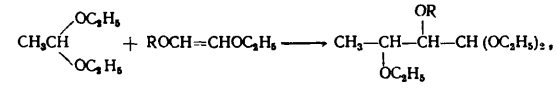
where X = Cl or Br.

Formaldehyde dimethyl acetal gives an addition product with keten[56], the yield being high:



The reaction is done in the presence of boron trifluoride between -60° and -80°.

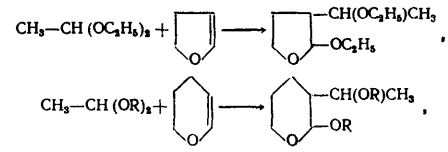
The reactions of acetaldehyde dialkyl acetals have been the most widely investigated. The dimethyl[5,57], diethyl[5,58], and dibutyl[32-34] acetals of acetaldehyde react smoothly with alkyl vinyl ethers. 2-Alkyl-substituted vinyl ethers react with an acetaldehyde acetal similarly to the unsubstituted vinyl ether — the substituent in the 2-position has no significant effect on the condensation[5,58]. However, addition products are not obtained with an alkyl 1-methylvinyl ether; the ether polymerises even in the presence of zinc chloride. Acetaldehyde acetal condenses with 1,2-diethoxyethylene and 2-ethoxy-1-phenoxyethylene at an initial component ratio of 1 : 1, giving a high yield of addition products according to the scheme[59]:



where R = $C_2H_5$ or $C_6H_5$.

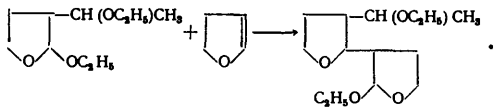
Obviously the ethoxy- or phenoxy-group in the 2-position to the acetal group deactivates the latter, preventing the formation of telomers.

Cyclic $\alpha\beta$-unsaturated ethers, such as dihydrofuran and dihydropyran, react with acetaldehyde dialkyl acetals to form derivatives of tetrahydrofuran and tetrahydropyran, respectively[60]:



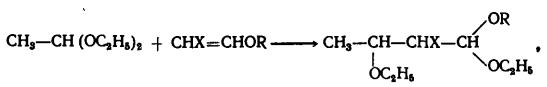
where R = $CH_3$, $C_2H_5$, or iso-$C_4H_9$.

Secondary condensation products are also formed:



However, the reactivity of the primary condensation products is less than for the initial acetaldehyde acetal, so that with a 1 : 1 ratio of the reagents there is a high yield of primary products (60–80%).

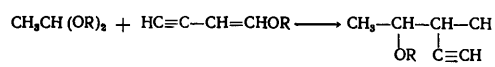
2-Chlorovinyl ethyl ether[55,61], 2-bromovinyl ethyl ether[30,55,61], and 2-bromovinyl butyl ether[30] react analogously to alkyl vinyl ethers with acetaldehyde diethyl acetal:



where X = Cl or Br and R = $C_2H_5$, or $C_4H_9$.

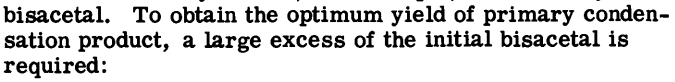
This reaction is interesting because the halogen in the vinyl ether neither reverses the order of addition of the acetal nor inhibits the reaction, although the presence of halogen atoms might be expected to change considerably the nature of the polarisation of the double bond.

Addition products of acetaldehyde acetals with 1-alkoxydienes have not been obtained. Under rigorous conditions (125–140°) alkyl 2-ethylvinyl ethers react according to the scheme[62]:



In the reaction of 1,1-dimethoxyethane with keten, methyl 3-methoxybutyrate is obtained as an addition product[63]. With diketen there is a complex reaction giving a mixture of three products[64].

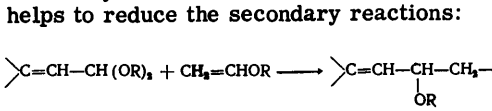
The acetals of propionaldehyde[58,56] and butyraldehyde[58] react with alkyl vinyl ethers analogously to acetaldehyde acetals. Vinyl ethers can also be condensed with saturated acetals of dialdehydes[66,67], for example, malonaldehyde bisacetal. To obtain the optimum yield of primary condensation product, a large excess of the initial bisacetal is required:



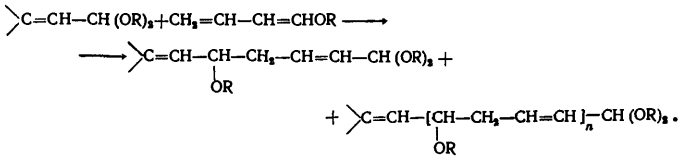
The bisacetal of glyoxal does not react with vinyl ethers under these conditions.

## 2. Reactions of Unsaturated Aliphatic and Alicyclic Acetals

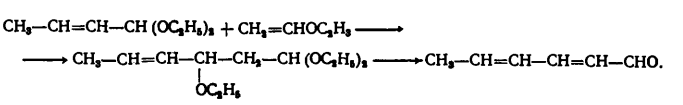
$\alpha\beta$-Unsaturated acetals readily add on to alkyl vinyl ethers[8–12], including also 1-substituted ethers[28,68], and give high yields of the addition products (sometimes over 90%). The reaction products here are 3-alkoxyacetals, whose reactivity is much less than that of the initial acetals, which helps to reduce the secondary reactions:



In addition, $\alpha\beta$-unsaturated acetals are able to add on to 1-alkoxydienes[28,37,69–72]. Addition at the 1,4-positions occurs and as a result of the reaction $\alpha\beta$-unsaturated acetals are regenerated, with reactivities similar to the original acetals. As a result, telomers are formed as well as the primary addition products:

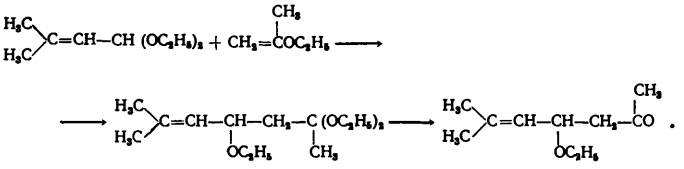


The reaction of $\alpha\beta$-unsaturated aldehydes is very widely used to make polyene compounds. Crotonaldehyde acetal reacts with ethyl vinyl ether in the presence of zinc chloride to form 1,1,3-triethoxyhex-4-ene, which on hydrolysis and elimination of ethanol gives sorbaldehyde[68]:

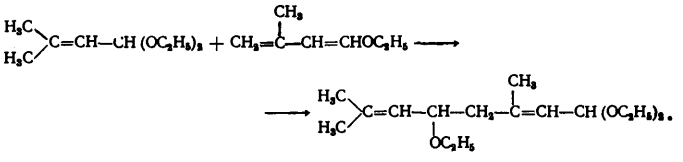


The reaction with ethyl isopropenyl ether also proceeds readily. The reactions of crotonaldehyde acetal with various 1-alkoxydienes, such as 1-ethoxybutadiene[70], 1-ethoxy-2-methylbutadiene and 1-ethoxy-3-methylbutadiene[73], and 1-ethoxypenta-1,3-diene[26], have also been studied.

3-Methylcrotonaldehyde acetal and ethyl isopropenyl ether form 2,2,4-triethoxy-6-methylhept-5-ene, in 60% yield, which on hydrolysis gives 4-ethoxy-6-methylhept-5-en-2-one[28]:

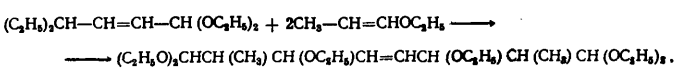


The latter was used in the synthesis of monoarylated polyene hydrocarbons[74]. The reaction of the ethyl acetal of 3-methylcrotonaldehyde with 1-ethoxybutadiene and 1-ethoxy-3-methylbuta-1,3-diene proceeds smoothly. The second combination gives an acetal of ethoxycitral[28,37]:

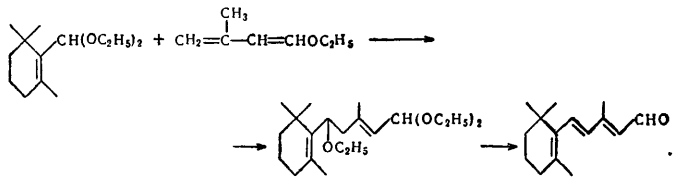


High yields of additions products are given by sorbaldehyde acetal with ethyl vinyl and ethyl isopropenyl ethers[68]. Products of the condensation of citral acetal with one and two molecules of 1-ethoxy-3-methylbuta-1,3-diene have been obtained[28].

The acetals of unsaturated dialdehydes react with unsaturated ethers to form addition products at both acetal groups[75–78], for example:

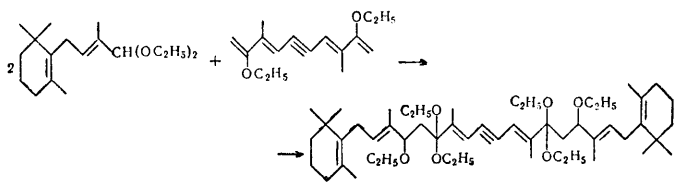


The $\alpha\beta$-unsaturated acetals of the alicyclic series react with unsaturated ethers quite analogously. For example, condensation products of cyclocitral acetal with 1-ethoxybutadiene and with 1-ethoxy-3-methylbuta-1,3-diene have been obtained[37]. From the latter reaction β-ionylideneformaldehyde [3-methyl-5-(2,5,5-trimethylcyclohex-1-enyl)penta-2,4-dienal (Ed. of Translation)], which is an intermediate in the production of Vitamin A, was isolated after hydrolysis and elimination of alcohol:



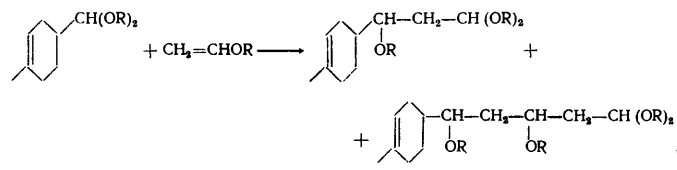
This synthesis path for β-ionylideneformaldehyde appears rather simple, but cyclocitral acetal itself is not readily available. Furthermore the reaction is complicated by the formation of telomers.

The reaction of $\alpha\beta$-unsaturated ethers with the acetal of 2-methyl-4-(2,6,6-trimethylcyclohex-1-enyl)but-2-enal — the so-called $C_{14}$ aldehyde — has been used for a series of syntheses of carotenoids. With ethyl vinyl ether the condensation product is formed in yields of up to 92%.[8] The bis-addition product of an acetal of the $C_{14}$ aldehyde with an unsaturated ether of such a complicated structure as 2,9-diethoxy-3,8-dimethyldeca-1,3,7,9-tetraen-5-yne has been obtained[79]:



The bis-addition product obtained was used to synthesise β-carotene. Apart from the $C_{14}$ aldehyde acetal, other analogous $\alpha\beta$-unsaturated alicyclic acetals have also been used for the synthesis of carotenoids[80,81]. The reaction of β-ionylideneformaldehyde acetal with 1-ethoxy-3-methylbuta-1,3-diene has been described[53].

Unsaturated cycloaliphatic acetals with the double bond distant from the acetal group react like saturated acetals. Thus, in the reaction of acetals of 4-methylcyclohex-3-enal with alkyl vinyl ethers a mixture of primary and secondary condensation products was obtained[82]:



where R = $C_2H_5$ or $C_4H_9$.

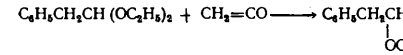
The yield of the primary condensation product is not high (~12%). Hence the double bond in the $\beta\gamma$-position does not activate the acetal group.

Acetals containing a triple bond in the $\alpha\beta$ position, such as propiolaldehyde acetal, do not react with unsaturated ethers.

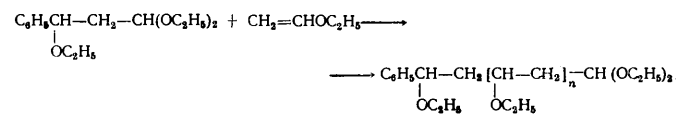
## 3. Reactions of Aliphatic-Aromatic and Aromatic Acetals

The reactions of acetals of the aliphatic-aromatic series with $\alpha\beta$ unsaturated ethers have been little studied. However, the available literature suggests that a phenyl ring in the 3-position in the acetal group no longer has any significant effect on the reactivity of the acetal and the reaction proceeds as for unsaturated aliphatic acetals.

Only condensation with keten has been described[63] for phenylacetaldehyde acetal. This reaction yields ethyl 3-ethoxy-4-phenylbutyrate:



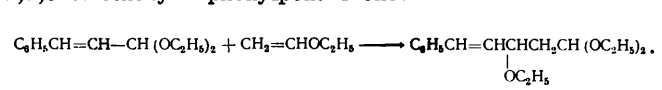
Mikhailov and Povarov[22] studied the reaction of 3-ethoxy-3-phenylpropanal acetal (obtained in the condensation of benzaldehyde acetal with ethyl vinyl ether) with ethyl vinyl ether. As a result they obtained a primary addition product 1,1,3,5-tetraethoxy-5-phenylpentane, in only 10% yield at a 1:1 ratio of the initial reagents and in 50% yield when the acetal was in threefold excess. In addition there was a telomerisation product:



where $n$ = 1, 2, or 3.

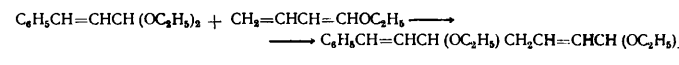
Analogously, in the condensation of 3-ethoxy-3-phenylpropanal acetal with ethyl propenyl ether 1,1,3,5-tetraethoxy-2-methyl-3-phenylpentane was obtained in 50% yield[17]. The reaction of 3-ethoxy-3-phenylbutanal acetal with ethyl vinyl ether has also been studied[72].

Aliphatic-aromatic acetals with a double bond in the $\alpha\beta$ position to the acetal group behave analogously to $\alpha\beta$ unsaturated aliphatic acetals in their reaction with unsaturated ethers. An example is the reaction of cinnamaldehyde acetal, which with ethyl vinyl ether and either boron trifluoride[47] or zinc chloride[69] readily forms 1,1,3-triethoxy-5-phenylpent-4-ene:



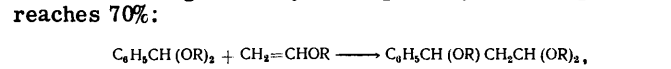
Methylcinnamaldehyde acetal also reacts smoothly with ethyl vinyl ether[72].

Like the aliphatic $\alpha\beta$-unsaturated acetals, cinnamaldehyde acetal reacts with 1-ethoxybutadiene, forming 1,1,5-triethoxy-7-phenylhepta-2,6-diene in good yield[69]:



Higher condensation products are also formed.

Of the aromatic acetals, the benzaldehyde dialkylacetals have been best studied as regards reaction with unsaturated ethers. In the presence of boron trifluoride, the dimethyl acetal[21] and diethyl acetal[22] form with alkyl vinyl ethers 3-alkoxy-3-phenylpropanal acetals, and even at a 1:1 molar ratio of the reagents the yield of primary addition product reaches 70%:



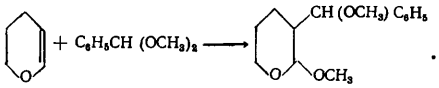
where R = $CH_3$ or $C_2H_5$.

Products of further condensation are also formed in small quantities, but their yield is insignificant, as the reactivity of 3-alkoxy-3-phenylpropanal acetals is much less than that of the original benzaldehyde acetal. Condensation with ethyl isopropenyl ether in the presence of zinc chloride[17] is even better and as a result a 4-ethoxy-4--phenylbutan-2-one acetal is formed in 81% yield. However, benzaldehyde acetals do not give addition products with 1-alkoxydienes under these conditions, which shows that although the aromatic acetals surpass the saturated acetals in reactivity they are less reactive than the $\alpha\beta$-unsaturated acetals. However, benzaldehyde acetal evidently reacts with alkoxydienes such as 3-ethoxy-1-phenylbuta-1,3--diene. This was explained[83] by the formation of 3,3,5-triethoxy-1,5-diphenylpent-1-ene:

$$C_6H_5CH(OC_2H_5)_2 + C_6H_5CH{=}CHC(OC_2H_5){=}CH_2 \longrightarrow C_6H_5CH{=}CHC(OC_2H_5)_2CH_2CH(OC_2H_5)C_6H_5.$$

As this equation shows, the addition to the alkoxydiene here takes place at the 1,2 positions of the conjugated diene system. Benzaldehyde bisethoxyethyl acetal — readily obtainable from benzaldehyde and Ethyl Cellosolve — gives an addition product with ethyl vinyl ether[46].

The reaction of benzaldehyde dimethyl acetal with the cyclic unsaturated ether dihydropyran, leads to the 2-methoxy-3-(methoxyphenylmethyl)tetrahydropyran[60]:



Benzaldehyde acetal reacts with alkyl 2-halogenovinyl ethers in the presence of boron trifluoride to form 3-alkoxy-2-halogeno-3-phenylpropanal acetals in high yields. The reactions are carried out either at 50°[30] or at higher temperatures (100–200°).[84] The halogen atom evidently makes the 3-alkoxy-2-halogeno-3-phenylpropanal acetal stable not only as regards further condensation but also to decomposition at high temperatures.

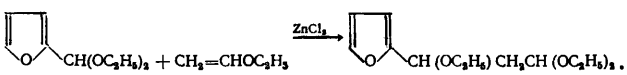
Esters of 3-ethoxy-3-phenylpropionic acid were obtained by reaction of keten with benzaldehyde acetal[63].

A mixed acylal benzaldehyde acetal also reacts with keten, esters of 3-ethoxy-3-phenylpropionic acid again being formed[85].

The reaction of terephthalaldehyde bisacetal with ethyl vinyl ether simultaneously at both acetal groups has also been described[86].

## 4. Reaction of Heterocyclic Acetals

Only a few representatives of the heterocyclic aldehydes have been studied in reactions with unsaturated ethers. Mikhailov and Ter-Sarkisyan[69] showed that furfural acetal reacts with ethyl vinyl ether to give (similar to benzaldehyde acetal) 3-ethoxy-3-furylpropanal acetal in high yield even at a 1:1 ratio of the initial reagents:



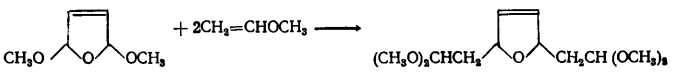
5-Nitrofurfural acetal reacts analogously[87].

Unlike benzaldehyde acetal, furfural acetal gives an addition product with 1-ethoxybutadiene, although the yield of the primary addition product is very moderate (23.7% on the converted acetal and ~5% on that taken).[69] Secondary condensation products are also formed. This is evidence of the somewhat higher reactivity of furfural acetal.

3-(Fur-2-yl)acrolein acetal reacts smoothly with ethyl vinyl ether, like an $\alpha\beta$-unsaturated acetal, and with 1-ethoxybutadiene, forming 1,1,3-triethoxy-5-(fur-2-yl)-pentene in 74.6% yield with the former and 1,1,5-triethoxy--7-(fur-2-yl)hepta-2,6-diene in 40.4% yield with the latter[69].

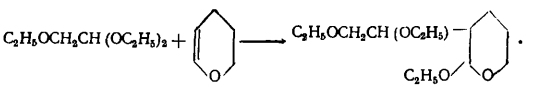
We must also remember the reaction of tetrahydro-4--keto-2,2-dimethylpyran diethyl acetal with ethyl vinyl ether, leading to 4-(2,2-diethoxyethyl)-4-ethoxytetrahydro--2,2-dimethylpyran[88].

The unusual heterocyclic bisacetal 2,5-dihydro-2,5-dimethoxyfuran has been shown to react with methyl vinyl ether, forming addition products at both acetal groups[89]:



## 5. Reactions of Substituted Acetals

Functional substituents have most effect only when they are situated at the 2-carbon atom with respect to the acetal group. More distant substituents do not affect the reactivity significantly. For example, 2-ethoxyacetaldehyde acetal does not condense with ethyl vinyl ether under ordinary conditions, while the vinyl ether polymerises[60]. 2-Ethoxyacetaldehyde acetal gives an addition product with dihydropyran but the yield (37%) is only half that for acetaldehyde acetal:



2-Bromoacetaldehyde acetal also does not form an addition product with ethyl vinyl ether[90].

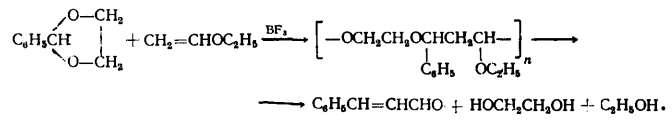
Mikhailov and Povarov[30] noted that acetals such as 1,1,3-trialkoxy-2-bromo-3-phenylpropane and 1,1,3-trialkoxy-2-bromobutane do not react with unsaturated ethers.

As already mentioned, the presence of an alkoxy-substituent in the 3-position to the acetal does not affect its reactivity. The presence of an ethoxycarbonyl group in the 3-position also does not affect the reactivity of crotonaldehyde acetal, which reacts with ethyl vinyl ether to form the ethyl ester of 1,1-diethoxy-2-methylbut-2-en-4-oic acid[91]. An addition product is formed similarly by 6,6-diethoxyhexanoic ester with ethyl vinyl ether[92]. 3,3-Dichloroacrolein, 5,5-dichloropenta-2,4-dienal, and 7,7-dichlorohepta-2,4,6-trienal acetals react smoothly with vinyl ethers[83,84]. Their behaviour does not differ from that of the corresponding unsubstituted, unsaturated acetals.

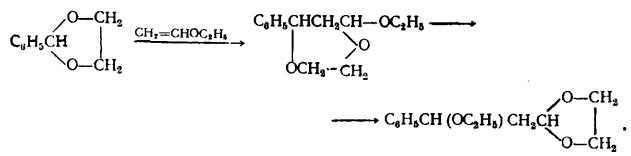
## 6. Reactions of Cyclic Acetals

Because of the special structure of the acetal group, cyclic acetals react uniquely with unsaturated ethers. It has been shown[47] that the reaction of benzaldehyde ethylene acetal [2-phenyl-1,3-dioxolan (Ed. of Translation)] in the

absence of a solvent leads to a polymer which in the presence of mineral acids is readily hydrolysed and splits off an alkoxy-group, giving cinnamaldehyde:

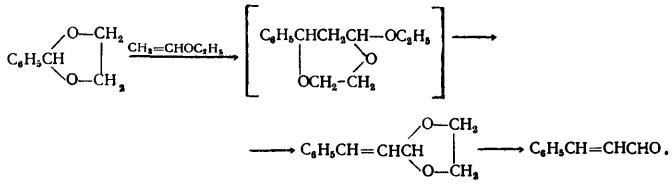


When the reaction is carried out in dilute solution an unstable primary condensation product can be isolated as a mixture with the stable isomer formed by rearrangement:



Aliphatic cyclic acetals and ketals† react analogously [95].

Reactions of cyclic acetals with alkyl vinyl ethers are used for the synthesis of several unsaturated aldehydes and ketones. The ethylene acetals of benzaldehyde, cinnamaldehyde, and 3-ethoxycarbonyl-2-methylacrolein have been condensed with ethyl vinyl and ethyl propenyl ethers, as also has been β-ionone ethylene ketal [96]. Different conditions were used to treat the reaction mixture and ethylene acetals were isolated from the reaction products hydrolysed further to the corresponding unsaturated aldehydes and ketones, for example:

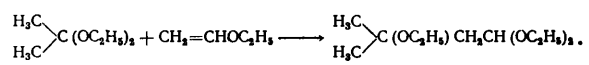


The mechanism of formation of cinnamaldehyde ethylene ketal (2-styryl-1,3-dioxolane) is not completely clear.

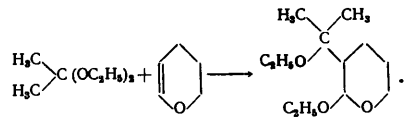
## 7. Reactions of Ketals†

The reactions of ketals with αβ-unsaturated ethers proceed mainly by analogy with the reactions of acetals, but at the same time are distinguished by special features.

2,2-Diethoxypropane with ethyl vinyl ether forms 1,1,3-triethoxy-3-methylbutane:

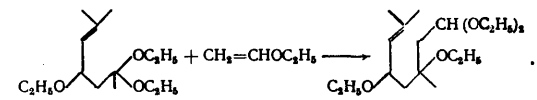


The reaction was performed in the presence of boron trifluoride both at 50° [89] and under milder conditions (at 5°) [51]. Reaction with methyl vinyl ether [21] and ethyl propenyl ether [88] have also been described. 2,2-Diethoxybutane reacts with ethyl vinyl ether analogously to 2,2-diethoxypropane [88]. 2,2-Diethoxypropane forms an addition product with dihydropyran [60]:



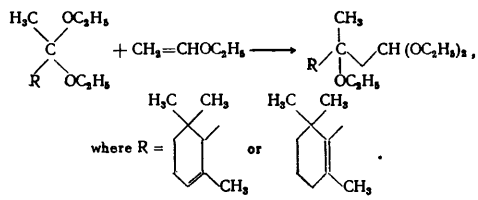
The ketals of cyclic ketones (cyclopentanone, cyclohexanone, pyranone) react with alkyl vinyl ethers by the usual scheme [88].

Ketals have frequently been used to synthesise terpene derivatives. Thus diethoxycitronellal acetal was obtained by condensing 2,2,4-triethoxy-6-methylhept-5-ene with ethyl vinyl ether [28]:



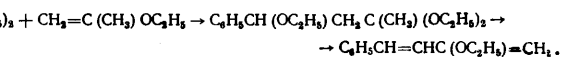
By condensing 2,2,4-triethoxy-6-methyl-hept-5-ene with ethyl vinyl ether, 1,1,3-triethoxy-3,7-dimethyloct-6-ene was obtained similarly, and was converted into citral by hydrolysis and the elimination of ethanol [29].

Mikhailov and Povarov [7] obtained ketals of α- and β-ionones and condensed them with ethyl vinyl ether:



The acetals obtained were converted into α- and β-ionylideneacetaldehydes.

In several instances the reactions of ketals are accompanied by elimination of alcohol, as ketals are more sensitive to the action of acid agents. For example, it has been reported that 1,3,3-triethoxy-1-phenylbutane formed by the reaction of benzaldehyde acetal, is partly converted into 3-ethoxy-1-phenylbutadiene by the elimination of the elements of the alcohol [83]:



This work also showed that 1,3,3-triethoxy-1-phenylbutane does not condense very well with ethyl vinyl ether.

Mikhailov and Ter-Sarkisyan [72] observed the formation of acetaldehyde acetal in the reaction of 1,1-diethoxy-1-phenylethane with ethyl vinyl ether, which was explained by the reaction of ethyl vinyl ether with the alcohol eliminated from the reaction product.

As already noted, cyclic ethylene ketals of acetone and ionone react with ethyl vinyl ether in a similar manner to cyclic acetals [96].

## 8. Reactions of Ortho-Esters

Ortho-esters — of which esters of orthoformic acid and, to a lesser extent, orthoacetic acid have been studied

† This name has been abandoned by IUPAC (Ed. of Translation).

— form addition products (bisacetals) with various $\alpha\beta$-unsaturated ethers, including 1-substituted ethers:

$$CR(OR')_2 + CH_2{=}CHOR' \rightarrow RC(OR')_2CH_2CH(OR')_2,$$

where R = H or $CH_3$.

At the same time they are evidently incapable of forming addition products with alkoxydienes. This is evidence that ortho-esters are more reactive than saturated acetals but less reactive than $\alpha\beta$-unsaturated acetals. That is, just the same as aromatic acetals. As with aromatic acetals, even at a 1 : 1 ratio of the initial reagents (ortho--ester and vinyl ether) the yield of the primary addition product is high (~ 75%) despite the fact that the addition product formed is a bisacetal capable of further addition. However, its reactivity is evidently less than that of the original ortho-ester.

Hultquist[97] brought about the first reactions using an orthoformic ester and ethyl vinyl ether. In later years many patents were taken out for the use of this reaction to synthesise bisacetals[98-113].

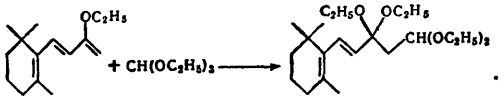
Protopova and Skoldinov[66] made a detailed study of the reaction between ethyl orthoformate and methyl vinyl, ethyl vinyl, propyl vinyl, and butyl vinyl ethers. They found that in addition to the primary addition product the products of further condensation are formed, for example, the bisacetal of ethoxyglutaraldehyde [1,1,3,5,5-pentaethoxypentane (Ed. of Translation)]:

$$CH(OC_2H_5)_3 + CH_2{=}CHOC_2H_5 \rightarrow (C_2H_5O)_2CH[CH_2CH]_n CH_2CH(OC_2H_5)_2,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OC_2H_5$$

where $n$ = 0, 1, 2, or over.

Yanovskaya and coworkers[114] brought about the reaction of triethyl orthoformate with ethyl propenyl, ethyl isopropenyl, ethyl 1,2-dimethylvinyl, cyclohexenyl ethyl, and 2-bromovinyl ethyl ethers. Whereas with vinyl ethers unsubstituted in the 1-position the reaction proceeds with 75% yields, the yield with methyl-substituted ether was appreciably less (35%). In the same work the reaction between orthoacetic ester and ethyl isopropenyl and 1,2-dimethylvinyl ethyl ethers was studied.

Orthoformic ester is capable of adding on to 1-substituted vinyl ethers of complex structure. Thus, it has been shown[115] that ethers of the enolic forms of $\alpha$- and $\beta$-ionones react with orthoformic ester. For example, the reaction for the ether of the $\beta$-ionone enol proceeds thus:



It was also found[116] that orthoformic ester reacts with keten to form an ester of 3,3-diethoxypropionic acid:

$$CH(OC_2H_5)_3 + CH_2{=}CO \rightarrow (C_2H_5O)_2CHCH_2C(=O)OC_2H_5.$$

The reaction of orthoformic ester with diketen is more complex[114].

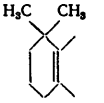
The addition of an ortho-ester to 1-chloro-1,2-diethoxyethylene has been described[117].

9. Reactions of Thioacetals

Mikhailov and Ter-Sarkisyan[118,119] investigated the reaction of thioacetals with ethyl vinyl ether. It appeared that thioacetals of aldehydes such as benzaldehyde, cinnamaldehyde, cyclocitral in the presence of boron trifluoride or zinc chloride react with ethyl vinyl ether by the same scheme as acetals:

$$RCH(SC_2H_5)_2 + CH_2{=}CHOC_2H_5 \longrightarrow RCH(SC_2H_5)CH_2CH\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix},$$

where R = $C_6H_5$, $C_6H_5CH{=}CH-$, or



The yields of the primary addition products are considerably less than for the corresponding acetals. The formation of secondary condensation products is also noted. The example of 1-ethoxy-1,3-bisethylthio-3-phenylpropane showed that monothioacetals react with ethyl vinyl ether with loss of an alkylthio-group and not of an alkoxy-group:

$$C_6H_5CH(SC_2H_5)CH_2CH\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix} + CH_2{=}CHOC_2H_5 \longrightarrow$$
$$\longrightarrow C_6H_5CH(SC_2H_5)CH_2CH(OC_2H_5)CH_2CH\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix}.$$

Even earlier, the reaction of trithioorthoformic ester with ethyl vinyl ether was investigated, also in the presence of boron trifluoride. This reaction leads to 1-ethoxy--1,3,3-trisethylthiopropane[120]:

$$CH(SC_2H_5)_3 + CH_2{=}CHOC_2H_5 \longrightarrow (C_2H_5S)_2CHCH_2CH\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix}.$$

Later the trithioorthoformic esters were condensed with ethyl vinyl and butyl vinyl esters and also with ethyl vinyl and phenyl vinyl sulphides[121]. The last gave bisthioacetals of malonaldehyde:

$$CH(SC_2H_5)_3 \xrightarrow{CH_2{=}CHSC_2H_5} (C_2H_5S)_2CHCH_2CH(SC_2H_5)_2$$
$$CH(SC_2H_5)_3 \xrightarrow{CH_2{=}CHSC_6H_5} (C_2H_5S)_2CHCH_2CH\begin{matrix}SC_2H_5\\SC_6H_5\end{matrix}.$$

## IX. RELATED REACTIONS

The progress in the investigation and application of the reactions of acetals with unsaturated ethers has entailed the realisation of a whole series of conversions of analogous nature, involving acetals, aldehydes, unsaturated ethers, and alkenes.

1. Reactions of Acetals with Alkenes

Several studies have shown that under the influence of boron trifluoride, acetals are capable of addition to alkenes just as they do to unsaturated ethers. With unsaturated

ethers the reaction proceeds in such a way that the alkoxy--group adds on to the 1-carbon atom of the ether.

The $\alpha$ carbon atom in unsymmetrical alkenes has a lower electron density than the 1-carbon atom of unsaturated ethers, therefore the order of the addition is the reverse. This corresponds to the orientation observable in the reaction of formaldehyde with alkenes[122]. For example, in the reaction of methylal with propene the main reaction product is 1,3-dimethoxybutane[123]:

$$CH_3OCH_2OCH_3 + CH_3CH{=}CH_2 \xrightarrow{BF_3} CH_3CH(OCH_3)CH_2CH_2OCH_3\ (39\ \%).$$

The reaction of methylal with 2-methylprop-2-ene, styrene, and $\alpha$-pinene is similar. With styrene, 1,3-dimethoxy-1--phenylpropane is formed in 72% yield. With ethylal these alkenes react more slowly. The reaction of acetals of acetaldehyde and higher aldehydes with 2-methylprop-1--ene is still more difficult. For example, in the reaction of acetaldehyde acetal the "normal" product of the addition — 2,4-diethoxy-2-methylpentane — was obtained in a yield of only 15.5%. Several other products were also obtained[124]:

$$CH_3CH(OC_2H_5)_2 + (CH_3)_2C{=}CH_2 \xrightarrow{BF_3} CH_2{=}C(CH_3)CH_2CH(OC_2H_5)CH_3 +$$

$$+ CH_3C(CH_3)(OC_2H_5)CH_2CHCH_3 + CH_3CH(OC_2H_5)C(C_2H_5O)=CH_2 + CH_3CH(OC_2H_5)CHCH_3 + (CH_3)_3COC_2H_5.$$

The reaction of ortho-esters with alkenes is of considerable interest. Copenhaver[125] took out a patent on the addition of ortho-esters to 2-methylprop-1-ene, indene, and cyclopentadiene. Another patent[126] described the reaction of trithioorthoformic ester with styrene in the presence of boron trifluoride at 50°.

The condensation of triethyl orthoformate with styrene[114] proceeds thus:

$$C_6H_5CH{=}CH_2 + CH(OC_2H_5)_3 \rightarrow C_6H_5CH(OC_2H_5)CH_2CH(OC_2H_5)_2.$$

but the yield of 1,1,3-triethoxy-3-phenylpropane does not exceed 5%, most of the styrene remaining unchanged.

## 2. Reaction of Aldehydes with $\alpha\beta$-Unsaturated Ethers

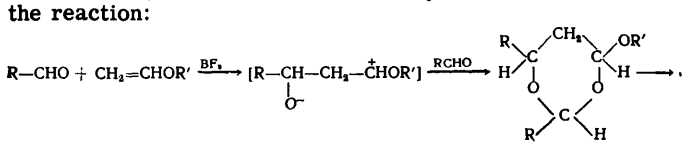
A considerable number of investigations[127-137] concern the reaction of aldehydes with $\alpha\beta$-unsaturated ethers. The mechanism of this reaction is somewhat similar to that of the reaction of cyclic acetals with vinyl ethers. As a result, a polymer is formed, the acid hydrolysis and destruction of which leads to unsaturated aldehydes:

$$R{-}CH{=}O + CH_2{=}CHOR' \xrightarrow{BF_3} R{-}CH(O{\cdot}BF_3){-}CH_2{-}CH(OR'){\rightarrow}$$

$$\rightarrow [-OCH(R){-}CH_2{-}CH(OR'){-}]_n \xrightarrow{H^+} R{-}CH{=}CH{-}CHO.$$

In this way, cinnamaldehyde was obtained in 60% yield from benzaldehyde and ethyl vinyl ether[127].

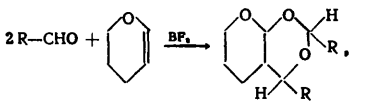
Saikachi and Ogawa[87] and Hoaglin and Hirsh[128] have shown that 1,3-dioxan derivatives may be intermediates in the reaction:



$$\rightarrow R{-}CH{=}CH{-}CHO + R{-}CHO + ROH.$$

Such an intermediate was isolated in the reaction with *p*-nitrobenzaldehyde[87]. An intermediate could not be isolated when furfural was used.

The reaction was also extended to cyclic unsaturated ethers. As it transpired[133], butyraldehyde and isobutyraldehyde react with dihydropyran to form 2,4-dipropyl- and 2,4-diisopropyl-hexahydropyrano[2,3-*d*]-*m*-dioxin respectively, with ~59% yields, according to the scheme:



where R = n-$C_3H_7$ or iso-$C_3H_7$.

It was also shown[130-132] that, depending on the aldehyde and catalyst, the reaction can go in another direction, with formation of alkoxyaldehydes. For example, in the condensation of crotonaldehyde with ethyl vinyl ether 3-ethoxyhex-4-enal was obtained in 46% yield:

$$CH_3{-}CH{=}CH{-}CHO + CH_2{=}CHOC_2H_5 \longrightarrow CH_3{-}CH{=}CH{-}CH(OC_2H_5){-}CH_2{-}CHO.$$

There are several patents on the use of this reaction[127-129], from which it appears that it can be employed with both aliphatic saturated and unsaturated aldehydes and also aromatic and heterocyclic aldehydes.

Krasnaya and Kucherov[134] showed that aldehydes also react with 1-alkoxydienes:

$$RCH{=}CHCHO + CH_2{=}C(R'){-}CH{=}CHOR'' \xrightarrow{BF_3}$$

$$\rightarrow RCH{=}CHCH(OR'')CH_2C(R'){=}CHCHO + RCH{=}CH[CH(OR'')CH_2C(R'){=}CH_2]CHO.$$

The reactions were carried out with crotonaldehyde, dimethylacrolein, citral, benzaldehyde, and furfural. The yields sometimes exceeded 40%.

Arens and his coworkers[135,136] found that aldehydes, and also ketones, are able, in the presence of boron trifluoride, to react with ethoxyacetylene and form esters of unsaturated acids:

$$R_2C{=}O \ldots BF_3 + HC{\equiv}COC_2H_5 \longrightarrow \left[R_2C(O{\cdot}BF_3){-}CH{=}C{-}OC_2H_5\right] \longrightarrow$$

$$\rightarrow R_2C{=}CHCOOC_2H_5.$$

Krasnaya and Kucherov[137] also used in this reaction such unsaturated aldehydes and ketones as crotonaldehyde, heptadienone, cyclocitral, etc., the yields of addition products reaching 67%.

## 3. Autocondensation of Acetals

Under the influence of boron trifluoride or zinc chloride acetals of saturated aldehydes dimerise with loss of a molecule of alcohol[138]:

$$R{-}CH(OC_2H_5)_2 + R{-}CH_2CH(OC_2H_5)_2 \xrightarrow{BF_3 \text{ or } ZnCl_2}$$

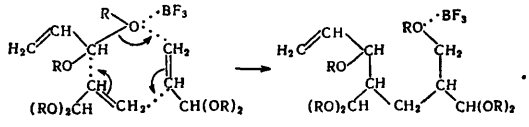
$$\rightarrow R{-}CH(OC_2H_5)CH(R)CH(OC_2H_5)_2 + C_2H_5OH.$$

1,1,3-triethoxybutane can be obtained by this reaction with yields of up to 50%.

The dimerisation of the acetals of $\alpha\beta$-unsaturated aldehydes takes place by addition at the double bond:

$$2R{-}CH{=}CH{-}CH(OR')_2 \longrightarrow R{-}CH{=}CHCH(OR')\overset{R{-}CH{-}OR'}{\overset{|}{C}}HCH(OR')_2.$$

For example, crotonaldehyde diethyl acetal gives a dimer of the above structure with a yield of up to 80%. Yufit and Kucherov[139] made a detailed study of the autocondensation of acrolein acetal and found that the dimer is obtained in 5–10% yield, the main product of the reaction being a trimer, whose formation they explained by the following mechanism of cyclic electron transfer in a six-membered ring:



The formation of a trimer here seems to be a self-contained reaction taking place in parallel with the formation of the dimer.

## 4. Autocondensation of Vinyl Ethers

Vinyl ethers are known to polymerise extremely readily in the presence of Friedel-Crafts catalysts[44], but low-molecular-weight polymerisation products have not been obtained. Hoaglin and coworkers[140] found that the use of boron trifluoride in conjunction with mercury(II) acetate enables polymerisation to be avoided and dimers, trimers, and tetramers of alkyl vinyl ethers obtained. Polymers are also formed but in reduced amounts. The products of the dimerisation are unsaturated acetals and ketals. The authors suggested that the mercury(II) acetate participated in the formation of the dimers thus:

$$CH_2{=}CHOC_2H_5 + Hg(OCOCH_3)_2 \rightleftarrows CH_2{-}\underset{\displaystyle HgOCOCH_3}{\underset{|}{C}}H{-}CH\begin{matrix}OC_2H_5\\OCOCH_3\end{matrix} \xrightarrow{CH_2=CHOC_2H_5}$$
$$\rightarrow CH_2{-}\underset{\displaystyle HgOCOCH_3}{\underset{|}{C}}H(OCOCH_3)CH_2CH(OC_2H_5)_2 \rightarrow$$
$$\rightarrow CH_2{=}CHCH_2CH(OC_2H_5)_2 + Hg(OCOCH_3).$$

The formation of trimers and tetramers evidently takes place as a result of the reaction of the acetals thus obtained with the alkyl vinyl ether by the usual mechanism. The dimer of ethyl vinyl ether — a vinylacetaldehyde acetal — was obtained in 72% yield, ethyl but-1-enyl ether gave a dimer in 30% yield, and ethyl isopropenyl ether gave only 11% yield.

The autocondensation of vinyl ethers has also been described in a Japanese patent[141]. In this work the autocondensation of methyl vinyl and ethyl vinyl ethers with catalysts such as boron trifluoride/mercury(II) acetate and boron trifluoride/mercury(II) oxide was studied.

Makin and Kruptsov[142] studied several complex catalysts, such as boron trifluoride/mercury(II) sulphate, iron(III) chloride/mercury(II) oxide, iron(III) chloride/mercury(II) acetate, and zinc chloride/mercury(II) oxide. The best results were obtained with boron trifluoride/mercury(II) acetate and boron trifluoride/mercury(II) oxide. With the last, the reaction mechanism is thought to be:

$$HgO + CH_2{=}CHOR \rightleftarrows CH_2{-}\underset{\displaystyle Hg{-}O}{\underset{|}{C}}HOR \xrightarrow{CH_2=CHOR}$$
$$\longrightarrow CH_2{-}\underset{\displaystyle Hg{-}O}{\underset{|}{C}}H{-}CH_2{-}CH(OR)_2 \longrightarrow CH_2{=}CHCH_2CH(OR)_2.$$

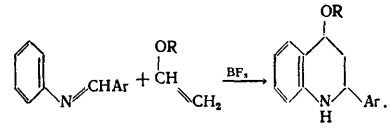
The authors investigated the autocondensation of ethyl vinyl, butyl vinyl, and pentyl vinyl ethers.

Apart from acetals and their sulphur analogues (thioacetals), nitrogen derivatives of carbonyl compounds, such as imines, have been used in the reaction with $\alpha\beta$-unsaturated ethers. Povarov and Mikhailov[143] showed that imines react with ethyl vinyl ether in an acetic acid medium; the reaction has many similarities to that with acetals and leads to 3-*N*-alkyl- or 3-*N*-aryl-aminoacylals (I). When the latter are split they give, like the 3-alkoxyacetals, an unsaturated aldehyde:

$$C_6H_5CH{=}NR \xrightarrow{H^+} [C_6H_5\overset{+}{C}H{-}NHR] \xrightarrow[-OCOCH_3]{CH_2=CHOC_2H_5}$$
$$\longrightarrow C_6H_5CH(NHR)CH_2CH\begin{matrix}OC_2H_5\\OCOCH_3\end{matrix} \xrightarrow[-RNH_2]{H_2O} C_6H_5CH{=}CHCHO.$$
(I)

where R = $-CH_2CH{=}CH_2$, iso-$C_4H_9$, or $C_6H_5$.

The same authors[144] found that in the presence of boron trifluoride, aromatic imines (Schiff bases) also react with $\alpha\beta$-unsaturated ethers, but here the reaction not only occurs at the carbonyl group, but also by addition of the $\alpha\beta$-unsaturated ethers in the 1,4 position to the diene system formed by the aromatic ring and the iminomethine group:



This reaction will not be discussed in this review.

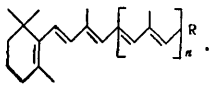
# X. SYNTHESES BASED ON THE REACTION OF ACETALS WITH $\alpha\beta$-UNSATURATED ETHERS

## 1. Synthesis of Isoprenoid Systems

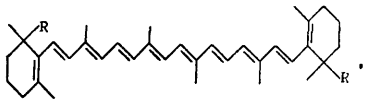
The use of the reaction of acetals with unsaturated ethers in the synthesis of isoprenoid systems seemed especially fruitful. Here above all mention must be made of the many papers and patents of Isler and his coworkers[8-13,145-160] and certain other patents[161-164]. With this reaction the authors obtained a series of yellow and red carotenoid pigments. The isoprenoid chain was built up by successive condensations of the initial acetals with ethyl propenyl and ethyl vinyl ethers:

$$RCH(OR')_2 \xrightarrow{CH_3CH=CHOR'} RCH(OR')CH(CH_3)CH(OR')_2 \xrightarrow[H_2O]{H^+}$$
$$\longrightarrow RCH{=}C(CH_3)CHO \xrightarrow{CH(OR)_3} RCH{=}C(CH_3)CH(OR')_2 \xrightarrow{CH_2=CHOR'}$$
$$\longrightarrow RCH{=}C(CH_3)CH(OR')CH_2CH(OR')_2 \xrightarrow[H_2O]{H^+}$$
$$\longrightarrow R\dot{-}CH{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH\dot{-}CHO, \text{ etc.}$$

By combining the reaction of acetals and unsaturated ethers with the Reformatski and Wittig reactions and with the acetylene synthesis, Isler and his coworkers obtained, in high yields, β-carotene, lycopene, zeaxanthin, cryptoxanthin, and other carotenoids of the type:

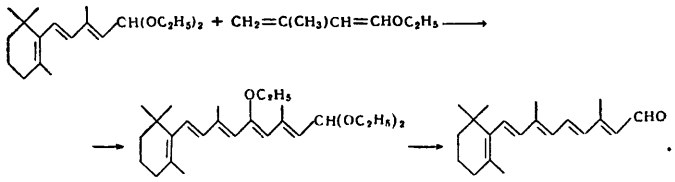


This method was also used to synthesise homologues of carotene[165]:



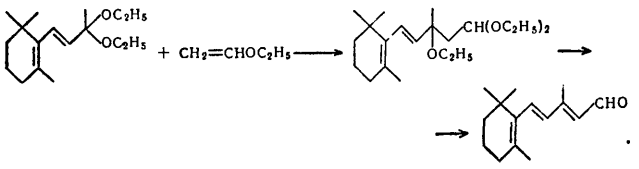
where R = $C_2H_5$ or iso-$C_4H_9$.

Krasnaya and Kucherov[53] arrived at the aldehyde of Vitamin A, by using the reaction of 1-ethoxy-3-methylbuta-1,3-diene with the acetal of β-ionylideneacetaldehyde:



Vitamin A itself was also obtained by reduction of the aldehyde.

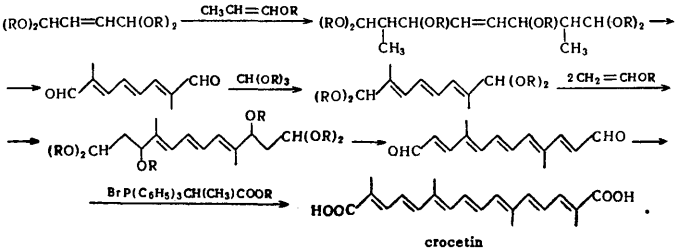
Mikhailov and Povarov[7] obtained an intermediate product in the synthesis of Vitamin A — β-ionylideneacetaldehyde — by condensation of β-ionone ketal with ethyl vinyl ether:



The condensation of acetals and ketals with unsaturated ethers has been used in the synthesis of bicyclodehydrofarnesenic acid[166], pseudoirone[67], citral[29], dihydrocitral[37], etc.

## 2. Synthesis of Unsaturated Dicarboxylic Acids

Isler and his coworkers[75,168] developed methods of synthesising polyene dicarboxylic acids, such as crocetin, and bixin. For this they used the reaction of bisacetals with ethyl propenyl and ethyl vinyl ethers in conjunction with subsequent Wittig reactions with a carbethoxyethylenephosphorane:

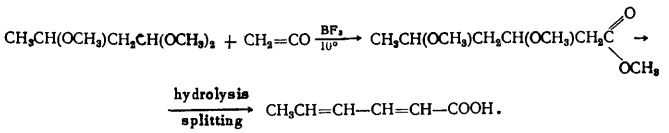


crocetin

Bixin was obtained by an analogous path.

Kucherov, Yanovskaya, and their coworkers[78,169-171] developed a path for synthesising polyenedicarboxylic acids of the corticrocin type containing either an even or an odd number of bonds in the chain, also providing a combination of the bisacetal condensation and the Wittig reaction.

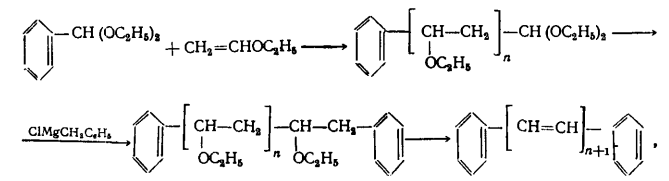
A convenient method of obtaining monobasic polyene acids is the reaction of 3-alkoxyacetals with keten[172]:



The yield of sorbic acid reaches 85%.

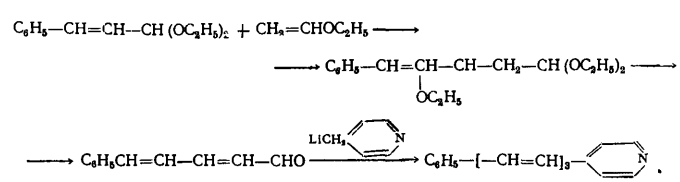
## 3. Synthesis of Arylated Polyene Hydrocarbons

Mikhailov and coworkers[15-17,36,74,173] developed new methods of synthesising arylated polyene hydrocarbons on the basis of the condensation of acetals with alkyl vinyl ethers and alkoxydienes. After Kuhn's well-known work, diphenylpolyenes from 1,4-diphenylbutadiene to 1,10-diphenyldecapentaene were obtained for the first time[15]:



where $n$ = 1, 2, 3, or 4.

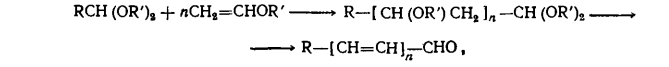
In addition, unsymmetrical diarylpolyenes[16], diphenylpolyenes methylated in various positions[17], and monoarylated polyenes[74] have been obtained. Mikhailov and Ter-Sarkisyan[173] obtained polyenes with heterocyclic substituents, by using phenylpolyenals obtained by the condensation of cinnamaldehyde acetal with ethyl vinyl ether or 1-ethoxybutadiene:



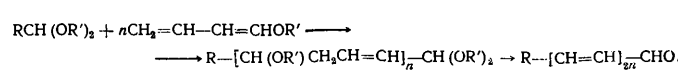
Arylated polyenes are of interest as organic luminophores.

## 4. Synthesis of Polyenals and 1-Alkoxypolyenes

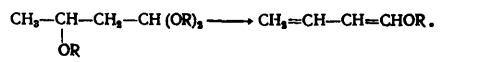
An extremely large number of syntheses of polyene aldehydes and ketones which previously were inaccessible or obtained with difficulty have been effected by the scheme:



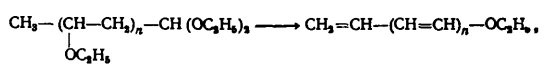
or by use of 1-alkoxydienes by the scheme:



Alkoxyacetals are now widely used to make 1-alkoxydienes, which are valuable intermediates in several syntheses:



Polyenes and other higher 1-alkoxypolyenes have been obtained by using the corresponding polyalkoxyacetals[25]:



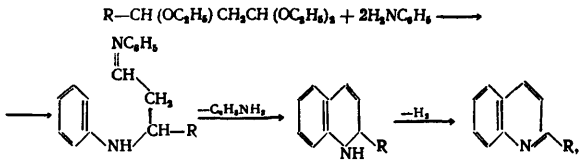
where $n$ = 2, 3, or 4.

5. Synthesis of Quinolines

$\gamma$-Ethoxyacetals of the type:

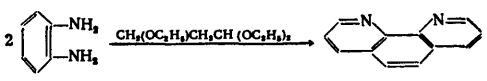


which can be obtained[65] by condensations with alkyl vinyl ethers, give quinoline derivatives on reacting with aromatic amines. By analogy with the suggested mechanism of the quinaldine synthesis, the reaction mechanism can be represented as follows:



where R = H, $CH_3$, $C_2H_5$, or $C_6H_5$.

With diamines, phenanthrolines are formed similarly:



The examples given do not exhaust all the fields of use of the reactions of acetals with unsaturated ethers.


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# THE OXIDATIVE AMMONOLYSIS OF ORGANIC COMPOUNDS

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## I. INTRODUCTION

Oxidative ammonolysis is a new catalytic process that combines the reactions of oxidation and ammonolysis. Each of these catalytic reactions has long attracted attention as very suitable for the technological design of methods of synthesising oxygen- and nitrogen-containing compounds; in these processes cheap raw materials, such as atmospheric oxygen and ammonia, may be used.

Catalytic oxidation of organic compounds was used as early as at the beginning of the twentieth century for the preparation of phthalic anhydride, anthraquinone, maleic anhydride and formaldehyde[1,2]. The replacement of expensive oxidising agents by air in the synthesis of these products was economically favourable; for this reason, a large number of papers appeared which described attempts to extent this method of synthesis to more and more organic compounds of different types. Apart from the development of new oxidative processes that found use in industry[3-10], much information was obtained on the mechanism of the reactions occurring. In particular it was shown that catalytic oxidation on oxide catalysts proceeds by a radical mechanism through a large number of intermediate stages comprising parallel and successive oxidations of the initial products and of stable and unstable intermediate products[11-15].

The catalytic ammonolysis of organic compounds has been less studied, but in this field, too, there is a fairly extensive literature[16-38]. As Andrussov showed, nitriles can be obtained directly from hydrocarbons by this reaction[39]. Catalytic ammonolysis of saturated hydrocarbons is effected in the vapour phase, as a rule, on oxide catalysts[28,29,40,41]; in contrast to the oxidation, it requires higher temperatures (500–1000°) and the yield of desired products (nitriles) generally does not exceed 20–25%. Ammonolysis of alkenes proceeds under somewhat milder conditions (400–600°)[32,42-44], but here the yield of nitriles is also low (up to 50%). The yield of nitriles is higher (up to 90%) in the ammonolysis of carboxylic acids under comparatively mild conditions[45], when the reaction may be carried out in the liquid phase in the presence of homogeneous and heterogeneous catalysts; the yield is not low even in the absence of a catalyst[45].

If ammonia is introduced into the reaction zone during the catalytic oxidation of naphthalene, phthalimide is formed in up to 50% yield instead of phthalic anhydride[47]. In the 1950's Erchak and Cosby and coworkers[48,50], and also Klimatis and Rasmussen[51,52] observed the formation of nitriles in the catalytic oxidation of alkenes, naphthene hydrocarbons, and alkylbenzenes in the presence of ammonia. Similar observations were made in the oxidation of pyridine homologues[53]. Oxides and salts of metals activated with carbon, silica gel, etc. were recommended as catalysts; the reaction could also be carried out without a catalyst. The yields of the corresponding aliphatic and aromatic nitriles never exceeded 50%, that is, they were the same as in catalytic ammonolysis.

On the other hand nitrogen-containing products were not observed when hydrocarbons, including *p*-cymene and cumene, were oxidised in the vapour phase[54,55].

Thus, up to 1950, there were only scattered observations indicating the possibility of preparing nitrogen-containing products by the catalytic oxidation of hydrocarbons in the presence of ammonia. However, there was no information in the literature on the mechanism of the reactions or on the part played by oxygen, ammonia, and catalysts in the process.

Systematic investigation of the catalytic oxidation of organic compounds of different classes in the presence of ammonia began only in the 1950's.[56-62] Experimental results showed that, when oxygen and ammonia are present simultaneously in the reaction zone, very complex parallel and successive coupled oxidations and ammonolyses of both the hydrocarbons and intermediate products occur. Oxidation takes a leading part in the process; because it proceeds by chain reactions, stable and unstable intermediates (free radicals, aldehydes, acids, etc.) that react readily with ammonia are accumulated. On the other hand, under the conditions of catalytic oxidation, ammonia too is easily converted into more active products, such as hydrazine and free radicals, which can react with hydrocarbons and intermediate products of their oxidation.

From such an interpretation of the mechanism of this complex process it received the name oxidative ammonolysis[57-59]. In recent years in non-Soviet literature the similar term "ammoxydation" has appeared[63,64] and the term "cyanodemethylation" has been used for a special case[65].

Oxidative ammonolysis is said to be used on an industrial scale for the preparation of acrylonitrile[66].

## II. OXIDATIVE AMMONOLYSIS OF AROMATIC HYDROCARBONS

As mentioned above, catalytic oxidation in the presence of ammonia in the aromatic series was first carried out by Wohl[47]. Using fused vanadium(V) oxide as a catalyst, he obtained phthalimide from naphthalene in 50% yield. Later it was shown that, under conditions of oxidative ammonolysis, naphthalene can also be converted into the *o*-phthalodinitrile. According to patent information[67], phthalodinitrile is formed in 88% yield (based on starting material)

when a catalyst of vanadium(V) oxide precipitated on aluminium oxide is used together with a naphthalene : ammonia : oxygen molar ratio of 1 : (4–20) : (9–40) at a reaction temperature of ~425°. In addition to vanadium(V) oxide, the reaction is catalysed by the oxides of molybdenum, chromium, cobalt, iron, manganese, copper, tin, tungsten, thorium, aluminium, and uranium. Air may be used instead of oxygen.

A method has also been proposed for the synthesis of benzonitrile from naphthalene[68,69]. The process is effected in two stages. In the first, naphthalene is oxidised to phthalic anhydride in the absence of ammonia on a vanadium oxide catalyst promoted by potassium sulphate. Ammonia (3–5 moles per mole of naphthalene) is added to the hot gases issuing from the convertor and they are passed over porous silica gel at 390–430° in a second reactor. The yield of benzonitrile is ~70%.

Benzonitrile is more conveniently synthesised by the oxidative ammonolysis of monoalkylbenzenes.

Toluene can be converted into benzonitrile by the action of air and ammonia over a wide range of conditions and on a variety of catalysts. At 480–550° the reaction goes even on silicon oxide and aluminium oxide or on activated carbon, but the yield of benzonitrile is then low[51,52]. Catalysts consisting of oxides of metals of variable valency are much more active. Moreover, they enable the reaction to be carried out at lower optimal temperatures, and, as a result, the proportion of pyrolysis by-products is reduced. For example, on a catalyst of oxides of vanadium, molybdenum, and phosphorus in the proportions 11.4 : 3.9 : 0.034 and with a feed of 2 moles of ammonia and 75 moles of air per mole of toluene and a temperature range of 430–450°, benzonitrile was obtained in 75 mole % yield; the total conversion of starting material was 95%.[50] Satisfactory results were also obtained with vanadium(V) oxide precipitated on alumina[70] or on aluminium oxide that had been heated to 1250°.[60,61] However, the best catalysts appear to be tin and titanium vanadates, on which the yield of benzonitrile reaches 89–90% of the theoretical based on toluene taken[71,73]. It is recommended that 6–10 moles of ammonia and 50–60 moles of oxygen (as air) should be used per mole of hydrocarbon.

The introduction of chlorine atoms into the aromatic nucleus appears to complicate the conversion of the methyl group into a nitrile group; according to Koopman[74,75], 2,6-dichlorotoluene gives the dichlorobenzonitrile in only 45–50% yield.

Tin and titanium vanadates may also be recommended for the preparation of benzonitrile from other monoalkylbenzenes. On a vanadium oxide catalyst ethylbenzene is converted into benzonitrile in only 53% yield[60,61], but on tin vanadate the reaction goes practically completely (93–96%)[71,73]. Cumene behaves in the same way; the yield of benzonitrile from it reaches 98%.[71,73] When n-propyl- and n-butyl-benzenes are used, the yield of benzonitrile is somewhat lower; phthalimide[73] in 15% yield is one of the products of oxidative ammonolysis of these hydrocarbons. Commercial mixtures of monoalkylbenzenes containing ethyl-, propyl-, and butyl-benzenes, which are difficult to separate, are also used for the preparation of benzonitrile. As a result of the oxidative ammonolysis of these so-called "polyalkyls", which are by-products of ethylbenzene and cumene production, benzonitrile is formed at the rate of 700–750 g per kilogramme of starting material[71,73]. It should be mentioned that, with other optimal conditions, the concentration of oxygen in the reaction gases has the greatest effect on the yield of benzonitrile from monoalkylbenzenes (Fig. 1)[73].

Great attention has been paid to the oxidative ammonolysis of *p*- and *m*-xylenes. Hydrogenation of the terephthalodinitrile and isophthalodinitrile formed gives *p*- and *m*-xylylenediamine[76–79], which are used as raw materials in the preparation of a variety of polyamides with melting points up to 300° and higher[80–83], and this has attracted the attention of research workers. Moreover, these aromatic dinitriles may be hydrolysed to free terephthalic and isophthalic acids or to various intermediate products with mixed functions[84,85].

A patent of Cosby and Erchak[50] shows that a mixed catalyst of oxides of vanadium, molybdenum, and phosphorus does not make the process selective enough; as a result oxidative ammonolysis of *p*-xylene on this catalyst gives *p*-toluonitrile and terephthalodinitrile at the same time, each in yield of not more than 25–26%.

By analogy with the monoalkylbenzenes the oxidative ammonolysis of *p*-xylene proceeds smoothly on fused tin vanadate[86]. It is characteristic that on this catalyst the degree of conversion of *p*-xylene can be controlled by changing the ratio of the components of the initial reaction mixture, the contact time and the reaction temperature. For example, at 330–350° with comparatively small feeds of air and ammonia the predominating reaction products are *p*-toluamide and *p*-toluonitrile, formed in yields of 15% and 55% respectively[87]. Under more drastic conditions terephthalodinitrile is obtained in 70–75% yield as the main product[56]. Still greater selectivity is shown by fused titanium vanadate and coprecipitated aluminovanadium catalyst, the use of which gives terephthalodinitrile practically free from *p*-toluonitrile and amide impurities[86]. Tin and titanium vanadates may be used not only in the fused state but also deposited on aluminium oxide[88,89].

The oxidative ammonolysis of *p*-xylene depends not only on the composition of the active phase of the catalyst, but also on the nature and method of preparation of the carrier. Hadley and coworkers, who studied the oxidative ammonolysis of alkylbenzenes on a catalyst of vanadium(V) oxide precipitated on aluminium oxide, found that the temperature used in the preliminary heating of the $Al_2O_3$ has a great effect on the yield of nitriles[61,64,90–92]. As Table 1 shows, the most satisfactory results were obtained with a catalyst the carrier of which had been roasted at 1250–1300°. Several catalysts based on aluminium oxide prepared in this way were obtained and by means of them

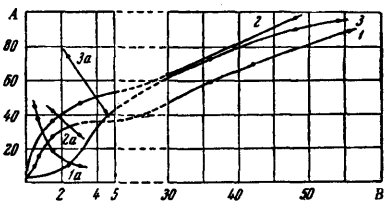



Fig. 1. Dependence of the yield of benzonitrile on the quantity of air in the oxidative ammonolysis of toluene (1), ethylbenzene (2), and cumene (3) on titanium vanadate[73]; 1*a*), 2*a*), and 3*a*) unreacted hydrocarbon. *A*) Yield of reaction products in %; *B*) quantity of oxygen (as air) in moles per mole of hydrocarbon.

TABLE. Effect of roasting temperature of aluminium oxide on the oxidative ammonolysis of *p*-xylene with a vanadium oxide catalyst[61]. Roasting time of carrier 22 h. $V_2O_5 : Al_2O_3$ = = 10 : 90 (wt.%), contact time 6 s. Xylene : ammonia : air = 1.5 : 6 : 92.5 (vol.%).

| Roasting temperature of carrier, °C | Reaction temperature, °C | Yield, % | | |
|---|---|---|---|---|
| | | p-toluonitrile | terephthalodinitrile | $CO_2$ |
| 1050 | 360 | 1 | 66 | 18 |
| 1050 | 380 | 1 | 53 | 28 |
| 1250 | 370 | 1 | 77 | 12 |
| 1250 | 395 | 1 | 47 | 38 |
| 1300 | 355 | 15 | 61 | 5 |
| 1300 | 375 | 1 | 74 | 14 |
| 1300 | 395 | 1 | 30 | 53 |
| 1325 | 370 | 1 | 70 | 19 |
| 1325 | 395 | 1 | 52 | 33 |
| 1400 | 355 | 29 | 37 | 6 |
| 1400 | 395 | 0 | 73 | 20 |

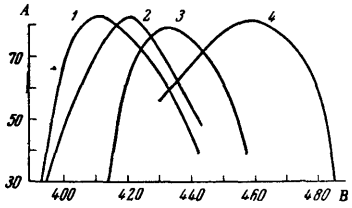



Fig. 2. Effect of thermal treatment of catalyst on the yield of terephthalodinitrile in the oxidative ammonolysis of *p*-xylene with a catalyst of vanadium oxides on aluminium oxide[94]. *p*-Xylene : $NH_3$ : $O_2$ = 1 : 4 : 13, contact time 3 s. *A*) Yield of reaction products, %; *B*) reaction temperature, °C. Roasting temperature of catalyst: 1) without roasting; 2) 500°; 3) 600°; 4) 700°.

terephthalodinitrile could be prepared in yields of 80% and more[88,93,94]. These workers also note that the thermal treatment of the finished catalyst is of great importance[94]. For example, increasing the roasting temperature of the catalyst does not affect the yield of terephthalodinitrile, but it extends the limits of the optimum temperature range of the reaction and moves it into a region of higher temperatures (Fig. 2).

Recently several publications have appeared on the oxidative ammonolysis of *p*-xylene with the use of dust catalysts[95,96]. This variation does not materially change other parameters of the process and has little effect on the yield of reaction products, although in one of the patents it is pointed out that the use of a fluid process makes it possible to reduce the consumption of ammonia to 3 moles per mole of xylene[95].

It has been proposed that water vapour should be introduced into the reaction zone with the object of increasing the yield of terephthalodinitrile, extending the optimum temperature range, and suppressing deep oxidation processes[56,86]. The effect of changes in the water feed on the enumerated characteristics of the process is shown in Fig. 3.

In addition to *p*-xylene, other *p*-dialkylbenzenes may be used as raw materials in the synthesis of terephthalodinitrile. Investigation of the oxidative ammonolysis

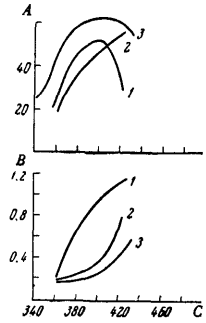



Fig. 3. Effect of quantity of water on the oxidative ammonolysis of *p*-xylene on tin vanadate[98]. $V_{hydrocarbon}$ = 50–52 g; $V_{air}$ = 2400 litres; $V_{NH_3}$ = 150–180 g per litre of catalyst per hour; contact time 0.4–0.6 s. *A*) Yield of terephthalodinitrile, %; *B*) yield of $CO_2$ in moles per mole of xylene; *C*) reaction temperature, °C. $H_2O$ (g): 1) 35; 2) 400; 3) 800 per × × litre of catalyst per hour.

of *p*-cymene[56,89], and of diethyl- and diisopropyl-benzene[59,94,97] has shown that the dinitrile may be obtained from them in 45 to 60% yield and only traces of the nitriles of the corresponding alkylbenzoic acids are formed.

In oxidative ammonolysis *m*-xylene behaves in the same way as *p*-xylene[64,98–101]. The process is usually carried out under analogous conditions with the same catalysts. The only difference is that the yield of isophthalodinitrile, and particularly of *m*-toluonitrile, is somewhat lower than in the case of the *p*-isomers. Attempts to increase the yield of these nitriles by varying the reaction conditions, or by using new types of catalysts and carriers, for example, platinum on oxides of the heavy metals and vanadium(V) oxide on silicon carbide, did not lead to the desired results[102].

The difference in the behaviour of the *p*- and *m*-isomers of xylene is explained by structural features of the *m*-xylene and of the products into which it is converted[99]. The relatively low yield of the monofunctional nitrogen derivatives of *m*-xylene is connected with the adsorption of the *m*-xylene on the catalyst by means of the two side groups, as a result of which the groups react at the same time. In contrast to *p*-xylene, the *m*-isomer is unsymmetrical and it is assumed that because of the joint orienting effect of the side groups the C–H bond at the carbon atom of the ring situated between the groups is weakened and is therefore susceptible to the action of oxygen to a greater degree than the other C–H bonds. With a high concentration of oxygen, this means destruction of the ring and the formation of aliphatic oxygen- and nitrogen-containing compounds, and combustion products.

Since the separation of *p*- and *m*-xylenes is difficult it has been proposed that commercial and other mixtures of these isomers should be used in oxidative ammonolysis with subsequent separation of the dinitriles with the aid of selective solvents. On a stationary or moving catalyst of vanadium oxides precipitated on aluminium oxide the composition of the mixture of xylenes taken does not appear to

affect the conversion of each of the components; the proportion of isomers in the starting material is the same as that in the dinitriles obtained[103,104]. The total yield of terephthalo- and isophthalo-dinitriles reaches 75% of the theoretical. On fused tin vanadate the behaviour of the isomers depends on the proportion of isomers in the starting material and the general picture of the process assumes a different character[105]. Fig. 4, which is given as an example, shows that, when the quantity of isomer in the mixture decreases, its degree of conversion increases. This applies to a great degree to *m*-xylene; in the pure state this is converted into isophthalodinitrile in 20–40% yield, but in a mixture with 9 parts of *p*-xylene the conversion of *m*-xylene is practically complete. It is noteworthy that in experiments with equimolar, or close to equimolar, mixtures deep oxidation is considerable and the yield of carbon oxides increases.

The oxidative ammonolysis of *o*-xylene proceeds in a peculiar manner. Because of the proximity of the methyl groups, the main products are usually phthalic anhydride and phthalimide, irrespective of the nature of the catalyst. With a molar ratio of ammonia : hydrocarbon of 2 : 1 and above, phthalimide begins to predominate. Under optimal conditions its yield may reach 65–70%[50,61] and even 75%,[106] based on the throughput of hydrocarbon. As a rule, only traces of *o*-toluonitrile and *o*-phthalodinitrile are formed. The formation of phthalodinitrile is promoted by a high concentration of ammonia and by the introduction of water vapour into the reaction zone[107]. With the ratio *o*-xylene: : $NH_3$ : $H_2O$ equal to 1 : (20–30) : (25–30) and an adequate supply of air, it may be obtained on tin vanadate in yields up to 45–50%. Only one worker has succeeded in obtaining phthalonitrile in a yield up to 60 wt.% with a feed containing less than 15 moles of ammonia per mole of *o*-xylene[100].

As a rule, oxidative ammonolysis of polyalkylbenzenes with three or more alkyl groups gives a mixture of aromatic nitriles. In particular, mesitylene on vanadium oxides or tin vanadates forms a mixture of mesitylenonitrile, uvitodinitrile, and trimesotrinitrile, the yields of which vary in the range 10–15, 20–25, and 20–25% respectively[60,101,108]. On dust vanadium oxide catalysts about 60% of mesitylene is converted into trimesotrinitrile[100].

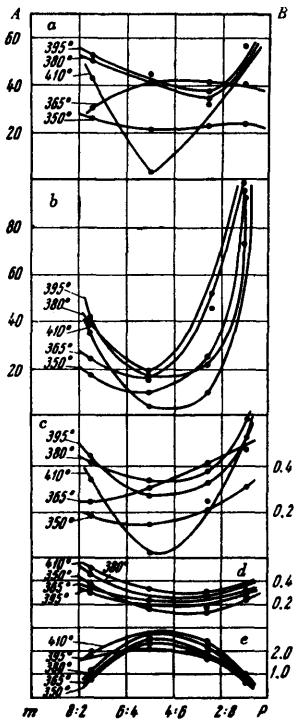



Fig. 4. Dependence of the yield of reaction products of oxidative ammonolysis on tin vanadate[105] on a mixture of *p*- and *m*-xylenes on the proportions of isomers in the mixture.
$V_{mixt}$ = 45–50 g, $V_{NH_3}$ = 130 g, $V_{H_2O}$ = 350–400 g, $V_{air}$ = 2350 litres per litre of catalyst per hour; contact time 0.5 s. *A*) Yield %; *B*) yield of HCN and $CO_2$ in moles per mole of xylene; *C*) composition of mixture of *p*- and *m*-xylenes.
*a*) Terephthalodinitrile; *b*) isophthalodinitrile; *c*) total yield of dinitriles; *d*) hydrocyanic acid; *e*) $CO_2$.

## III. OXIDATIVE AMMONOLYSIS OF CYCLOALKANES AND CYCLOALKENES

Alkyl-substituted cycloalkanes and cycloalkenes are dehydrogenated under the conditions of oxidative ammonolysis on oxide catalysts to aromatic hydrocarbons, which are then converted into the corresponding nitriles. Only nitriles of aromatic acids are found in the catalysates, which indicates that the reaction proceeds in two stages. Thus, benzonitrile was obtained from methylcyclohexane[49] and the terephthalodinitrile from dimethylcyclohexane[109]. The oxidative ammonolysis of various terpene hydrocarbons has been studied on various catalysts[110–112]. In all cases the main product was terephthalodinitrile. The yield was 48–50% from α-pinene, dipentene, and *d*-limonene, and 15–30% from menthol, borneol, terpin hydrate, [*p*-menthane-1,8-diol (Ed. of Translation)], α-terpinolene, terpinen-4-ol, and isopulegol.

## IV. OXIDATIVE AMMONOLYSIS OF ALKENES

The oxidative hydrolysis of alkenes to the nitriles of unsaturated acids is of exceptional importance. It is considered[66] that on the basis of this one of the most economic methods can be developed for the synthesis of vinyl cyanides, in particular acrylonitrile, the monomer for high-quality chemical fibres, synthetic rubber, and other polymers. Intensive work on the oxidative ammonolysis of propene is being carried on in the Soviet Union[113], the United States[66,114,115], Great Britain[64], and other countries. Several variants of the oxidative ammonolysis of propene to acrylonitrile have been described; these have been developed in the search for a more economic process and they differ mainly in the proportion of propene to ammonia. Acrylonitrile can be obtained in 65% yield, based on hydrocarbon used, or 72% based on hydrocarbon consumed, with a feed of 3 or more molecules of ammonia per mole of propene and a large excess of oxygen on cobalt, tin or antimony oxide catalysts, and also on mixed catalysts of molybdenum, tellurium, bismuth and phosphorus oxides[116–121]. Water vapour is an essential component of the reaction mixture; it is used in a molar ratio to propene of 0.25 to 10.[116] In all papers it is noted that the yield of acrylonitrile increases with increasing concentration of ammonia.

When a high concentration of ammonia is used, a considerable part of it passes through the convertor without change, and it may interact in the scrubbers with acrylonitrile to form various amino-derivatives. Cyanethylation of water also occurs in the scrubber system with the formation of hydracrylonitrile and 2,2'-oxydiacetonitrile; other secondary processes, due to the presence of unreacted ammonia, lead to the undesirable consumption of acrylonitrile. To avoid this, the ammonia coming from the reactor is preferably neutralised with sulphuric acid.

In another variant, an equimolar mixture of propene, ammonia and oxygen are passed over the catalyst, or the reaction is carried out with insufficient ammonia and air [116,120,122,123]. The conversion of ammonia is relatively high, side reactions are at a minimum, and unreacted propene is returned to the reaction. The yield of acrylonitrile, based on hydrocarbon consumed, varies between 60 and 75%. Methods of synthesising acrylonitrile from allyl chloride have also been described [124,125]; in a two-stage method propene is first oxidised in the gaseous phase by air to acrolein, after which ammonia is added to the reaction gases and they are passed over a catalyst (oxides of molybdenum, phosphorus, or other elements of variable valency) at 350–400°. [126]

## V. OXIDATIVE AMMONOLYSIS OF ALKYLPYRIDINES

In recent years a considerable amount of work has been done on the oxidative ammonolysis of alkyl derivatives of pyridine. The reaction is of interest because the cyanopyridines formed can be rapidly hydrolysed to give a good yield of free pyridinecarboxylic acids or their amides [127,128], many of which are widely used in the pharmaceutical industry [129]. According to published information the reaction conditions for 3- and 4-picolines differ little from the conditions for the oxidative ammonolysis of the alkylbenzenes. The reaction goes well with 1–3% of picoline and 3–10 vol.% of ammonia in the air feed, a contact time of 0.5–3 s, and a temperature of 350–420°. Vanadium(V) oxide [53,130–133], titanium and tin vanadates [134–137], iron [138,139], silver [138], a mixture of vanadium oxides with oxides of molybdenum and phosphorus [53,140] or with potassium sulphate [139], iron niobates [138], etc. may be used as catalyst. The catalyst may be fused or precipitated on a carrier and used as 3–5 mm granules or as a dust. As a rule, nicotinic acid and isonicotinic acid nitriles are obtained in a stable yield of 60 to 85% based on the weight of picoline taken, or 75 to 95% based on the picoline consumed. Some amides of pyridinecarboxylic acids, hydrogen cyanide, and carbon oxides are also formed. The oxidative ammonolysis of 3- and 4-ethylpyridines proceeds in the same way, although the yield of nitriles is somewhat lower (30–50%) [53]. The nitrile of picolinic acid has been obtained from 2-picoline in the same yield [132,138,141]. The presence of pyridine in the reaction products indicates that, under the given conditions, the side group in the $\alpha$-position can be eliminated and replaced by a hydrogen atom [141].

On oxidative ammonolysis the dialkyl pyridines only give the nitriles of the alkylpyridine acids and nitriloamides in small quantities. Thus, 2,6-dimethylpyridine (lutidine) gives 6-methylpyridine-2-nitrile and 2-cyanopyridine-6-carboxamide; 5-ethyl-2-methylpyridine (collidine) gives 5-methylpyridine-2-nitrile and 2-cyanopyridine-5-carboxamide [53,138,142]. By analogy with 2-picoline, in oxidative ammonolysis of 5-ethyl-2-methylpyridine a side group is eliminated from the $\alpha$-position and as a result nicotinonitrile appears amongst the reaction products. When a catalyst consisting of vanadium oxides precipitated on aluminium oxide is used, the yield of nicotinonitrile is 37%, based on the 5-ethyl-2-methylpyridine passed through [53].

Because of the difficulty of separating 3- and 4-picolines from the corresponding coal-tar fractions, attempts have been made to subject various commercial mixtures to oxidative ammonolysis. From the 3-picoline fraction, which contains ~30% of other alkylpyridines, nicotinonitrile was obtained on a dust-like vanadium-oxide catalyst in 83% yield, based on the pure isomer [143]. Commercial 4-picoline, containing ~8% of impurities, is converted into isonicotinonitrile in almost 88% yield. From a mixture of 3- and 4-picolines in close to equimolecular proportions, nitriles were obtained in practically the same ratio; the yield varied between 55 and 85%, depending on the conditions of the reaction [144,145]. Oxidative ammonolysis of a commercial product consisting of 3-picoline (33.8%), 4-picoline (35.7%), and lutidine (27.4%) gave a mixture of nitriles in 59.9% yield; the mixture consisted of 31% of nicotinonitrile, 51% of isonicitinonitrile, 11% of 6-methylpyridine-2-nitrile, and 7% of picolinonitrile [143].

## VI. SOME QUESTIONS CONNECTED WITH THE MECHANISM OF OXIDATIVE AMMONOLYSIS OF ORGANIC COMPOUNDS

A number of workers quite rightly consider that amino-compounds are the primary products of the reaction of hydrocarbons and ammonia [33,146]; these products are then dehydrogenated to nitriles:

$$R{-}CH_3 + NH_3 \rightarrow R{-}CH_2NH_2 \rightarrow R{-}CN,$$
$$R{-}CH_2{-}R' + NH_3 \rightarrow R{-}CHNH_2{-}R' \rightarrow R{-}CN.$$

With alkenes the first stages of the process are connected with the addition of ammonia to the double bond:

$$R{-}CH{=}CH{-}R' + NH_3 \rightarrow R{-}CHNH_2{-}CH_2{-}R' \rightarrow R{-}CN.$$

The orientation of the $NH_2$-group may differ according to the nature of the radicals R and R'. This question has been extensively considered in the literature, but is still not finally elucidated [26,32,33]. Moreover, in $\alpha$-alkenes the amino-group often combines, according to Markovnikov's rule, with the carbon atom attached to other carbon atoms [44,147–150]:

$$R{-}CH{=}CH_2 + NH_3 \rightarrow R{-}CHNH_2{-}CH_3 \rightarrow R{-}CN.$$

Nitriles with an unchanged carbon skeleton are formed from $\alpha$-alkenes in very small quantities; as a rule, they require special conditions, for example, high pressure [150–153]:

$$R{-}CH{=}CH_2 + NH_3 \rightarrow R{-}CH_2{-}CH_2NH_2 \rightarrow R{-}CH_2{-}CN.$$

Amino-compounds appear in fact to be the intermediate products of ammonolysis of hydrocarbons, as they have been separated in very small quantities and identified by a number of workers [16,151–154].

It is thought by some that a similar reaction also occurs in the oxidative ammonolysis of hydrocarbons [57,59,58,155]. Although the direct ammonolysis proceeds under very drastic conditions (at 500–600°) with a very small yield of nitriles, in the presence of oxygen the optimal temperature is sharply reduced and the conversion of starting material increases.

Paushkin and Osipova regard ammonolysis as a free--radical process in which both hydrocarbon and $NH_2$ radicals take part[32]. This point of view is in agreement with other results on ammonolysis, in particular those dealing with the thermal synthesis of aniline from benzene and ammonia[156], or the ammonlysis of benzene in the silent electric discharge[157], that is, in conditions under which the reactions proceed through free radicals.

In the presence of oxygen the rate of generation of hydrocarbon radicals by a catalyst surface increases[158]. The rate of formation of $NH_2$ radicals also increases[159-161]. The rate of formation of the latter may be so high that hydrazine appears in the reaction products[162]. In the presence of silver oxide at 300–400°, hydrazine can be obtained by the oxidation of ammonia in up to 20% yield[163,164]. This obviously leads to an increase in the rate of formation of amino-compounds.

Moreover, as has been noted above, amino-compounds are present in small quantities in the products of the reaction of hydrocarbons with ammonia. This is explained by the fact that at high temperature in the presence of metallic or oxide catalysts they are rapidly dehydrogenated to nitriles. Experiments on the dehydrogenation of benzylamine on a nickel catalyst have been described[165,166]. On tin and titanium vanadates, benzylamine is converted into benzonitrile in 45–50% yield[167]. The nitriles of aliphatic acids are obtained in still higher yields from various aliphatic amines on nickel, palladium, platinum[168-171], molybdenum oxide[172] chromium oxide[173], and aluminium oxide[174,175]. Oxygen to a still higher degree promotes the further conversion of amino-compounds, in particular the dehydrogenation of these compounds to nitriles. Even aniline under the action of air on thallium oxides is subjected to oxidative dehydrocondensation to azobenzene and phenazine[176]. Methallylamine with air in the presence of a silver catalyst gives 76 mole % of acrylonitrile[177,178], and on titanium vanadate, with an equimolecular quantity of oxygen and 8–10 moles of ammonia, benzylamine is converted almost quantitatively into benzonitrile[167].

If the possibility of dehydrogenating amines is excluded, they may accumulate in the reaction products. An example of this is the formation of aniline on the ammonolysis of benzene in the presence of iron, nickel, or copper catalysts[179], and cobalt or iron oxides[180].

Andrussov[181-184], Wendlandt[185], and other workers[186] have come to the conclusion that intermediate amino-compounds may also be formed in the catalytic synthesis of hydrogen cyanide from methane and ammonia in the presence of oxygen. Since the process starts with the oxidation of ammonia, they suggest that methylamine and methylenimine stages precede the formation of nitroxyl [sic (Ed. of Translation)]:

$$NH_3+O_2 \longrightarrow NH_2O_2 \xrightarrow{-H_2O} HNO \xrightarrow[-H_2O]{+CH_4} NH{=}CH_2 \xrightarrow{-H_2} HCN.$$

$$NH_3+O \longrightarrow NH_2O \xrightarrow[-H_2O]{+CH_4} H_2N{-}CH_3 \xrightarrow{-H_2} NH{=}CH_2$$

The synthesis of hydrocyanic acid is carried out at a temperature of ~1000° on metallic catalysts (platinum and alloys of platinum with rhodium, iridium, ruthenium, etc.) under specific conditions that differ substantially from oxidative ammonolysis. It may be thought that for this reason the hypothetical scheme given with the participation of nitroxyl cannot be considered as applying to the mechanism of oxidative ammonolysis of hydrocarbons.

Under conditions of oxidative ammonolysis ammonia may be oxidised to nitrogen oxides[187-190], and these could react with hydrocarbons to give carboxylic acid nitriles. Toluene and the xylenes readily react with oxides of nitrogen at 400–700° in the presence of dehydrogenating catalysts (for example, silver), to give the corresponding aromatic nitriles[191]. Isonicotinonitrile is formed from 3-picoline. There are reports of the construction of an industrial plant for the preparation of acrylonitrile from propene and nitrogen monoxide[192]. Nitro-compounds appear to be intermediate products in this reaction. In this connection, it should be noted that Wohl[47], Green[193], and also Zal'kind and Kesarev[194] observed the formation of phthalimide in the vapour-phase oxidation of nitronaphthelenes on various oxide catalysts in the absence of ammonia. The routes considered above with participation of amines and nitro-compounds are not the only ones in oxidative ammonolysis. It has been shown that with a sufficient concentration of oxygen in the presence of oxide catalysts the initial hydrocarbon may be subjected to oxidation to oxygen--containing compounds, which then participate in the formation of nitriles[57-59,72,73,86,98,99,107,155]. Later this point of view was confirmed by many workers[64,120].

It is well known that the catalytic vapour-phase oxidation of hydrocarbons leads to the formation of peroxide compounds, aldehydes, ketones, alcohols, acids, anhydrides, lactones, and other oxygen-containing products[1,11,12,15]; the products depend on the structure of the initial compound. Many of these compounds have also been found in the oxidative ammonolysis of hydrocarbons. The yield of these compounds depends on temperature, ammonia concentration, time of contact, and other parameters, but under certain conditions they may accumulate in considerable amounts (see Figs. 5-8).

At a high temperature in the presence of catalysts nearly all the oxidation products of hydrocarbons mentioned are capable of reacting at some rate or other with ammonia, giving amines, imines, amides, and acid nitriles.

The simplest route is that through an acid stage:

$$R{-}COOH \longrightarrow R{-}COONH_4 \longrightarrow R{-}CONH_2 \longrightarrow R{-}CN.$$

An extensive literature is devoted to the vapour-phase ammonolysis of acids and this method has long been considered very convenient for the synthesis of nitriles of the most varied structure. Methods of preparing nitriles from aromatic[196-199], aliphatic[200-205], and heterocyclic[206-208] acids have been described, as well as methods of preparing dinitriles from acid anhydrides[209-211] and imides[212-214], also imides from anhydrides[210], methods of dehydrating amides[200,208,215,216], etc. Ammonolysis is carried out on oxide catalysts, preferably catalysts with dehydrating activity at ~500°, and, as a rule, a large excess of ammonia is used.

On catalysts of metals of variable valency at 350–450° in the presence of air, that is, under oxidative ammonolysis conditions, the degree of conversion of acids into nitriles is low. The cause of this is connected not with the amide dehydration stage, the rate of which is sufficiently high, but with the formation of the amide group from the carboxyl[195,217,218]. The fact is that under the given conditions the acids not only react with ammonia to form amides, but they are also decarboxylated. Dilution of the reaction mixture with air, which finally leads to a reduced concentration of acid and ammonia in the reacting gases, promotes this side reaction.

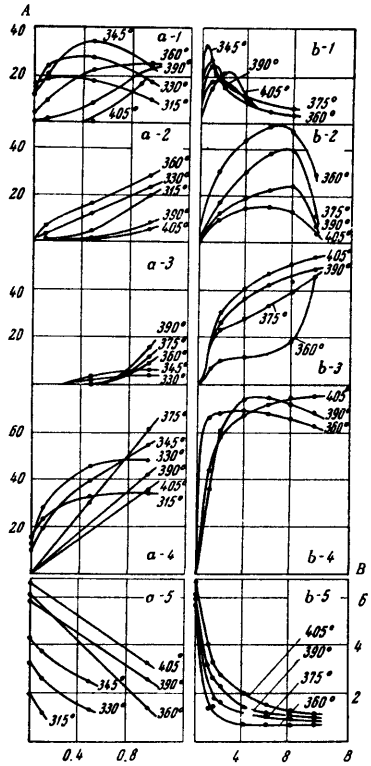


Fig. 5. The effect of ammonia additions on the yields of products of oxidative ammonolysis of *p*-xylene on tin vanadate[86].
$V_{hydrocarbon}$ = 50–52 g, $V_{air}$ = 2400 litres, $V_{H_2O}$ = 350–400 g per litre of catalyst per hour. Contact time = = 0.4–0.6 s. *A*) Yield %; *B*) yield of $CH_2O$, HCN, CO, and $CO_2$ in moles per mole of xylene; *C*) moles $NH_3$ per mole of xylene. *a*) Up to 1 mole of $NH_3$; *b*) up to 10 moles of $NH_3$ per mole of xylene. 1) Terephthalic acid; 2) *p*-toluonitrile; 3) terephthalodinitrile; 4) total yield of $C_8$ products; 5) total yield of gaseous products.

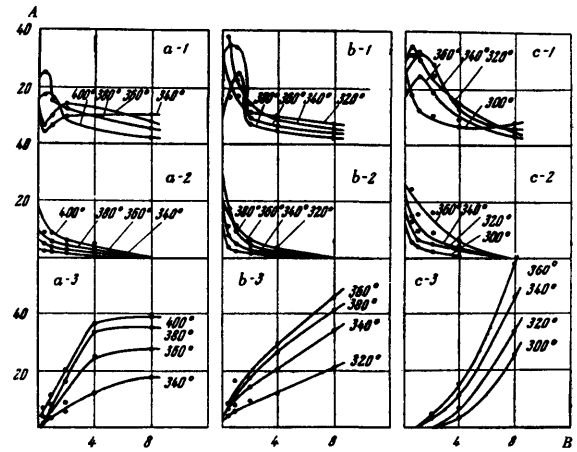


Fig. 6. Effect of ammonia additions on the yield of products of the oxidative ammonolysis of toluene (*a*), ethylbenzene (*b*), and cumene (*c*) on tin vanadate[73].
$V_{hydrocarbon}$ = 30 g, $V_{air}$ = 2200 litres, $V_{H_2O}$ = 250 g per litre of catalyst per hour. *A*) Yield %; *B*) moles of $NH_3$ per mole of hydrocarbon. 1) Benzoic acid; 2) maleic anhydride; 3) benzonitrile.

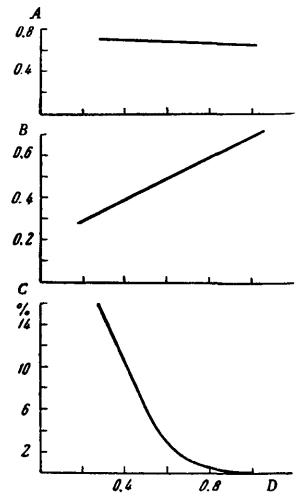


Fig. 7. The effect of the quantity of ammonia on the oxidative ammonolysis of propene in the presence of oxide catalyst[120], $C_3H_6 : O_2 : H_2O$ = = 1 : 1.5 : 1. Contact time = 2 s, $t$ = 450°. *A*) Total degree of propene conversion; *B*) degree of propene conversion into acrylonitrile; *C*) yield of aldehydes, %; *D*) moles of $NH_3$ per mole of propene.

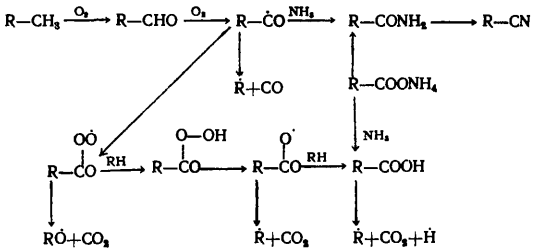
This special feature in the ammonolysis of acids has been used to prepare benzonitrile from phthalic anhydride and phthalimide; when these, mixed with ammonia and air, are passed over oxide catalysts they undergo decomposition with opening of the five-membered ring and elimination of one of the side groups[219–221]. The two-stage synthesis of benzonitrile from naphthalene described above is based on the same principle[68–69].

In the gas phase, aldehydes react with ammonia in two main directions. One of them, which was already studied by Chichibabin, is cyclisation with the formation of pyridine derivatives at a temperature of ~500°, often without a catalyst or with catalysts of the aluminium-oxide or silica type[222–227].

Ammonolysis of aldehydes on oxides of metals of variable valency gives acid nitriles. Thus benzonitrile is obtained in 40% yield from benzaldehyde and ammonia on thorium oxides[228,229]. On a copper catalyst the yield of benzonitrile was 46%,[230] and on titanium and tin vanadates nearly 90%.[231,232] On chromium and cobalt catalysts propionaldehyde is converted into propionitrile in 50–70% yield[233,235]. The preparation of methacrylonitrile[230], heptanenitrile (oenanthonitrile), 3,3,5-trimethylcapronitrile[236], acrylonitrile[237], and nitriles of a number of other carboxylic acids[238,239] by the direct ammonolysis of aldehydes on vanadium and molybdenum oxides, etc. has also been reported.

In contrast to the ammonolysis of acids, when aldehydes react with ammonia the addition of oxygen or air not only accelerates the process but also suppresses many side reactions. In the presence of air, benzonitrile, for example, is formed from benzaldehyde in 93.6% yield[62,72] and acrolein is converted into acrylonitrile (50–70% yield) on nearly all types of oxidative catalysts, including vanadium[237,240], molybdenum[241-243], chromium, manganese[126], and various mixed catalysts[244-246].

In this connection, the authors of this review concluded that when the methyl group is subjected to oxidative ammonolysis, the nitriles are formed through an amide stage, usually not from acids but from aldehydes[57-59,72,247]:



Similar interpretations on the role of aldehydes, in particular the role of acrolein in the oxidative ammonolysis of propene to acrylonitrile have been put forward by Hadley[64]. However, he considers that ammonia reacts with the carbonyl group by an aldimine mechanism:

$$R{-}CHO + NH_3 \longrightarrow R{-}CH{=}NH \longrightarrow R{-}CN.$$

Ketones as well as aldehydes may be intermediates in the oxidative ammonolysis of hydrocarbons with a side-chain having two or more carbon atoms[248-250]. The vapour-phase reaction of ketones with ammonia has been little studied. In one of the earlier papers it is reported that the ammonolysis of acetophenone and propionphenone on thorium oxide gives small amounts of the corresponding ketimines, which were isolated only as hydrochlorides[251]. On tin and titanium vanadate catalysts, acetophenone reacts with ammonia by a Chichibabin-type reaction, giving 2,4,6-triphenylpyridine in 35% yield based on ketone taken or 98% on ketone consumed[252]. Oxidative ammonolysis, even with very small air feeds, of acetophenone gives benzonitrile as the only product; the yield exceeds 70%.[72]

Therefore in oxidative ammonolysis of hydrocarbons the sequence for the conversion of the alkyl group into the nitrile group depends on the process conditions (hydrocarbon : $NH_3$ : $O_2$ ratio) and on the structure of the initial compounds. On the basis of data from the literature and experimental results, the authors of the present review have proposed a scheme of the basic probable stages in the oxidative ammonolysis of toluene, ethylbenzene, and cumene[72] (See Fig. 9).

Alcohols may also be intermediates in the catalytic vapour-phase oxidation of hydrocarbons. Ammonolysis of alcohols leads to the formation of amines or nitriles according to the conditions.

Sabatier and Mailhe were amongst the first to show the possibility of forming alkylamines by the ammonolysis of alcohols[253,254]. In the 1930's a series of papers of Shuikin and coworkers[255-257] on the study of the reaction of alcohols with ammonia in the presence of mixed oxide dehydration catalysts, began to appear. In these papers it was shown, in particular, that butylamine could be obtained in 35–40%

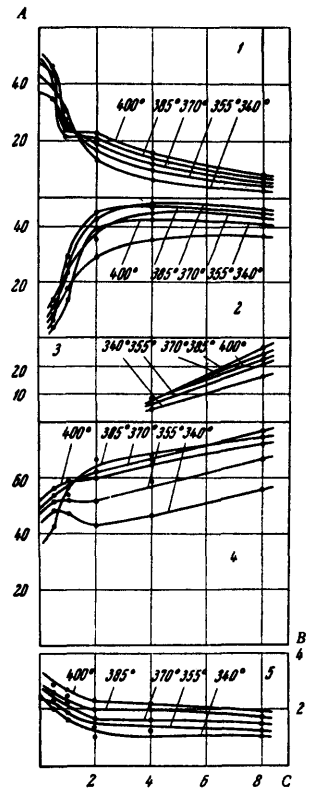



Fig. 8. Dependence of the yield of products of the oxidative ammonolysis of *o*-xylene on the reaction temperature and quantity of ammonia on a tin vanadate catalyst[107]. $V_{xylene}$ = 55–60 g, $V_{air}$ = 2500 litres, $V_{H_2O}$ = = 40 g per litre of catalyst per hour. Contact time = 0.6 s. *A*) Yield %; *B*) yield in moles per mole of xylene; *C*) moles $NH_3$ per mole of xylene. 1) Phthalic anhydride; 2) phthalimide; 3) *o*-phthalodinitrile; 4) total yield of $C_8$ reaction products, %; 5) total yield of gaseous products in moles per mole of xylene.

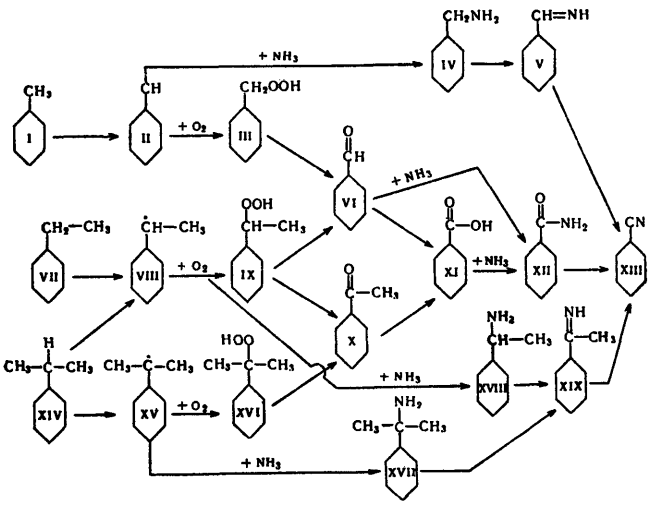



Fig. 9. Reaction scheme for the oxidative ammonolysis of monoalkylbenzenes[72].

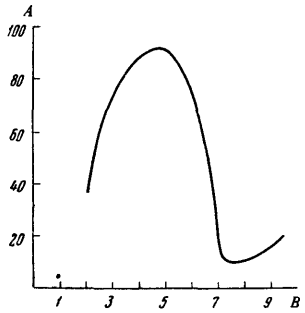



Fig. 10. Dependence of nitrile content of catalysate on the number of carbon atoms in the alcohol molecule[261]. Catalyst $Ni/Al_2O_3$, Ni content = 7.5%. *A*) Nitrile content of catalysate, %; *B*) number of carbon atoms in alcohol molecule.

yield from butanol at 380–420° on aluminium oxide. This reaction goes quite satisfactorily on catalysts of such natural materials as alumina and bauxite[258].

The position of the hydroxyl group has a great effect on the ammonolysis of alcohols[259]. Thus, in the butyl alcohol series the primary alcohol reacts fastest and the tertiary alcohol gives amines in only negligible amounts.

The use of dehydrogenating catalysts changes the direction of the reaction and nitriles become the main products of the ammonolysis of alcohols. Popov showed that, when butyl alcohols react with ammonia in the presence of platinised silica gel, butyronitrile is formed in yield up to 27%.[259] On a nickel catalyst, ethanol, propanol, butanol, and benzyl alcohol give the corresponding nitriles in 50 to 90% yield[260-262]. Similar activity is shown by copper and silver catalysts[263,264]; the sulphides of zinc, tungsten, nickel, titanium, and chromium[265]; aluminomolybdenum oxide catalyst[266]; and oxygen-free zinc salts[267].

In a study of the ammonolysis of various aliphatic alcohols Popov and Shuikin[261] found that on a nickel catalyst the greatest amount of nitrile is obtained from alcohols with four or five carbon atoms (Fig. 10).

According to available patent information[246,268], in the presence of dehydrogenating and oxidative catalysts, especially when oxygen is present in the reaction zone, the formation of nitrile from alcohol and ammonia should proceed through the intermediate aldehyde:

$$R{-}CH_2OH \xrightarrow{-H_2} R{-}CHO \xrightarrow{+NH_3} R{-}CONH_2 \xrightarrow{-H_2O} R{-}CN$$

It has been noted above that in the oxidative ammonolysis of hydrocarbons the addition of water vapour has a favourable effect on the yield of nitriles[50,86,116,242].

The introduction of water vapour into the reaction zone also promotes the formation of carbonyl and carboxylic derivatives in the vapour-phase catalytic oxidation of hydrocarbons with atmospheric oxygen[250,269-271]. It has been shown by direct experiments that toluene, benzil, and benzaldehyde on oxides of vanadium at 350–420° in the absence of air react with water to form benzoic acid and other oxygen compounds[272]. In this connection it has been suggested that the favourable action of water on the oxidative ammonolysis of hydrocarbons is also connected with the participation of water in the formation of intermediate oxygen-containing compounds[247].


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# REACTION OF ACETYLENE AND ALKYNYL COMPOUNDS WITH AMINES AND AMMONIA

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## 1. INTRODUCTION

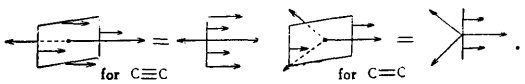
In the last few decades there has been a considerable extension of the studies in the field of the chemistry of unsaturated amines. Thanks to the presence of several reaction centres in their molecules (the amino-group, multiple bonds), unsaturated amines exhibit high reactivity and can serve as starting compounds in the synthesis of more complex nitrogen-containing substances of various classes, including high-molecular-weight materials.

Many unsaturated amines and derivatives obtained from them and based on them are of interest as physiologically active substances.

One of the main methods for obtaining unsaturated amines is by the direct action of amines and ammonia on acetylene and alkyne derivatives.

Alkynes are capable of two types of reaction with amines: addition of the amines to triple bonds and replacement of the active alkynyl hydrogen by an aminomethyl group (Mannich reaction).

The addition of amines and ammonia to alkynes can be classified as a nucleophilic addition to a triple bond. Bohlmann [1] attributed the tendency of a triple bond to participate in nucleophilic addition to the asymmetry of the electron density. During the formation of each electronic bond the centre of gravity of the electron density is displaced towards the centre of the bond. The overlap integrals are a measure of this displacement to a first approximation. If the displacement is represented by vectors leaving the plane perpendicular to the bond and passing through the nucleus of the carbon atom, an almost symmetrical picture is obtained for ethylene, but there is distinct asymmetry for acetylene:




Since this also implies asymmetry of the spherical positive field of the nucleus, the carbon atoms in alkynes already possess in their ground state an approximately electrophilic character. On passing to the polyynes the electropositive character of the terminal carbon atoms increases owing to mesomerism:

$$-\overset{\delta+}{C}\equiv C-[C\equiv C]_n- \longleftrightarrow -\overset{+}{C}=C=[C=C]_n-.$$

However, these views do not explain the influence on the reactivity of the triple bond of various substituents in alkynes.

The many experimental results on the reaction of alkynes with amines show that the reactivity of the alkynyl group and the direction of the addition to it depend essentially on the electronic structure of the substituent, on the amine reacting, and on the conditions.

A possible hypothesis is that in many instances the reaction is brought about through the formation of intermediate complexes of the alkynes with the amines, the catalyst, and the solvent.

This review is intended to survey the literature on the reactions of acetylene and alkyne derivatives with amines and ammonia and to throw light on the fundamental mechanisms of these reactions.

## 2. REACTION OF ACETYLENE WITH AMINES AND AMMONIA

### (a) Reaction of Acetylene with Amines

The reaction of acetylene with amines proceeds in the presence of catalysts on heating and under pressure. Acetylene reacts with primary and secondary aliphatic amines in the presence of copper acetylide under pressure at 80–100° with formation of butynylamines [2–5]. It is thought that vinylamines are the intermediates in this reaction:

$$R_2NH + CH\equiv CH \rightarrow [R_2NCH=CH_2] \rightarrow R_2NCH(CH_3)-C\equiv CH.$$

The yields of butynylamines from secondary amines reach 60–80%; primary amines do not react so well with acetylene. Under these conditions hexamethylenediamine reacts at one amino-group.

Acetylene and primary amines in the presence of zinc or cadmium acetate under pressure at 120–140° form ethylideneimines [6], and not *N*-vinylamines, as Reppe and coworkers had reported [3]:

$$RNH_2 + CH\equiv CH \rightarrow [CH_2=CHNHR] \rightarrow CH_3C(=NR)H.$$

In the presence of water at 60–70° and 20 atm, acetylene also reacts with trimethylamine to form neurine [3,7] [trimethylvinylammonium hydroxide (Ed. of Translation)] in good yield:

$$(CH_3)_3N + CH\equiv CH + H_2O \rightarrow [(CH_3)_3N^+-CH=CH_2]\,OH^-.$$

Amines of structure RNHX, in which R is an alkyl, aryl, aracyl, or ester radical, and X is a chloro-, bromo-, iodo-, cyano-, nitro-, sulpho-, or nitro-aryl group, condense with acetylene in the liquid phase in the presence of a mercury catalyst — $Hg(OAc)_2$ and $H_2SO_4$ — to give *N*-vinyl compounds of general formula $RN(CH=CH_2)X$. [8]

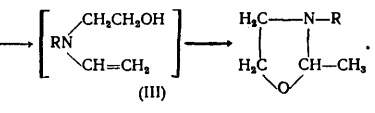
Amino-alcohols react with acetylene in the presence of alkaline catalysts (alkali, alkali metal alkoxides) under pressure at 120–160° to form the corresponding vinyl ethers [9–13]:

$$R_2NCH_2CH_2OH + CH\equiv CH \longrightarrow R_2NCH_2CH_2OCH=CH_2,$$

where R = H, alkyl, or aryl.

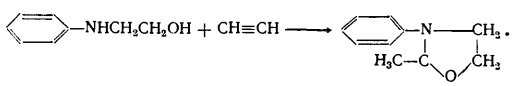
Watanabe and Conlon [14] showed that amino-alcohols with the structure $RNH(CR_2)_nOH$, where R = H or alkyl and $n$ = 2 or 3, with acetylene under pressure, at 100–200°, in the absence of traces of water give 2-methyloxazolidine ($n$ = 2) and perhydro-2-methyl-1,3-oxazine ($n$ = 3), or their derivatives (when R = alkyl) with yields of 5–75%. A vinyl ether is not formed under these conditions. The authors suggest the following mechanism for the reaction:

$$RNHCH_2CH_2OH + CH\equiv CH \longrightarrow \underset{(I)}{} \left[RN^+(CH_2CH_2OH)(CH=CH^-)\right] \underset{(II)}{} \longrightarrow \left[RN(CH_2CH_2OH)(CH=CH_2)\right] \underset{(III)}{} \longrightarrow$$

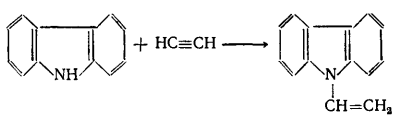


The intermediate compound (II) can be converted into the reaction product directly or through compound (III). Watanabe and Conlon did not give a convincing demonstration of the existence of (III). They represented the reaction mechanism as a special case of vinylation in which the acetylene first attacks the nitrogen of the amino-group (and not the oxygen), analogously to the reaction of aqueous tertiary amines with acetylene, as a result of which a trialkylvinylammonium hydroxide is formed. In the presence of a strongly basic catalyst at 140–150° acetylene under pressure with 2-methylaminoethanol forms a mixture of 2-methylaminoethyl vinyl ether (50%) and 2,3-dimethyloxazolidine (25%).

Aromatic amino-alcohols do not react with acetylene under these conditions. However, in the presence of cadmium acetate 2-methyl-3-phenyloxazolidine is formed from 2-anilinoethanol and acetylene[3]:



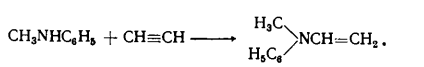
Stable *N*-vinyl compounds are obtained in the reaction of acetylene with nitrogen-containing heterocyclic compounds having a hydrogen atom on nitrogen, such as pyrrole, indole, carbazole, and imidazole[3,5]. The reaction proceeds in the presence of a strongly alkaline catalyst under pressure at 100–200° with yields up to 99%:



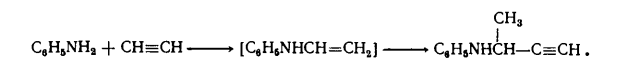
In the presence of alkaline catalysts at 100–200° diarylamines (diphenylamine, phenyl-α- and phenyl-β-naphthylamines) form relatively stable *N*-vinyl compounds[3]:

$$(C_6H_5)_2NH + CH{\equiv}CH \longrightarrow (C_6H_5)_2NCH{=}CH_2.$$

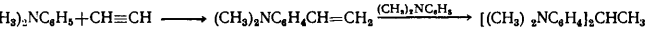
Vinyl derivatives and acetylene also form aralkylamines in the presence of potassium or zinc dust at 185°. *N*-methylaniline gives *N*-methyl-*N*-vinylaniline in 44% yield[4]:



When acetylene and aniline react in the presence of copper acetylide at 20–60° under pressure, 3-anilinobutyne is obtained in 25% yield[2]:



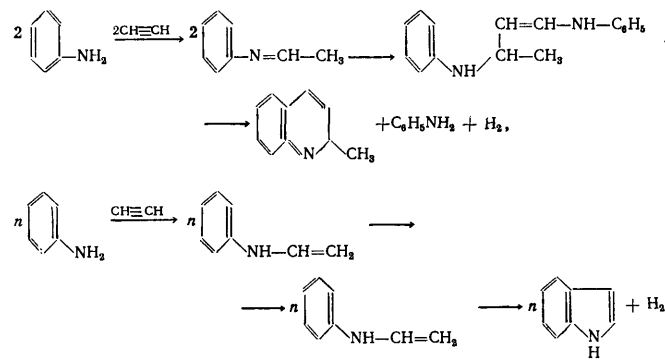
Tertiary aralkylamines are alkylated by acetylene in the aromatic nucleus in the presence of aluminium chloride[15]:



The *p*-dimethylaminostyrene which might be expected from the scheme is not observed in the reaction products.

Kozlov and coworkers[16] showed that acetylene can condense with primary aromatic amines under pressure, and without it at room temperature, or on heating, not above 30°, in the presence of various catalysts: copper(I) chloride, mercury(II) chloride, copper acetylide, or mercury salts of organic acids. Quinaldine, indole, quinoline, and their derivatives are formed.

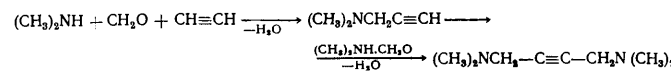
The authors suggest that the formation of quinaldine and indole in the reaction of aniline and acetylene in the presence of copper(I) chloride proceeds through an ethylidene--base and vinylaniline thus:



An analogous scheme was proposed for the reaction of acetylene and ethylaniline in the presence of mercury(II) chloride[17]. However, the authors did not provide convincing proof[16,17].

In the vapour phase at 400° in the presence of tetraethyl lead, aniline and acetylene give indole[18,19]. On an aluminosilicate catalyst at 450°, aniline and acetylene form quinoline in 50% yield[20].

Acetylene condenses with aliphatic amines and formaldehyde only under the influence of catalytic amounts of copper acetylide; with aqueous dimethylamine the products are *NN*-dimethylprop-2-ynylamine and a little *NNN'N'*-tetramethylbut-2-ynylenediamine[5,21,22]:



The reaction does not take place without a catalyst, even at elevated temperatures. Dimethylammonium chloride does not undergo this reaction[23].

(b) Reaction of Acetylene with Ammonia

The catalytic condensation of acetylene with ammonia leads to the formation of a mixture of heterocyclic bases (piperidine bases, α- and γ-picolines, pyrrole, pyridine derivatives, aniline, benzonitrile, etc.) or acetonitrile[3,24].

Among the bases we can single out 5-ethyl-2-methylpyridine, which is formed when the catalyst employed is a nickel complex or a cobalt compound[3]. Vinylamine is probably an intermediate in the reaction of acetylene and ammonia.

If the reaction is carried out in the presence of ammonium acetate at 170–200° and 20–30 atm, 5-ethyl-2-methylpyridine is obtained in up to 90% yield[24].

In the presence of cadmium catalysts, picolines can be obtained in good yield together with other pyridine bases[25,26].

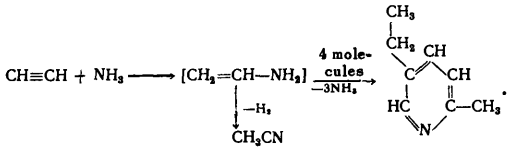
By passing mixtures of acetylene, ammonia, and hydrogen at 350° over zinc oxide and thorium oxide on

silica gel, and then over nickel on silica gel at 150°, condensates containing mainly piperidine and 2-aminoethanol are obtained. When mixtures of acetylene, hydrogen, and ammonia are heated to 650°, pyridine, pyrrole, aniline, and benzonitrile are formed as well as naphthalene and other hydrocarbons [27].

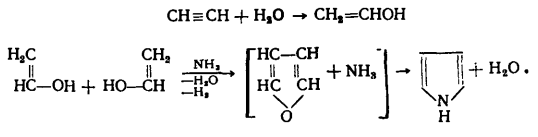
In glazed clay or quartz tubes at > 700° acetylene and ammonia form hydrogen cyanide [28].

On passing mixtures of ammonia and ethylene at 300–500° over catalysts consisting of alumina, zinc oxide, chromium(III) oxide, and 0.15% NaOH, or on using a zirconium catalyst, acetonitrile is formed in theoretical yield [29]. Other catalysts can also be used for this reaction: thorium oxide, $(ZnOH)_2CO_3$ (zinc oxide precipitated from sodium carbonate), zinc nitrate on kaolin, a mixture of sodium carbonate and alumina, carbon monoxide with hydrogen, and also molten salts ($ZnCl_2$–KCl–NaCl; $CdCl_2$–KCl–NaCl; $PbCl_2$–KCl–NaCl; $FeCl_3$–KCl–NaCl; and $SnCl_2$–KCl). [30–33] The yields of acetonitrile when these catalysts are used are 60–90%. Sometimes small quantities of MeCH=NH, pyridine bases, and hydrogen cyanide are formed.

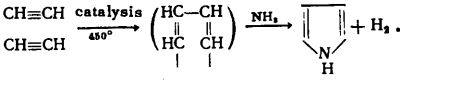
Reppe found that the reaction of acetylene and ammonia can be represented as follows [3]:



Chichibabin showed [34] that when acetylene and gaseous ammonia are passed over oxides of Al, Fe, Cr, Ti, Th, or Si on kaolin, or over aluminium phosphate at > 300°, the products are α-picoline, γ-picoline, 3-ethyl-2-methyl pyridine, pyrrole, and piperidine bases, the production of which he explained by the intermediate formation of acetaldehyde [34]. However, the formation of cyclic nitrogenous bases, for example, pyrrole, can take place in the presence of traces of moisture, as Yu'rev noted [35], by another mechanism, namely:



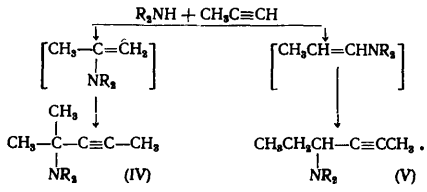
A third path of pyrrole synthesis was subsequently suggested [36]:



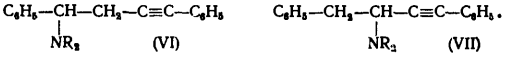
## 3. REACTION OF ALKYL- AND ARYL-ALKYNES WITH AMINES

Like acetylene, alkyl- and aryl-alkynes add on aliphatic amines in the presence of catalysts and on heating [37]. The direction of the reaction is determined by the nature of the substituents on the alkyne as well as by the structure of the amine being added and the conditions of the reaction. Thus, diethylamine reacts with propyne in the presence of cadmium or zinc acetate on heating to 120°, forming *NN*-diethyl-1,1-dimethylbut-2-ynylamine in 80% yield [37].

Alkylalkynes add on amines in accordance with the Markovnikov rule. Of the two possible butynylamines, (IV) and (V), only the *NN*-dialkyl-1,1-dimethylbut-2-ynylamine (IV) was isolated:

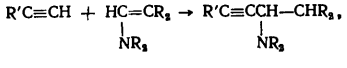


Phenylacetylene adds on secondary amines in the presence of copper(I) chloride at 100°; with morpholine, 3-morpholino-1,4-diphenylbut-1-yne and 1-morpholino-1,4-diphenylbut-3-yne are formed [38]. Compounds (VI) and (VII) were isolated from the products of the reaction between phenylacetylene and secondary alkylamines, showing that the amines add on to phenylacetylene in two ways



This suggests that, as for acetylene, when alkyl- or aryl-alkynes react with aliphatic amines, the corresponding enamines are formed as intermediates [37,38].

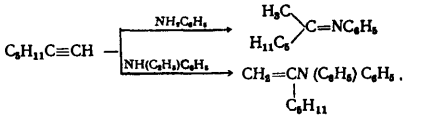
Brannock and coworkers [39] confirmed the formation of an intermediate enamine in the reactions of acetylene, alkyl-, and aryl-alkynes with amines. They continued the reaction of alkynes with enamines and obtained the expected alkynylamines:



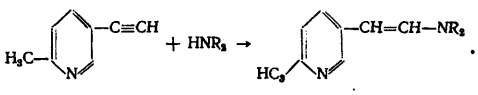
where R′ = H, $C_4H_9$, $C_6H_5$, $CH_3CO_2CH_2$, etc.

The process takes place on heating, without catalysts, but catalytic amounts of copper(I) chloride accelerate the reaction so much that it sometimes becomes explosive.

Alkyl alkynes react with aromatic amines in the presence of boron trifluoride or mercury(II) oxide [40]. Under these conditions hept-1-yne gives an anil with primary aromatic amines and a vinyl derivative with secondary aromatic amines:



Pyridylacetylenes behave similarly to the alkyl- and aryl-alkynes in reactions with amines. As Kost and coworkers showed [41], the activity of the triple bond of 5-ethynyl-2-methylpyridine in these reactions is higher than that of phenylacetylene. Actually, 5-ethynyl-2-methylpyridine adds on secondary amines on heating to 180° with up to 70% yields of β-addition products:



Bromophenylacetylene reacts with secondary amines in the cold, addition and substitution taking place simultaneously [42]:

Hexafluorobut-2-yne gives addition products with primary and secondary alkylamines at 20°.[43] Thus with cyclohexylamine it forms *N*-cyclohexyl-1,1,1,4,4,4-hexafluorobut-2-enylamine:

$$F_3CC{\equiv}CCF_3 + C_6H_{11}NH_2 \rightarrow F_3CCH{=}CCF_3NHC_6H_{11}.$$

Other halogenobutynes react analogously:

$$Cl_2CHC{\equiv}CCHF_2. \quad Cl_2CHC{\equiv}CCH_3.$$

The aminomethylation of alkyl- and aryl-alkynes at the labile alkyne hydrogen takes place comparatively readily on heating, although for alkyl alkynes it would be natural to expect retardation of the process. The explanation of this behaviour must probably be sought in Arens' work on the chemistry of alkoxyalkynes (see Section 4).

On heating to 80–100° with dialkylamines and formaldehyde, hex-1-yne forms[44,45] the corresponding alkyne derivatives in 75–81% yield:

$$C_4H_9C{\equiv}CH + R_2NH + CH_2O \rightarrow C_4H_9C{\equiv}CCH_2NR_2 + H_2O.$$

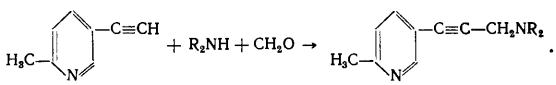
With secondary aliphatic amines and formaldehyde at 100°, phenylacetylene forms *NN*-dialkyl-3-phenylprop-2-ynylamines in yields of up to 80%:[5,46]

$$C_6H_5C{\equiv}CH + NHR_2 + CH_2O \rightarrow C_6H_5C{\equiv}CCH_2NR_2 + H_2O.$$

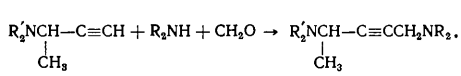
4-Phenylbut-1-yne reacts with secondary amines and paraformaldehyde in the presence of copper(II) acetate at 100° to form the corresponding compound in 76% yield[47]:

$$C_6H_5CH_2CH_2C{\equiv}CH + (CH_3)_2NH + CH_2O \xrightarrow{-H_2O} C_6H_5CH_2CH_2C{\equiv}CCH_2N(CH_3)_2.$$

The condensation of 5-ethynyl-2-methylpyridine with secondary amines and formaldehyde proceeds in the presence of potassium hydroxide on boiling in dioxan; the yields of amino-derivatives reach 92%:[41]



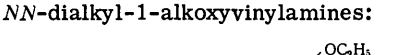
Dialkylaminoalkyl alkynes react with secondary amines and formaldehyde on heating in dioxan; alkynyldiamines are formed in 55–70% yield[48]:



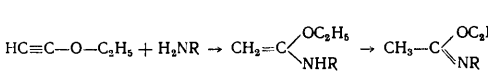
## 4. REACTION OF ALKOXYALKYNES AND ALKYNYL SULPHIDES WITH AMINES AND AMMONIA

Alkoxyalkynes react slowly with aliphatic amines on heating; the reaction can be accelerated by addition of water.

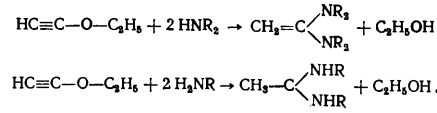
The amines add on to the $\alpha$ carbon atom in accordance with the polarisation of the alkoxyalkyne molecule. The structure of the final reaction product depends on the nature of the amine and the conditions of the reaction[49–51]. Thus secondary amines taken in equimolecular amount react to give *NN*-dialkyl-1-alkoxyvinylamines:



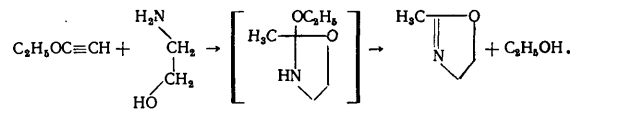
Under these conditions primary amines form the tautomeric iminoethers:



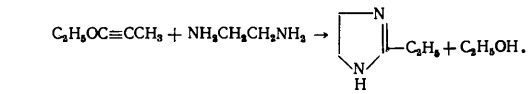
With an excess of the amine, nucleophilic replacement of the alkoxy-group proceeds as well as the addition:



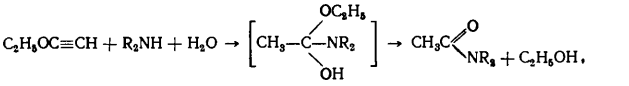
Bifunctional nucleophilic compounds, such as diamines, amino-alcohols, and amino-sulphides, give heterocyclic addition products when heated with ethoxyacetylene[49,52]:



The introduction of a methyl group into ethoxyacetylene retards the reaction with diamines and lowers the yield of addition products. The reaction is accelerated on addition of mercuric oxide. Ethylenediamine gives 2-ethyl-2-imidazoline[52,53]:



The addition of amines to alkoxyalkynes in the presence of water leads to the formation of *N*-substituted acetamides with a yield of up to 89%.[49,51,54] The authors suggest that the intermediate compound in this reaction is a derivative of orthoformic acid. When an amine of high basicity is used, the reaction is exothermic:



where R is H or alkyl.

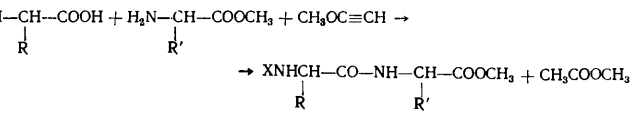
Amines of low basicity, such as aniline and diphenylamine, do not react in this way. They mainly act as catalysts for the hydration of ethoxyacetylene:

$$C_2H_5OC{\equiv}CH + H_2O \xrightarrow[\text{or } (C_6H_5)_2NH]{C_6H_5NH_2} CH_3COOC_2H_5.$$

In the presence of alkoxyalkynes, acids react smoothly (at 25–50°) with amines to form amides in quantitative yield[49,55]:

$$C_2H_5OC{\equiv}CH + RCOOH + H_2NR' \rightarrow RCONHR' + CH_3COOC_2H_5.$$

This reaction can be used for the synthesis of peptides:



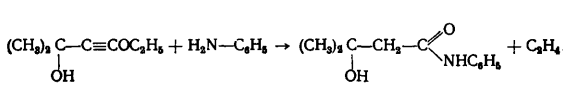
Ethoxyacetylene also reacts with tertiary amines in the presence of water to form trialkyl-(1-ethoxyvinyl)ammonium hydroxides in 55–73% yields[49,56].

The reaction with higher aliphatic amines is very slow — several months are required — but with trimethylamine and triethylamine it occurs readily even at room temperature:

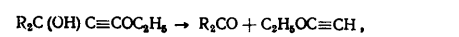
$$C_2H_5OC{\equiv}CH + N(CH_3)_3 + H_2O \rightarrow [CH_2{=}C(OC_2H_5)N(CH_3)_3]^+OH^-.$$

The compound which is formed is analogous to the vinyl derivative obtained by Reppe from acetylene, water, and a tertiary amine[3].

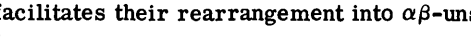
4-Ethoxy-2-methylbut-3-yn-2-ol and aniline form anilides of β-hydroxy-acids in 40% yield[49,57]:



Whereas diethylamine catalyses the decomposition of the tertiary 3-ethoxyprop-2-yn-1-ols:



nitroaniline facilitates their rearrangement into αβ-unsaturated ethers:

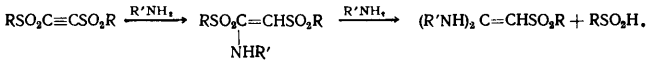


Alkynyl sulphides also react with amines on heating, to form addition products. Thus, ethyl ethynyl sulphide and diethylamine give an addition product in 65% yield[49,51].

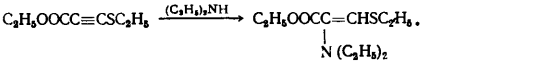
As Arens showed, the sulphide group can act as either a donor or an acceptor of electrons. A nucleophilic reagent adds on to the β carbon atom of an alkynyl sulphide in accordance with the polarisation of its multiple bond:



Alkynyl sulphones react with amines to form addition products; with an excess of the amine the sulphonyl group can be replaced by an amino-group[49,58]:

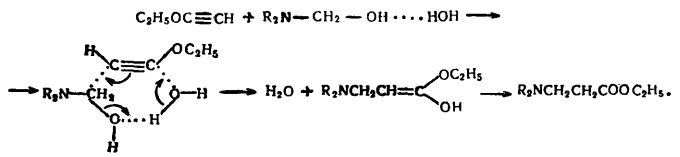


Ethyl ethylthiopropiolate adds on amines at the α carbon atom. Thus when it is heated with diethylamine an addition product is obtained in 74% yield[59]:

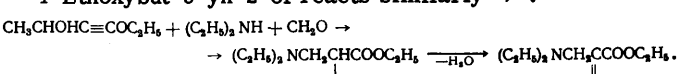


Ethylthiopropiolanilide and 1-ethylthiobut-1-yn-3-one react with amines in a similar manner[60].

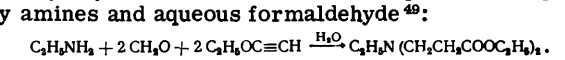
Alkoxyalkynes react readily with amines and formaldehyde. Thus, ethoxyacetylene reacts with diethylamine and aqueous formaldehyde at room temperature[49,61], when ethyl 2-diethylaminopropionate is obtained instead of a Mannich base. Arens assumes that here aminomethanols are formed, which react in a hydrated form with the ethoxyalkyne. During this the hydrogen atom of the alkyne is not replaced by an aminomethyl group, but there is electrophilic addition at the triple bond, which takes place according to this scheme:



4-Ethoxybut-3-yn-2-ol reacts similarly[49,62]:



Ethoxyalkynes form bis-addition compounds with primary amines and aqueous formaldehyde[49]:

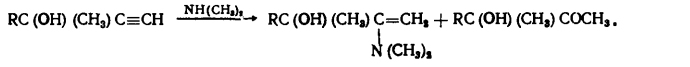


Electrophilic addition to the triple bond can probably also explain the ease of reaction of alkyl alkynes with amines and formaldehyde compared with acetylene; the decomposition of the intermediate addition product here leads to the formation of a Mannich base.

Ethylthioacetylene, unlike ethoxyacetylene, reacts with diethylamine and formaldehyde only on boiling in dioxan[63]. The product is formed by replacement of the alkynyl hydrogen by an aminomethyl group, the yield being quantitative.

## 5. REACTION OF ALKYNYL ALCOHOLS, THEIR DERIVATIVES, AND ALKYNYL OXIDES WITH AMINES AND AMMONIA

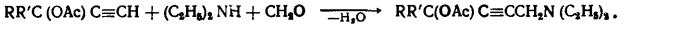
The published information on the addition of amines to the triple bond of alkynyl alcohols is restricted to the work of Vartanyan and Badanyan[64], who reported that when 2-methylbut-3-yn-2-ol or but-3-yn-2-ol are heated with aqueous dimethylamine at 100–120° vinyl amino-alcohols are formed, which are partly hydrolysed under the conditions of the experiment:



1-Ethynylcyclohexan-1-ol and 4-ethynylperhydro-2,2-dimethylpyran-4-ol react analogously.

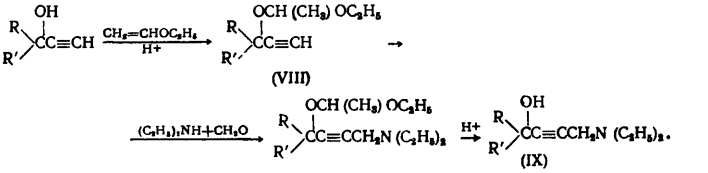
Alkynyl alcohols and their derivatives react with amines under aminomethylation conditions at the alkynyl hydrogen atom.

Whereas α-ethynylmethanols themselves react with secondary amines and formaldehyde at 80° to form the corresponding compounds in low yields, their acetates form Mannich bases in 50–90% yields[45,65]:



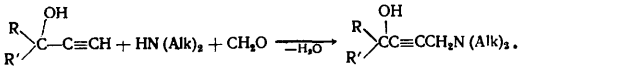
However, this method of obtaining amino-alcohols is inapplicable when R and R′ are aromatic radicals, as the corresponding alkynyl alcohols are unstable in acid and alkaline media.

Shvekhgeimer[66] used an indirect path for the synthesis of the amino-derivatives of alkynyl alcohols:

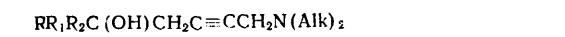


The reaction of the acetals (VIII) with paraformaldehyde and diethylamine occurs when the mixture is heated in dioxan for many hours, and leads to the formation of aminoacetals (IX) with 75–97% yield.

Libman and Kuznetsov aminomethylated tertiary ethynylmethanols in the presence of copper compounds at 80–90°. The reaction is rapid and the yield 80–95%:[67]



Under these conditions amino-alcohols of the structure



are synthesised in 83–95% yield[68].

Pent-4-yn-1-ol reacts with diethylamine and formaldehyde on heating to 40–50° in the presence of copper salts, forming 6-diethylaminohex-4-yn-1-ol in 69% yield[69,70]:

$$HOCH_2CH_2CH_2C{\equiv}CH + (C_2H_5)_2NH + CH_2O \rightarrow HOCH_2CH_2CH_2C{\equiv}CCH_2N(C_2H_5)_2.$$

The following alkoxy- and acyloxy-derivatives of alkyl alkynes also undergo aminomethylation:

$C_2H_5OCH_2C{\equiv}CH$;[71] $(C_2H_5O)_2CHC{\equiv}CH$;[72] $R_1OCR_2R_3(CH_2)_nC{\equiv}CH$;[73] $CH_3(AcO)CHC{\equiv}CH$, $C_6H_5(OAc)CHC{\equiv}CH$;[74] $AcO(CH_2)_2C{\equiv}CH$;[75] $R_1R_2C(OR_3)C{\equiv}CH$.[76]

The low reactivity of the labile hydrogen of alkynyl alcohols in reactions involving substitution by the aminomethyl group is attributed by some to the electron-donor influence of the hydroxyl[67]. Displacement of the electrons of the hydroxyl group towards the side of the alkynyl hydrogen is believed to deactivate it, hindering protonation.

The addition of amines and ammonia to oxides of alkynes and but-1-en-3-ynes does not take place at the triple bond but by opening of the oxide ring according to Krasuskii's rule[77–81].

## 6. REACTION OF ALKYNYL AND BISALKYNYL KETONES WITH AMINES AND AMMONIA

Alkynyl and bisalkynyl ketones, and also alkynyl diketones readily add amines at the triple bond. The amino-group enters the $\beta$ position to the carbonyl group. The latter is a strong acceptor of electrons and intensifies the electrophilic nature of the triple bond, facilitating nucleophilic addition.

Alkynyl ketones add on primary and secondary amines and ammonia even at room temperature, forming 2-aminovinyl ketones in 36–97% yield[82–84]:

$$RCOC{\equiv}CR' + NHR_2'' \rightarrow RCOCH{=}CR'NR_2'',$$

where R is alkyl or aryl.

With conjugated ethynylene–vinylene ketones, the addition of the amine proceeds under analogous conditions at the triple bond[83]:

$$RCOCH{=}CH{-}C{\equiv}CH \xrightarrow{NH(C_2H_5)_2} RCOCH{=}CH{-}CH{=}CHN(C_2H_5)_2,$$

where R is alkyl.

Ketones in which the carbonyl group is between a double and triple bond also add ammonia to the triple bond[83]:

$$RCH{=}CH{-}CO{-}C{\equiv}CH \xrightarrow{NHR_2'} RCH{=}CHCOCH{=}CHNR_2'.$$

Alkynyl diketones also react readily with amines and ammonia. Dibenzoylacetylene forms the corresponding addition products with amines and ammonia[85,86]:

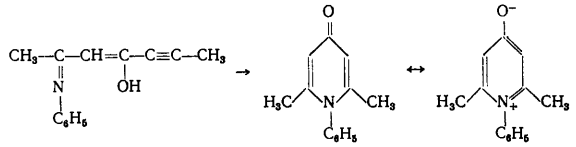
$$C_6H_5COC{\equiv}CCOC_6H_5 \xrightarrow{RNH_2} C_6H_5CO(RNH)C{=}CHCOC_6H_5$$
$$\xrightarrow{NH_3} C_6H_5CO(NH_2)C{=}CHCOC_6H_5,$$

where R is alkyl or aryl.

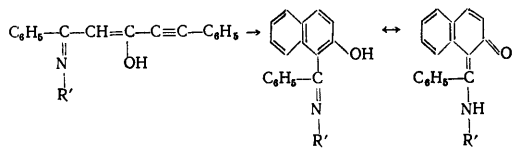
Bisalkynyl ketones readily add on ammonia and primary and secondary amines in the cold or on heating to 50°:[87–91]

$$R{-}C{\equiv}C{-}CO{-}C{\equiv}C{-}R \xrightarrow{R'NH_2} R{-}C{=}CHCOC{\equiv}C{-}R \rightleftarrows R{-}C{-}CH{=}C{-}C{\equiv}C{-}R$$
$$\underset{R'}{|}NH \qquad\qquad R{-}\underset{\|}{N} \quad \underset{OH}{|}$$
$$\xrightarrow{R_2'NH} R{-}C{=}CHCOC{\equiv}C{-}R \rightleftarrows R{-}C{=}C{=}C{-}C{\equiv}C{-}R$$
$$\underset{NR_2'}{|} \qquad\qquad \underset{NR_2'}{|}\ \underset{OH}{|}$$

The addition products of the secondary amines are thermally stable. On heating to 150° the addition products of primary amines isomerise into a 4-pyridone, when R is an alkyl radical:



When R is an aryl radical the isomerisation proceeds in two directions; in addition to a pyridone an isomeric cyclic compound is formed[87–93]:



With aniline, the reaction starts at 150° and sometimes ends with an explosion.

The ketone $CH_3C{\equiv}CCOC{\equiv}CC_6H_5$ adds on aniline at both triple bonds, forming a mixture of two substances (XI) and (XII) with a total yield of 75%:[93]

$$CH_3C{\equiv}CCOC{\equiv}CC_6H_5 \xrightarrow{C_6H_5NH_2} \begin{cases} CH_3C(NHC_6H_5){=}CHCOC{\equiv}CC_6H_5 \ (XI) \\ CH_3C{\equiv}CCOCH{=}C(NHC_6H_5)C_6H_5 \ (XII) \end{cases}$$

Substance (XI) preponderates in the mixture; the proportion of (XII) does not exceed 2%.

## 7. REACTION OF ETHYNYLCARBOXYLIC ACIDS AND THEIR ESTERS WITH AMINES AND AMMONIA

Like alkynyl ketones, ethynylcarboxylic acids and their esters react readily with amines, forming unsaturated compounds with the amino-group in the $\beta$-position to the carboxy-group[94–99]:

$$R{-}\overset{\beta}{C}{\equiv}\overset{\alpha}{C}{-}C\begin{matrix}=O \\ OR'\end{matrix} + HNR_2'' \rightarrow RC(NR_2'')=CH{-}COOR'.$$

Postovskii and coworkers have shown that cyclic secondary amines add on to propiolates, tetrolates, phenylpropiolates, and ethynyldicarboxylates when cooled with ice, followed by heating to 30–60°.[98,99] Monoaddition products are formed in 16–78% yield:

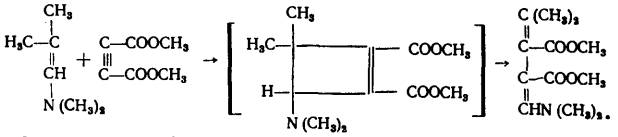
$$RC{\equiv}C{-}COOR' + HN\Big\} \rightarrow R{-}C{=}CH{-}COOR',$$
$$\qquad\qquad\qquad\qquad\qquad\quad \underset{N}{|}\Big\}$$

where $N\Big\}$ represents the residue of the cyclic amine.

Ethynyldicarboxylates also react readily with amines. Thus, diethyl ethynyldicarboxylate adds on benzylamine and aniline at room temperature, forming diethyl *N*-benzylaminofumarate and diethyl anilinofumarate, the yield being 63% in each instance[100]:

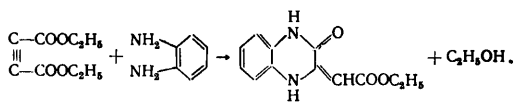
$$\begin{matrix} C{-}COOC_2H_5 \\ \| \\ C{-}COOC_2H_5 \end{matrix} \xrightarrow{C_6H_5CH_2NH_2} \begin{matrix} CH{-}COOC_2H_5 \\ \| \\ C(NHCH_2C_6H_5)COOC_2H_5 \end{matrix}$$
$$\xrightarrow{C_6H_5NH_2} \begin{matrix} CH{-}COOC_2H_5 \\ \| \\ C(NHC_6H_5)COOC_2H_5 \end{matrix}.$$

Brannock and coworkers [101] showed that ethynyldicarboxylates react with tertiary enamines at the double bond:

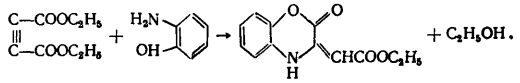


The reaction of ethynyldicarboxylic acid and its esters with bifunctional compounds, such as *o*-phenylenediamine, *o*-aminophenol, ethylenediamine, and *o*-aminobenzenethiol leads to the formation of heterocyclic compounds [102,103]. The reaction proceeds in stages: initially one amino-group reacts, forming an addition product, which then cyclises.

Diethyl ethynyldicarboxylate reacts at room temperature with *o*-phenylenediamine to form ethyl 1,2,3,4-tetrahydro-3-oxoquinoxalin-2-ylideneacetate:



Diethyl ethynyldicarboxylate and *o*-aminophenol give ethyl 3,4-dihydro-2-oxobenzo[*b*]-[1,4]-oxazin-3-ylideneacetate:



Acetylenedicarboxylic acid and *o*-phenylenediamine form 1,2,3,4-tetrahydro-3-oxoquinoxalin-2-ylideneacetic acid.

## 8. REACTION OF BUT-1-EN-3-YNES AND THEIR DERIVATIVES WITH AMINES AND AMMONIA

The addition of amines to but-1-en-3-yne takes place in the 1,4 position with formation of an intermediate allene derivative, which is isomerised into a diene or alkynylamine [104,105].

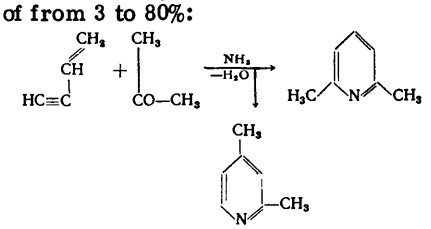
But-1-en-3-yne adds on secondary aliphatic amines on heating to 100° in aqueous solution under pressure, forming alleneamines. When the reaction occurs with an excess of the amine, then the alleneamine formed rearranges into an alkynylamine [104,105]:

$$CH_2{=}CH{-}C{\equiv}CH + R_2NH \rightarrow CH_2{=}C{=}CH{-}CH_2NR_2 \rightarrow CH_3C{\equiv}CCH_2NR_2.$$

Primary amines react analogously.

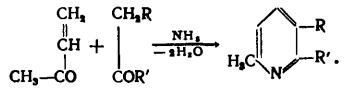
But-1-en-3-yne reacts with ammonia at 250° under the influence of a lead–cadmium catalyst deposited on aluminium oxide; aliphatic amines, picoline, and collidine are formed [105].

Vereshchagin showed [106-108] that but-1-en-3-yne condenses with ammonia and ketones at 350–400° in the presence of cadmium catalysts to form substituted pyridines in yields of from 3 to 80%:



The reaction mechanism is:

$$CH_2{=}CH{-}C{\equiv}CH + H_2O \rightarrow CH_2{=}CH{-}CO{-}CH_3$$



During the reaction of but-1-en-3-yne with piperidine, morpholine, and methylaniline in the presence of copper compounds, nitrogen-containing unsaturated bases used in rubber production are formed [105].

The reaction of but-1-en-3-yne with lithium dialkylamides can be used to obtain addition products which on treatment with water form amines with a terminal ethynyl group [105,109,110]:

$$CH{\equiv}C{-}CH{=}CH_2 \xrightarrow{R_2N{-}Li} H{-}C{=}C{=}CH{-}CH_2NR_2 \rightarrow$$
$$\rightarrow Li{-}C{\equiv}C{-}CH_2{-}CH_2NR_2 \xrightarrow{H_2O} CH{\equiv}C{-}CH_2CH_2NR_2.$$

With alkyl substituted but-1-en-3-ynes the final product is an *NN*-dialkyl-4-alkylbuta-2,3-dien-1-amine:

$$R{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{R_2N{-}Li} R{-}CLi{=}C{=}CH{-}CH_2NR_2 \xrightarrow{H_2O}$$
$$\rightarrow R{-}CH{=}C{=}CH{-}CH_2NR_2.$$

The yields of these compounds reach 45–55%. But-1-en-3-yne is an exception, which mainly forms a dimer under the conditions of this reaction.

But-1-en-3-yne reacts with secondary amines and formaldehyde (in dioxan) at 100° under pressure to form the corresponding bases [111]:

$$CH_2{=}CH{-}C{\equiv}CH \xrightarrow{R_2NH,\ CH_2O} CH_2{=}CH{-}C{\equiv}C{-}CH_2NR_2 + H_2O.$$

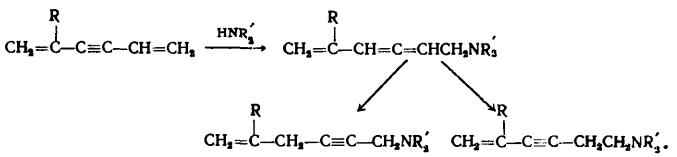
The yield varies from 9 to 91% with various amines.

Nazarov and Mistryukov showed [112] that thoroughly purified paraformaldehyde and diethylamine hardly react with but-1-en-3-ynes. It is only when catalytic quantities of iron salts [iron(III) chloride] are added to the reaction mixture that aminomethyl derivatives are formed smoothly with yields of up to 90%:

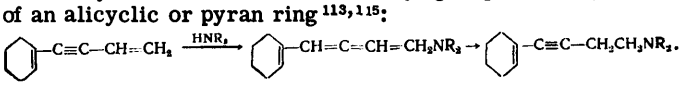
$$-\overset{|}{C}{=}\overset{|}{C}{-}C{\equiv}CH \xrightarrow[CH_2O]{(C_2H_5)_2NH} -\overset{|}{C}{=}\overset{|}{C}{-}C{\equiv}C{-}CH_2N(C_2H_5)_2 + H_2O.$$

The reaction takes place on heating in dioxan solution.

Hexa-2,5-dien-3-yne adds on secondary amines in the 1,4 position when heated in a sealed tube to 95–100°. [113,114] The triene amine formed undergoes isomerisation in two directions; as a result, hexa-5-en-2-ynyl and hexa-5-en-3-ynyl amines are obtained:

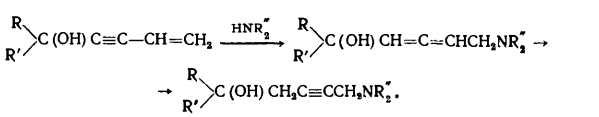


In a similar way dimethylamine adds on to hexa-1,5-dien-3-ynes in which one of the vinyl groups forms part of an alicyclic or pyran ring [113,115]:



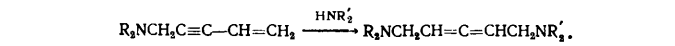
As Vartanyan and coworkers have shown, the addition of amines to but-1-en-3-ynyl alcohols [116-118] and their esters [119] takes place in the 1,4 position on heating them with an

aqueous solution of the amine, and leads to the formation of allene amino-alcohols, which isomerise into alkynyl amino-alcohols (yield > 50%):

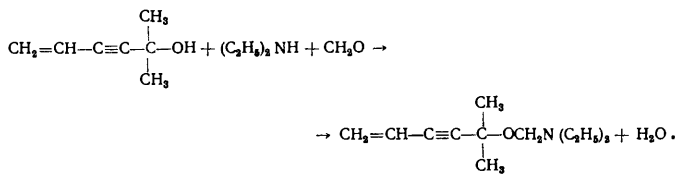


But-1-en-3-ynyl piperidols [120], tetrahydro-4-pyranols, and tetrahydro-4-thiopyranols [121], but-1-en-3-ynyl phenols and their ethers [122] behave analogously.

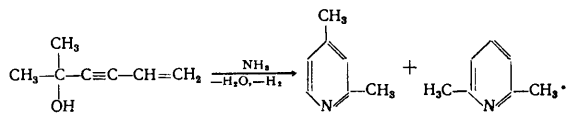
Dialkylaminomethylbut-1-en-3-ynes add on amines in the 1,4 position. The allene diamines formed do not isomerise into alkynyl diamines [123]:



But-1-en-3-ynyl alcohols undergo aminomethylation on boiling in dioxan or benzene, forming aminomethyl vinyl-alkynyl ethers with 43–71% yield [124]:



Tertiary but-1-en-3-ynyl alcohols undergo catalytic condensation with ammonia at 285–470°. Cadmium and chromium compounds are mainly used as catalysts. Pyridine bases are formed in low yield [106–108,125]:



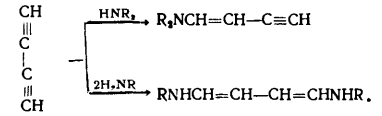
Secondary vinylethynylmethanols on condensation with ammonia on cadmium catalysts at 400° decompose into aldehydes and but-1-en-3-ynes [126]. The aldehyde formed reacts with ammonia to form pyridine bases. Vinylacetylene does not participate in this reaction.

## 9. REACTION OF BUTA-1,3-DIYNE WITH AMINES

The first patent communication of this reaction stated that buta-1,3-diyne reacts with diethylamine at 45° in the presence of copper or silver salts to form diethylaminobutenyne [127].

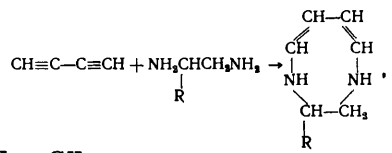
Later Petrov and his coworkers showed that the reaction of buta-1,3-diyne with secondary amines is effected in the cold without a catalyst in benzene solution to form *NN*-dialkylbut-1-en-3-ynamines [128].

The results of systematic investigation of the reaction of diacetylene with amines and amino-alcohols were given by Shostakovskii and his coworkers [129–137]. They showed that buta-1,3-diyne reacts with aliphatic amines at room temperature on passing the buta-1,3-diyne through the amine. Evidently the strongly basic amines show a catalytic action on the course of this reaction. The direction of the addition of the amines to buta-1,3-diyne depends essentially on the nature of the amine. Secondary amines add on in the 1,2 position to form *NN*-dialkylbut-1-en-3-ynamines in 60–70% yield. Primary amines react with buta-1,3-diyne under analogous conditions, adding on in the 1,2 and 3,4 positions, and forming *NN'*-dialkylbuta-1,3-diene-1,4-diamines in 80% yield [130,132,135]:



Unsaturated primary and secondary amines, such as allyl- and diallyl-amines, react similarly [137].

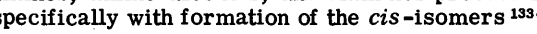
Buta-1,3-diyne reacts much more vigorously with bifunctional compounds (diamines and 2-aminoethanol) than with aliphatic amines [134]. The products of the reactions with propylenediamine and ethylenediamine are heterocyclic compounds: 1,2,3,4-tetrahydro-2-methyl-1,4-diazocine and 1,2,3,4-tetrahydro-1,4-diazocine respectively. The yields are 55–70%:



where R is H or $CH_3$.

Buta-1,3-diyne reacts with 2-aminoethanol at the two triple bonds, forming a linear product of addition in the 1,4 position [134].

Dialkylamino-alcohols react with buta-1,3-diyne by adding on to the triple bond in the 1,2 position [129,131]. The reaction is exothermic, without the participation of a catalyst, and leads to the formation of the corresponding ethynyl vinyl ethers with 80–90% yield:



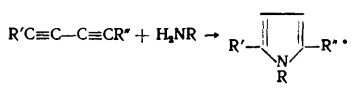
All the above-mentioned reactions of buta-1,3-diyne with amines, amino-alcohols, and diamines proceed stereospecifically with formation of the *cis*-isomers [133–135].

These reactions show the astonishing difference in the behaviour of buta-1,3-diyne and acetylene when they react with amines, amino-alcohols, and diamines. The exceptional ease of reaction of alkylamines and 2-aminoethanols with buta-1,3-diyne is apparently due, above all, to the fact that nucleophilic addition at the triple bond of buta-1,3-diyne is activated by the second ethynyl group, which behaves in relation to the first as an electron-acceptor substituent.

But here it is impossible not to consider also the role of the second component, that is, the amino-compound, which possesses basic properties. Thus, aromatic amines (aniline, methylaniline) under analogous conditions do not react, since their basic properties are diminished owing to the delocalisation of the lone pair of $p$ electrons of the nitrogen with the $\pi$ electrons of the nucleus.

The reaction of buta-1,3-diyne with aliphatic alcohols free from amino-groups takes place only at 70–100° under the influence of an alkaline catalyst [138,139].

Disubstituted buta-1,3-diyne R'C≡C–C≡CR", where R' and R" are aliphatic, aromatic, or heterocyclic radicals, reacts with primary aliphatic and aromatic amines in the presence of small quantities of copper(I) chloride to form trisubstituted pyrroles [140]:



Buta-1,3-diyne can react with a mixture of a secondary amine and paraformaldehyde in the presence of copper or silver salts [141]. It is suggested that the reaction proceeds through the intermediate formation of an aminomethanol, leading to mono- and di-substituted products:

$$CH{\equiv}C{-}C{\equiv}CH + HOCH_2NR_2 \xrightarrow[-H_2O]{} CH{\equiv}C{-}C{\equiv}CCH_2NR_2 \rightarrow$$

$$\xrightarrow[-H_2O]{HOCH_2NR_2} R_2NCH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH_2NR_2.$$

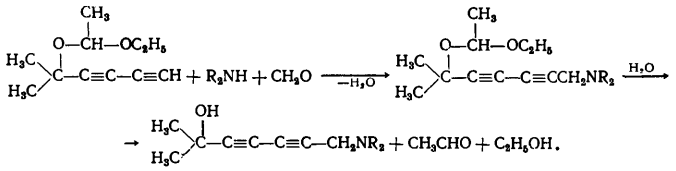
Alkadiyne compounds with isolated triple bonds react with amines and formaldehyde in dioxan solution with a copper catalyst at 80–100° and bisalkynyl ethers react at 80° to form the corresponding diamines [142–144]:

$$CH{\equiv}C{-}(CH_2)_n{-}C{\equiv}CH + 2\,R_2NH + 2\,CH_2O \rightarrow$$

$$\xrightarrow[-2H_2O]{} R_2NCH_2C{\equiv}C{-}(CH_2)_n{-}C{\equiv}CCH_2NR_2,$$

$$(CH{\equiv}CCH_2)_2O + 2\,R_2NH + 2\,CH_2O \xrightarrow[-2H_2O]{} (R_2NCH_2C{\equiv}CCH_2)_2O.$$

The acetal derivative and acetate of 2-methylhexa--3,5-diyn-2-ol react readily on heating with amines and formaldehyde at their labile hydrogen atom; diyne amino--alcohols are formed in good yield [145]:



## 10. REACTION OF BUTENYNES CONTAINING A HETEROATOM IN THE α-POSITION TO MULTIPLE BONDS, WITH AMINES

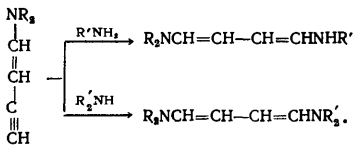
In recent years there has been an investigation of compounds of structure

$$RXCH{=}CH - C{\equiv}CH,$$

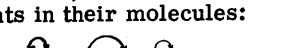
where X = O, N, or S, made in connection with the progress of work on the chemistry of buta-1,3-diyne.

The ability of these compounds to enter into nucleophilic additions is less than that of buta-1,3-diyne and approaches the reactivity of but-1-en-3-yne derivatives.

The addition of amines to butenyneamines takes place at the 3,4 position, and as a result of the reaction, 1,4-substituted dienes are formed with yields up to 80%. [132,133,135] The yield of the reaction product and the conditions of the reaction are determined by the nature of the amine being added:



The addition of amines to a triple bond of butenyneamines, despite Markovnikov's rule, does not correspond with the electron displacements in their molecules:



The displacement of the electron density in butenyneamines, due to the delocalisation of the electron pair of the nitrogen atom over the enyne system, is confirmed by the investigation of the intensities and positions of the absorption bands of the C≡C and ≡C–H stretching vibrations in these compounds and also by the determination of the dipole moment for *NN*-diethylbut-1-en-3-yne-1-amine [146–149].

These reactions can be also regarded as electrophilic additions of an ammonium ion to the position of greatest electron density [150]:

$$\overset{+}{R}NH_3 \ldots \overset{-}{H}C{\equiv}C{-}CH{=}CHNR_2 \rightarrow H(NHR)C{=}CH{-}CH{=}CHNR_2.$$

The formation of positively-charged ions is evidently explained by transfer of a proton in consequence of the autoprotolysis of the amines, which here act as amphiprotic solvents:

$$2\,RNH_2 \rightleftarrows [RNH]^- + [RNH_3]^+.$$

The formation of ammonium ions can be made possible by the presence of traces of moisture. For example, it is well known [49] that the addition of amines to alkoxyalkyne is catalysed by water.

The addition of amines to oxygen- and sulphur-containing analogues of ethynylvinylamines under analogous conditions has not been accomplished.

Whilst this review was being considered by the editors a work was published on the addition of aqueous and dry amines to dimethyldiacetylenemethanol [151].


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# THE MECHANISM OF THE ELEMENTARY ACT OF HOT REACTIONS

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## I. INTRODUCTION

Hot atom chemistry dates from the discovery, made by Szilard and Chalmers in the nineteen-thirties, that as a result of a nuclear reaction, radioactive atoms leave the original molecule and are found partly in a chemical form which can be separated from the initial form. Fermi showed that the reactivity of these atoms is associated with the considerable recoil impulse produced when the second particle is ejected in the nuclear process. Although the first work in the field of the chemistry of hot atoms (as atoms exhibiting appreciable kinetic energy came to be called) was devoted chiefly to the practical utilisation of the Szilard–Chalmers method for the preparation of enriched specimens of radioelements, the main attention was subsequently directed to the secondary effects associated with the chemical action of hot atoms. Here two directions have been distinguished.

Part of the work is carried out with the aim of finding an effective method for preparing labelled compounds, particularly those which are difficult to obtain by ordinary chemical synthesis or by isotopic exchange. The possibilities of the hot synthesis of organic compounds labelled with tritium and carbon have been discussed in reviews by Nesmeyanov and coworkers[1–3].

Another direction in hot atom chemistry involves the investigation of the mechanism of the elementary act of the atom–molecule collision and the subsequent reactions brought about by the transfer of the excess of energy from the atom to the molecule. Since the publication of reviews by Nesmeyanov and Borisov[4,5] in 1957 and earlier, no attempt has been made in the Soviet literature to examine the achievements made in this direction. The present paper examines the results obtained in recently published work. Particular attention is paid to the theoretical interpretation of the results. The review does not reflect completely all directions of study in hot atom chemistry: the main attention is paid to work whose results lead to definite conclusions regarding the mechanism of hot reactions.

At the present time, hot atom chemistry is attracting increasing attention as a branch of high-energy chemical kinetics. This is indicated by the two international conferences held in Prague in 1960 and in Vienna in 1964.

## II. SOME PHYSICOCHEMICAL PRINCIPLES OF HOT ATOM CHEMISTRY

### 1. The Possibility of Applying the Theory of Absolute Reaction Rates to High-Energy Chemical Processes

The first problem arising in the theoretical interpretation of the results of experiments in hot atom chemistry is the extent to which the ideas of an intermediate complex as the transition state of the reacting atom–molecule system are applicable to the reactions of high-energy atoms. The Arrhenius–Eyring equation is:

$$k \simeq z \exp[-E/RT] \simeq pz \exp[-E/RT] \simeq \chi pz \exp[-E/RT], \quad (1)$$

where $z$ is the number of active collisions, $p$ a steric factor, and $\chi$ the transmission coefficient, with $\chi = \rho\sigma$, where $\rho$ is the probability of transition between potential surfaces, and $\sigma$ the reflection coefficient (the reflection coefficient is related to the rate of deactivation in the transition state). This equation can be used to calculate reaction rate constants if the following conditions are satisfied: (1) the reaction A + BM → [AB]M → AB + M is adiabatic, that is, takes place on one potential surface; (2) the potential energy surface has a range corresponding to the existence of the activated complex; (3) equilibrium is established between the reacting substances and the complexes; and (4) the transmission coefficient is constant and close to 1.

Lack of agreement between experimental data and theoretically calculated values for the rates of chemical reactions is attributed to the fact that the intermediate and final products are formed initially with an irregular distribution of energy in the vibrational degrees of freedom. Vibrational--rotational non-equilibrium distributions may also arise as a result of inelastic collisions of the second type (extinction of electronic-excited states on collision). Deviations from "ordinary" kinetics are observed in processes accompanying the combustion of reactive fuels, rapid explosion reactions, etc.[6]

The pictorial model representation of a chemical reaction as the movement of a configurational point over a potential energy surface[7,8] is untenable in the study of reactions initiated by the collisions of fast atoms, in which the duration of the interaction is much less than the rate of energy transfer from the local point of collision to the molecule as a whole. From this it follows that conditions 1–4 can hardly be applicable to reactions initiated by the collisions of hot atoms, in view of the marked non-equilibrium character of the process of energy transfer on collision. Theoretical studies of non-equilibrium processes are at present in the development stage[9,10].

A specific feature of hot atoms is that they approach the range of the energy of chemical interaction "from above", from the direction of higher energies. On retardation, the hot atom passes successively through energy levels until it falls into an energy range below the activation energy for the reaction. In ordinary kinetics, the atoms which reach $E = E_{act}$ "from below" (that is, the active atoms) are able to take part in a chemical interaction which proceeds on a definite surface corresponding to $E = E_{act}$. The hot atom has at its disposal a set of potential surfaces (possibly with facilitated transition between them) and this makes it very difficult to calculate the probability of chemical interaction by means of a model which represents the

course of the reaction in the form of the movement of a configurational point.

Since the reaction of hot atoms with molecules leads to their stabilisation in definite chemical forms, some hot atom–molecule transition state must exist.

The aim of hot atom chemistry is to determine the nature of this transition state and the energy at which bond formation between the hot atom and the molecule takes place, and to investigate the influence of various factors on the course of hot reactions.

## 2. Reactions of Excited Molecules and Processes of Excitation Energy Transfer

As shown in Section I.1, the ideas of "ordinary" kinetics provide little basis for understanding the high reactivity of hot atoms. Irrespective of the way in which a chemical bond is formed by a hot atom on collision with a molecule, however, it is undoubtedly the case that the primary "labelled" molecule is excited. Stabilisation of this molecule can take place only with dissipation of the excitation energy. Most information on this question, particularly in recent years, has been given by radiation chemistry. The deviations, observed in a number of studies, from the law of radiation-chemical additivity in the radiolysis of binary systems can be attributed to a process involving the transfer of the excess of energy from the initially excited molecule fragments [11–15]. Analysis of experimental data on "large" and "small" deviations from additivity showed that in the first case the rate of transfer of energy is greater than the number of collisions with inhibitor by a factor of at least 10 (inhibitor concentration $< 0.01$ M). It is evident that the excitation energy is "thrown" 50–70 Å during the lifetime of the excited molecule. These processes can take place only under conditions where the excitation spectra of two components of the mixture overlap. This condition can be realised in practice by selecting substances with similar chemical structures.

If the action of radiation on a substance leads to the formation of molecular ions, the solution of the problem of energy transfer becomes possible if the following conditions are satisfied: (1) the inhibitor has a complex system of levels (an almost continuous spectrum) in the region of the excitation energy of the main component; (2) the medium is transparent, that is, the excitation levels of the molecular fragments (in particular, ions) formed during radiolysis lie below the first excitation electronic level of the main molecule. Brodskii [13] showed that the probability of inhibition is determined by the equation

$$W = kN^{2/3}\left(1 + \frac{N^{2/3}}{\omega^2} + \frac{N^{4/3}}{\omega^4}\right), \qquad (2)$$

where $N$ is the concentration of inhibitor, and $\omega$ the excitation energy. The available experimental data show good agreement with Eqn. (2) over a wide range of concentrations. Since the excitation energy cannot always be determined accurately, use is made of another equation, previously established experimentally:

$$G = k r^3 = k\left(\frac{1}{\sqrt[3]{N}}\right)^3, \qquad (3)$$

where $G$ is the radiation yield, and $r$ the mean distance between the inhibitor molecules, expressed in the number of molecules of the main substance. Eqn. (3) is a first approximation of the more general equation (2). The physical nature of the phenomenon described by Eqn. (2) is the existence of a mechanism of energy transfer analogous to sensitised fluorescence–non-radiative electromagnetic transition [15].

"Small" deviations from additivity are attributed to the direct transfer of energy through the formation of a donor–acceptor complex according to the scheme: $A^* + B \rightarrow \rightarrow [AB]^* \rightarrow A + B$, where the complex breaks down to non-excited particles.

Simple energy transfer on collision $A^* + B \rightarrow A + B^*$ either is very difficult or does not take place at all. This important experimental fact was established in an analysis of the radiation-chemical yields in the cyclohexane–benzene system and in the study of the intensity of fluorescence in the cyclohexane–terphenyl, benzene–terphenyl, and cyclohexane–benzene–terphenyl systems [11]. Since the chief primary particles in radiolysis are excited and ionised molecules, the part played by benzene in the complex $[AB]^*$ is assumed to involve the following processes: (1) the benzene brings about the conversion of the electronic excitation of the cyclohexane molecules; and (2) the benzene removes the charge from the cyclohexane molecule, since the ionisation potential of benzene is lower by 1.8 eV.

From the viewpoint of the formation of donor–acceptor complexes, it is also possible to explain the "large" deviations from additivity, observed at low concentrations of added acceptor, if we assume the existence of associates consisting of molecules of the main substance; in this case the collision of an inhibitor molecule with an associate is equivalent to a collision with an initially excited molecule.

The explanation of the results of radiolysis, however, even for a well-studied system such as the cyclohexane–benzene system, is ambiguous, since the benzene may react with thermal hydrogen atoms:

$$C_6H_6 + H^{\cdot} \rightarrow C_6H_7^{\cdot} \rightarrow \text{polymer}$$

(pyridine shows analogous behaviour in mixtures with benzene [16]).

Moreover, according to Swallow's hypothesis [17] (based on the data of Inokuti on cross-sections for the interaction of electrons with benzene molecules), radiation may be selectively absorbed in a mixture of two components, so that the concentration dependence of the yields of radiolysis products shows marked departure from linearity. Thus departure from additivity in the radiolysis of binary systems does not provide sufficient basis for concluding that energy transfer from the initially excited molecules occurs and influences the yield of radiolysis products.

If Swallow's model were applicable, the radiolysis of a cyclohexane–benzene binary mixture in the gaseous phase at low pressures should give the same effect as that given in the liquid phase. Since the gas-phase radiolysis showed differences from the regular features observed for condensed systems [18], doubt was cast on the applicability of Swallow's hypothesis.

Since the transfer of excitation energy assumes the existence of long-lived states — and this has not been proved spectroscopically — some authors suggest that the deviation from the law of radiation-chemical additivity is due to the formation of hot hydrogen atoms during radiolysis. The energy of the hydrogen atoms formed during radiolysis varies from fractions of 1 eV to 1–3 eV. These atoms are capable of detaching hydrogen from organic compounds with consequent breakdown of the primary distribution of radiolysis products [19,20].

The most appropriate viewpoint is that which allows for the principal effects observed: one of the observed (or assumed) effects may play a major part, depending on the nature of the compounds and the relative concentration of the components[21].

The processes of excited molecule stabilisation are apparently accompanied by intramolecular energy transfer. This was proved by experiments on the radiolysis of alkylbenzenes. The yield of radicals from the compounds $C_6H_5R$ (where R= alkyl) is less than that from the mixture $C_6H_6$ + RH. This indicates a process of effective energy transfer from the side chain into the phenyl ring. At the same time, analysis of the radiolysis products of alkylbenzenes indicated that the greatest tendency to undergo rupture is shown by the bond formed by the second carbon atom in the side chain, that is, the $C_6H_5CH_2^{\cdot}$ radical is formed in highest yield, irrespective of the length of the chain. This can be attributed to transfer of excitation energy from the benzene ring into the side chain, or simply to the high "vulnerability" of the $\alpha$ position in intramolecular energy migration.

The yields of the products of hot reactions also show deviation from the additivity law, suggesting that the process of energy transfer from the excited labelled products takes place.

## 3. The Retardation of Hot Atoms (Physical Interpretation)

It has recently been assumed that the retardation of hot atoms in the range of energies in which the reactions of hot atoms do not take place obeys the laws derived from the assumption of elastic particle collisions. In this case the retardation spectrum can be calculated using the equations describing the process of neutron thermalisation[22,23].

The fraction of the energy remaining on a recoil atom (m) after collision with another atom (M) is

$$E'/E = \frac{m^2 + M^2 + 2mM\cos\theta}{(m+M)^2}. \quad (4)$$

The minimum fraction is

$$\alpha = \left(\frac{m-M}{m+M}\right)^2. \quad (5)$$

The loss of energy or the fraction of the energy transferred to an atom of the medium is equal to

$$E''/E = \frac{2mM}{(m+M)^2}(1-\cos\theta). \quad (6)$$

The maximum loss is

$$\beta = \frac{4mM}{(m+M)^2}, \quad (7)$$

where $\theta$ is the scattering angle of the centre of mass in the system. The extent of the deviation from spherical scattering can be estimated from the mean value of the cosine of the angle of scattering in a laboratory system of coordinates ($\overline{\cos\varphi}$):

$$\overline{\cos\varphi} = \int_0^{\pi} \cos\varphi\,\lambda(\theta)\,d\theta = \int_0^{\pi} \frac{(M\cos\theta + m)}{\sqrt{m^2 + M^2 + 2mM\cos\theta}} \frac{1}{2}\sin\theta\,d\theta, \quad (8)$$

where $\lambda(\theta)d\theta$ is the probability of scattering.

For the case of the retardation of tritium recoil atoms in a hydrogen-containing medium, expression (8) becomes

$$\overline{\cos\varphi} = \frac{1}{2}\int_{-1}^{+1} \frac{y+3}{\sqrt{1+6y+9}}\,dy, \quad (9)$$

where $y = \cos\theta$, and $dy = -\sin\theta d\theta$.

Solution of integral (9) gives $\overline{\cos\varphi} = 0.9$, that is, the scattering of tritium recoil atoms in hydrogen-containing media is markedly anisotropic.

The number of collisions necessary for retardation of a given energy $E$ from an initial energy $E_0$ is

$$k = \frac{\ln\frac{E_0}{E}}{\xi}, \quad (10)$$

where $\xi$ is the logarithmic energy decrement

$$\xi = \overline{\ln\frac{E}{E'}} = 1 + \frac{\alpha}{1-\alpha}\ln\alpha. \quad (11)$$

For a chemical two-component compound or binary mixture of substances, the logarithmic decrement is

$$\xi = f_1\xi_1 + f_2\xi_2 = \frac{N_1\sigma_1\xi_1 + N_2\sigma_2\xi_2}{N_1\sigma_1 + N_2\sigma_2}, \quad (12)$$

where $N_1\sigma_1$ and $N_2\sigma_2$ are the macroscopic scattering cross-sections ($N\sigma = \Sigma_S$), $N_1$ and $N_2$ the mole fractions, $\sigma$ the microscopic scattering cross-section, and $f_1$ and $f_2$ the geometric probabilities of collision with the first and second components of the mixture.

The beam of hot atoms which have reached the energy level $E$ is defined by the expression

$$n(E) = \frac{q}{\xi E\Sigma_s}, \quad (13)$$

where $q$ is the number of recoil atoms generated, in $cm^3 \times s^{-1}$. Expression (13) is applicable if $E \ll E_0$, that is, if the recoil atom has undergone at least several collisions with other atoms. A more precise criterion for the applicability of Eqn. (13) is that $E < \xi^3 E_0$. If this is not so, it is necessary to make allowance for the fact that the function $n(E)$ shows discontinuities at $E = \xi^n E_0$, where $n = 1, 2, 3\ldots$ (collision density oscillations).

A more accurate hot atom distribution than that given by formula (13) can be found by the two-group approximation method (Placzek[22] and Temkin[13]). The equations obtained are extremely cumbersome, and simple expressions can be obtained only when the tracks of the hot atoms overlap. This last condition is not satisfied, however, for hot atoms obtained by nuclear reactions.

Eqn. (13) is applicable to the retardation of recoil atoms on atoms with similar masses, and also when it is desired to find the value of $n(E)$ at a distance from the initial recoil energy. These conditions are generally realised in the study of reactions brought about by hot atoms.

If the hot atoms undergo chemical reactions in the energy range from $E_2$ to $E_1$, the retarded atom spectrum loses a fraction of recoil atoms equal to

$$1 - \exp\left[-\int_{E_1}^{E_2} \frac{p(E)}{\xi}\frac{dE}{E}\right], \quad (14)$$

where the exponent expresses the probability of avoiding hot reactions in the range $E_2$–$E_1$, and $p(E)$ is the chemical reaction excitation function. The latter is dependent on

energy and apparently has resonance character. This makes it possible to apply the basic formulae from the theory of neutron retardation (4)–(14) not only to the case of retardation through collision, but also to the derivation of equations for the yields in chemical reactions of hot atoms.

The theory of neutron retardation as applied to the collisions of hot atoms was recently developed by Hsiung and Gordus[24] for isotropic and anisotropic scattering with selection of two interaction potentials (rigid-sphere collisions and Lennard-Jones potential). It was shown that isotropic scattering with respect to the centre of mass with selection of the Lennard-Jones interaction potentials is achieved only for simple atomic systems (H + $H_2$, H + He) and then naturally coincides with the isotropic scattering for the elastic scattering of particles. For more complex systems, for example, the collision H + $CH_4$, the deviation from isotropy is significant. Thus in real systems where retardation of hot atoms takes place, the loss of energy will be dependent on the energy.

If by definition $\xi = \overline{\ln \frac{E}{E'}}$, Eqn. (11), we have

$$\xi = \int_{\alpha E}^{E} \ln \frac{E}{E'} \lambda(E, E')\, dE,$$

where $\lambda(E, E')$ is the scattering function[24]. Eqn. (11) was obtained for isotropic scattering with respect to the centre of mass, when the probability of scattering is

$$\lambda(E, E') = \frac{1}{2} \sin\theta d\theta.$$

## III. CHEMICAL REACTIONS OF HOT ATOMS

The general considerations discussed in Section II naturally do not resolve the problems facing hot atom chemistry. The theory of the kinetics of the reactions of hot atoms includes many problems, each of which is still far from being solved (non-equilibrium processes of energy transfer in hot-atom collisions, the dissociation of molecules, reaction excitation function, etc.). This explains the difficulty and ambiguity of the interpretation of results in hot atom chemistry. In recent years some progress has been made in this direction. Special experiments aimed at investigating the part played by individual factors influencing the yield of hot reactions have eliminated to a considerable extent the ambiguity and indefinite nature of the results.

The greatest number of papers has been published on the chemistry of hot atoms of tritium, the halogens, and carbon in organic systems, by Rowland and coworkers[25], Wolfgang and coworkers[26], Willard and coworkers[27], Nesmeyanov and coworkers[3,28–30], and Wolf and coworkers[31].

### 1. Mechanism of the Reactions of Hot Tritium Atoms

It is now regarded as firmly established that in reactions of hot atoms no transition complex with regular energy distribution exists; this also follows from the theory of the non-equilibrium processes of kinetic energy transfer on collision between a hot atom and a molecule. An exception is those systems in which, after the primary act of collision and transfer of energy, states with lives long enough ($10^{-7}$–$10^{-8}$ s) for the even distribution of energy throughout the degrees of freedom are produced†. The substances which have been studied in this connection include cyclopropane[32], cyclobutane[33], and unsaturated compounds[34–36].

The reactions of tritium recoil atoms with molecules containing saturated carbon–carbon bonds generally take place by direct single-stage interaction between the recoil atom and individual atoms (more accurately, chemical bonds‡); this primary process does not involve other atoms. The latter merely provide the spatial limitation in the attack by the hot atom.

With this approach to the mechanism of the reactions of hot atoms, it becomes possible to compare the results of experiments with calculation. The main assumptions of the theory[37] are as follows. Of the total number of hot atoms ($N_s$) only part ($N_h$) react in the energy range $E_2$–$E_1$, in which the probability of chemical reaction on collision $p_i(E)$ differs from zero:

$$R_{ij} = N_h / N_s = \int_{E_1}^{E_2} f_j p_i(E)\, n(E)\, dE, \qquad (15)$$

where $R_{ij}$ is the yield of the $i$-product of the hot reaction from the $j$-component, $f_j$ the probability of collision with the given component, $f_j = N_j \sigma_j / \Sigma N\sigma$ ($N_j$ is the mole fraction of the $j$-component, and $\sigma_j$ the collision micro-cross-section), $n(E)dE$ the hot atom spectrum (the number of collisions between $E$ and $E + dE$), and $p_i(E)$ the probability of reaction on one collision with a molecule of the $j$-component with the formation of the $i$-labelled product. It is evident that in the range $E > E_2$, $n(E)$ is equal to the flow of hot atoms in the absence of absorption, that is, it can be calculated from formula (13): $1/\xi E$ ($\Sigma_s$ is assumed to be constant). When chemical reactions take place, the atoms taking part in the chemical reactions are "eaten out" of the spectrum in the range $E_2$–$E_1$. It is assumed that the fraction of atoms not taking part in the reaction is proportional to

$$\exp\left[-\int_{E}^{E_2} f\, p(E)\, n(E)\, dE\right] \qquad (16)$$

[see Eqn. (14)]. The flow of hot atoms when chemical reactions take place is then equal to

$$n(E) = \frac{1}{\xi E}\left\{\exp\left[-\Sigma \int_{E}^{E_2} f p(E)\, n(E)\, dE\right]\right\} \qquad (17)\S$$

(the sum with respect to all components of the mixture).

Substitution of Eqn. (17) into (15) and expansion of integral $\int_{E_1}^{E_2} \frac{p(E)}{E} dE$ into a series leads to an expression of the form

$$R = 1 - \exp\left[-\frac{f}{\xi} I\right], \qquad (18)$$

† In this case also, however, the primary act does not involve the formation of an intermediate complex. Here a "pseudo-complex" is formed, since the course of the reaction is determined by the second, slow stage of energy redistribution.

‡ See p. 685 for more details.

§ The integral in expression (17) is the resonance integral in the theory of neutron retardation[22,23]; see elsewhere[28,38] for more details.

where

$$I = \int_{E_1}^{E_2} \frac{p(E)}{E} dE. \qquad (19)$$

The quantity $R$ signifies the yield of all products containing recoil atoms and formed by hot reactions. For the yield of an individual labelled compound from a two-component system (the second component being an inert moderator), we obtain the expression

$$R_{1i} = \frac{f_1}{\xi} I - \frac{f_1^2}{\xi^2} K, \qquad (20)$$

where

$$I = \int_{E_1}^{E_2} \frac{p_i(E)}{E} dE, \qquad (21)$$

and

$$K = \int_{E_1}^{E_2} \frac{p_i(E)}{E} \left[ \int_{E}^{E_2} \frac{p(E)}{E} dE \right] dE. \qquad (22)$$

Here $p_i(E)$ is the probability of a hot reaction on one collision between a hot atom and a molecule with the formation of an $i$-labelled product, and $p(E)$ the probability of formation on collision of all labelled products. If the second component is not inert, we have

$$K = \int_{E_1}^{E_2} \frac{p_i(E)}{E} \left[ \int_{E}^{E_2} \frac{f_1 p_1(E) + f_2 p_2(E)}{E} dE \right] dE,$$

where $p_2(E)$ is the probability of chemical reaction with the formation of all labelled products on collision with a molecule of the second component.

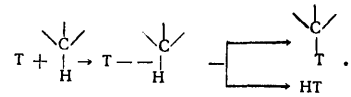
It follows from (20) that the dependence of $(\xi/f)R_{1i}$ on $f/\xi$ should be given by a straight line. The intercept on the axis of ordinates gives the value of the integral (21), that is, the probability of chemical reaction with the formation of a definite labelled product, and the slope gives the value of integral (22) as the probability that the hot atom enters any chemical compound in general.

This model was verified for the case of hot tritium atoms in the methane–inert gas system. The mean value of the probabilities of the hot chemical reaction of tritium atoms with methane with the formation of $CH_3T$:

$$\overline{p(E)} = I/\ln\frac{E_2}{E_1}, \qquad (23)$$

was found to be 0.12. The quantities $f$ and $\xi$ were calculated from the masses and dimensions of the atoms and molecules in the approximation corresponding to elastic transfer of energy.

It was shown that the mechanism of elastic collisions is not applicable to the reactions of hot tritium atoms [39]. An important problem in this connection is the following: how does the transfer of energy from the hot atom to the molecule, leading to chemical reaction, take place? The agreement between the experimental data and calculation according to formula (20) for the yield of the product of hydrogen replacement is best [40] if it is assumed that the tritium atom collides with a mass which is smaller than the mass of the methane molecule but greater than the mass of the hydrogen atoms. If the role of this "effective mass" is assigned to the chemical bond between the atoms in organic compounds, the process of formation of compounds labelled with tritium can be represented schematically as follows.



This conclusion follows from the following experimental facts: (1) the yield of product formed by the rupture of any bond is proportional to the total number of bonds of this type; the ratio of the yields $HT/CH_3T$ in the reactions of hot tritium atoms with carboxylic acids [41] and alcohols [42] is directly proportional to the ratio: (number of C–H bonds) ÷ ÷ (number of $C-CH_3$ bonds); (2) the reactions of tritium recoil atoms are not accompanied by Walden inversion [43] and the isomeric configuration is also preserved [32,33,44]; (3) 90% of the activity of the tritium is distributed between the labelled mother compound RT and active hydrogen HT. The ratio of the yields HT/RT (hydrogen abstraction/hydrogen replacement) in the reactions of hot tritium atoms with hydrocarbons agrees with the expression

$$\frac{HT}{RT} = \frac{n}{n_1(1-\Omega) + n_2(1-\Omega)^2 + n_3(1-\Omega)^3}, \qquad (24)$$

where $n$ is the total number of hydrogen atoms in the molecule, $\Omega$ the steric hindrance in the reaction of hydrogen replacement, and $n_1$, $n_2$, and $n_3$ the numbers of primary, secondary, and tertiary hydrogen atoms.

The experimental data are compared with the results calculated from formula (24) in Table 1. [26]

These facts give grounds for concluding that hot tritium atoms react with the bonds between the C and H atoms and that attack along the C–H bond (more accurately, at small angles to this bond; in this case there is no steric hindrance so that the yield of HT is proportional to the total number of hydrogen atoms) leads to the abstraction of

TABLE 1. The part played by steric factors in the abstraction and replacement of hydrogen by hot tritium atoms.

| Substance (hydrocarbon) | Abstraction / replacement: calculated ratio | observed experimentally |
|---|---|---|
| $CH_4$ | 1 | 1 |
| $C_2H_6$ | $\frac{1}{1-\Omega} = 1.82$ | 1.82 |
|  | $\frac{1}{1-\Omega} = 1.82$ | 1.40 |
|  | $\frac{10}{9(1-\Omega)+(1-\Omega)^3} = 1.95$ | 1.95 |
|  | $\frac{4}{3(1-\Omega)+(1-\Omega)^3} = 2.05$ | 2.0 |
|  | $\frac{10}{6(1-\Omega)+4(1-\Omega)^2} = 2.2$ | 2.0 |
|  | $\frac{14}{6(1-\Omega)+8(1-\Omega)^2} = 2.4$ | 3.3 |
|  | $\frac{12}{9(1-\Omega)+2(1-\Omega)^2+(1-\Omega)^3} = 2.1$ | 2.0 |

$\Omega$ is the steric parameter in replacement reactions: $\Omega = 0.45$ is the choice made to give agreement between calculation and experiment for the case of ethane.

hydrogen in the form HT, whereas attack in a perpendicular direction (more accurately, at high angles to the bond; the steric hindrance increases with increase in the angle of attack and amounts to $\Omega = 0.45$ for primary hydrogen) leads to the replacement of hydrogen.

The theory whose main conclusions have been examined above has been called the "collision model" [37]. For the gaseous phase, this model was confirmed for the case of recoil halogen atoms [45-47].

It follows from the collision model that the decisive factors for reactions of hot atoms in the gaseous phase are: the steric hindrance to approach to the bond, the form of the function $p(E)$, and the hot atom spectrum in the range $E_2 - E_1$, where $p(E) > 0$. The value of the bond energy is unimportant from the viewpoint of the "collision model".

The collision model was developed by Wolfgang for multicomponent systems [48] and may now form a basis for the development of a theory of the kinetics of high-energy reactions. The case of the gas-phase reactions of tritium recoil atoms, $^3He(n,p)T$ with ethane, butane, neopentane, and hydrocarbon mixtures with the addition of a moderator has shown [49] the applicability of the Wolfgang equation — a combination of formulae (12) and (18): [48]

$$-1/\ln(1-R) = \xi_p/I + \xi_M/I\,\frac{1-f_p}{f_p}, \qquad (25)$$

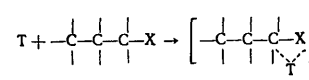
where $\xi_p$ is the mean loss of energy for the collision of tritium with a molecule of the main component, and $\xi_M$ is the same for the collision with a molecule of the inert moderator, for example, helium.

These results [49] show that the ratio of the molar activity of ethane to the molar activity of neopentane for the neutron irradiation of a $^3He + C_2H_6$ + neo-$C_5H_{12}$ mixture *increases* with *decrease* in the ethane concentration, that is, the reactivity of the ethane molecules in the replacement of H by T increases (or that of neopentane decreases) with decrease in its concentration. The same effect of increase in the relative activity of tritium-substituted ethane is achieved by adding the moderator helium to the mixture being studied (at the same molar ratios). It was concluded that hot reactions are extremely sensitive to change in the spectrum of the retarding atoms, the mean energy losses for retardation in identical substances differing considerably. Data on the magnitude of the energy losses on collision of tritium with molecules of ethane, butane, and neopentane, and also the integral probabilities of chemical reaction with the formation of labelled ethane, butane, and neopentane in the reactions of hot tritium atoms, are given in Table 2 (the data were calculated relative to the value of $\xi$ He — the mean loss of energy by tritium on collision with helium, for example, $\xi$ ethane = $= 3.64\xi$ He).

TABLE 2. Mean energy loss for the collision of hot tritium atoms with ethane, n-butane, and neopentane. Integral probabilities of replacement and abstraction of hydrogen by hot tritium atoms. (Conditions [49]: 1 cm $^3He$, 2–4 cm $O_2$, 1 atm of substances, integral neutron beam $10^{15}$).

| Hydrocarbon | $\xi$ | $I_{RT}$ | $I_{HT}$ |
|---|---|---|---|
| Ethane | 3.64 | 2.1 | 0.55 |
| n-Butane | 5.05 | 2.78 | 0.79 |
| Neopentane | 5.8 | 2.93 | 0.59 |

The collision model does not reveal the nature of the phenomenon of energy transfer on collision and formation of a chemical bond, that is, a transition state leading to the hot reaction is excluded. At the same time the concept which considers the process of establishment of chemical bonds through a transition complex is more familiar to the chemist [25]. Since there is no significant difference in the yields of compounds labelled with tritium relative to change in the phase state and pressure in the gaseous phase (that is, deactivating collisions after the "marking" process do not influence the distribution of the activity), this complex should exist for a period of not more than $10^{-13}$–$10^{-14}$ s ("collision complex"), that is, for the duration of one or two vibrations of the bond:



The breakdown of the "collision complex" may be determined by the C–X bond energy, but the bond energy is apparently not so important. The reaction of hot atoms takes place in the range 15 eV–$E_{act}$, and the recoil atoms approach "from above" the energy values where the probability of reaction has maximum values. A change in the magnitude of the bond energy by several tenths of an electron volt cannot greatly influence the yield of labelled compound, since the greater part of the reactions are assumed to take place in the range 3–8 eV. Since the abstraction (of hydrogen) takes place at lower energies than substitution, as observed in experiments to find models for the collisions of atoms and molecules in the tritium + hydrocarbon system (tritium gas at $t = 1200$–$1800°$), [50] change in the C–X bond energy should be revealed as a change in the yield of the abstraction (in the form XT).

In fact, Rowland, the author of the latest theory, was able to show that the proportion of the activity of the tritium in the form HT is consistent with the energy of the C–H bond [51]; a paradoxical feature is that neopentane was not "fitted" into the relationship found for other hydrocarbons until new data were published on the energy of the C–H bond in neopentane.

It follows from the experiments of Rowland and coworkers [51] that the chemistry of hot tritium atoms gives an accuracy in the determination of the energy of the chemical bond which is no less than that given by the ordinary methods of "ordinary" chemistry.

In this connection, some doubt may be cast on the aspect of the collision theory dealing with the competing reactions of hydrogen abstraction and replacement, particularly for systems in which the hot atom spectrum contains an appreciable proportion of epithermal and "slightly hot" atoms. Such atoms in the range 0.5–3 eV have a greater tendency to take part in hydrogen abstraction, and in this range the C–H bond energy influences the yield of HT.

There are apparently no fundamental contradictions between the "collision model" [26,37] and the "collision complexes" [25]; at any rate, the experimental data can be explained equally successfully from both viewpoints. Let us take an example. Isotopic effects have been observed [39,53-58] in the reactions of tritium recoil atoms with simple dueterated compounds (Tables 3 and 4): the processes of replacement and abstraction of hydrogen by tritium ions

TABLE 3. Isotopic effect in reactions of hot tritium atoms with simple and deuterated compounds[58].

a. Abstraction of HT or DT

| Ratio of yields | Substance | | | |
|---|---|---|---|---|
| | $CH_2D_2$ | $CH_3CD_3$ | $CH_4+CD_4$ mixture | $CH_3F+CD_3F$* |
| HT/DT | 1.32±0.01 | 1.34±0.01 | 1.28±0.02 | 1.26±0.05 |

b. Replacement of H and D by T

| $CH_3T/CD_3T$ | $CH_2TF/CD_2TF$* | $C_4H_9T/C_4D_9T$** |
|---|---|---|
| 1.31±0.05 | 1.33±0.04 | 1.21±0.05 |

* Derived from experiments with mixtures of $CH_3F$ (or $CD_3F$) and cyclobutane.

** Derived from experiments with mixtures of n-$C_4H_{10}$ (or n-$C_4D_{10}$) and $CH_4$.

TABLE 4. Isotopic effect in reactions of tritium recoil atoms with simple and deuterated methyl fluoride[40].

| Replacement | Yield of products from | | H-system / D-system |
|---|---|---|---|
| | $CH_3F$ | $CD_3F$ | |
| H (D) | 12.4 | 10.1 | 1.23±0.02 |
| F | 4.2 | 3.2 | 1.30±0.02 |
| H (D), F | 2.9 | 2.1 | 1.4 ±0.06 |
| 2 H (2 D) | 1.3 | 0.9 | 1.4 ±0.09 |

(Yield given for the total absolute activity of tritium.)

For the abstraction of hydrogen (or deuterium) the isotopic effect = = 1.17 ± 0.03.

take place preferentially by 30% compared with the same processes for deuterium.

Since the loss of energy on retardation is not the same even for a homologous series of substances[49], the magnitude of the isotopic effect is investigated by carrying out experiments on the action of hot tritium atoms simultaneously in a mixture of two substances such that the spectra of the retarded atoms are the same[58]. For example, determination of the yield of $CH_2TF$ from $CH_3F$ and of $CD_2TF$ from $CD_3F$ and calculation of the ratio $CH_2TF/CD_2$. .TF (Table 3a) were carried out in a study of mixtures of $CH_3F$ and $CD_3F$ with a large quantity of cyclobutane. The yield of $CH_3T$ and $CD_3T$ from $CH_4$ + cyclobutane and $CD_4$ + + cyclobutane mixtures was determined in analogous fashion. The ratio $CH_3T/CD_3T$ was found[58] to be equal to 1.31 ± 0.05, which agrees with the ratio $\frac{CH_3T/CD_3T}{CH_4/CD_4}$ obtained from direct experiments with a $CH_4$ + $CD_4$ mixture[56].

From the viewpoint of the collision model, the isotopic effect observed in reactions of tritium recoil atoms with methane and deuteromethane can be attributed to a difference in the retarding power of the simple and deuterated compounds[40].

We are however, faced with the question of how the isotopic effect arises in the reaction of hot tritium atoms with $CH_2D_2$ $\left(\frac{HT}{DT}=1.32\right)$, with $CH_3CD_3$ $\left(\frac{HT}{DT}=1.34\right)$, and in a $CH_4$ + $CD_4$ mixture ($CH_3T/CD_3T$ = 1.26), where the recoil atom spectra are the same for the replacement and abstraction of H and D.

Some part is possibly played by a slight difference in the values of the C–H and C–D bond energies, but it is then difficult to explain the existence of the isotopic effect for the replacement of fluorine by tritium atoms in $CH_3F$ and $CD_3F$ ($CH_3T/CD_3T$ = 1.3 [40]), where the C–F bond energy is the same in both compounds.

Recent work by Rowland and coworkers[57] has shown that in the $CH_4$ + $D_2$ system the ratio of the specific activities $DT/D_2/CH_3T/CH_4$ remains unchanged with change in the ratio of the gas pressures by a factor of 15. This indicates, firstly, that the hot tritium atoms not only react with $CH_4$ in the high-energy range to give $CH_3T$, but also are effectively retarded, on collision with methane, to low energies, which are, however, higher than the activation energy for exchange with deuterium (0.5 eV); and secondly, that the $p(E)$ curve for the replacement of hydrogen in methane by hot tritium atoms lies in a higher energy range and does not overlap the range for the reaction T + + $D_2$ = TD + D. This makes possible the appearance of an "integral" isotopic effect associated with the difference in the energy dependence of the probabilities of the chemical reactions, which, like the change in the retardation parameter $\xi$, explains so successfully the difference in the yields of the products of the replacement (or abstraction) of H and D.

A pictorial representation of the dynamics of the collision of hot tritium atoms with methane molecules may be provided by the collision of "a sphere against a cushion" [57], in which an appreciable proportion of the kinetic energy of the hot atom is lost.

It has now been established that the magnitude of the mean energy loss on collision changes sharply in the range of chemical interaction[49,57]. The corresponding theoretical approach to this problem has already been mentioned (see Section II. 3).

The importance of the study of isotope effects in the reactions of hot tritium atoms is related to the fact that this may reveal the mechanism of bond formation in the reactions of highly energetic atoms with molecules. It is of interest to determine the decisive factor in the production of isotopic differences in the replacement of hydrogen and deuterium by tritium: the process of replacement on collision or the secondary process of bond formation after the ejection of hydrogen and deuterium, that is, whether the important reaction is

(1) $$T+CH_4 \rightarrow CH_3T+H,$$

or the recombination of radicals in direct proximity

(2) $$T+CH_4 \rightarrow CH_3 \,\vdots\, T+H.$$

It is suggested that the answer may be obtained by studying the yields of H and D replacement by tritium in $CH_2D_2$:

(3) $$T+CH_2D_2 \rightarrow CHTD_2+H,$$

(4) $$T+CH_2D_2 \rightarrow CH_2DT+D.$$

If the chief part is played by direct replacement, the yield of reaction (3) should be 30% greater than the yield

of reaction (4) (since the replacement of hydrogen is preferred to the replacement of deuterium to the extent of 30%). If the main part is played by the secondary isotopic effect (recombination in direct proximity), reaction (4) should be preferred to reaction (3) to the extent of 10%, since on the recombination of radicals in direct proximity to one another, an important part is played by the "inertial mechanism" of replacement, namely: the rate of recombination is greater, the smaller the mass of the fragment (see Section IV. 7). At present, however, the technical difficulties of separating the products of reactions (3) and (4) have not been overcome.

In concluding this section we may note the following feature. The magnitude of the isotopic effect, obtained in the reactions of tritium recoil atoms with simple and deuterated compounds, amounts on the average to 1.3–1.4 (H-system/D-system) and is extremely close to the ratio of the fundamental vibration frequencies of the C–H and C–D bonds (with the assumption that the force constants are equal)

$$\nu_{C-H}/\nu_{C-D} = \sqrt{\frac{f}{m_H}}\Big/\sqrt{\frac{f}{m_D}} = \sqrt{2} \simeq 1.4.$$

This ratio of the rate constants for the chemical reactions of hydrogen and deuterium replacement is obtained if in the transition complex the dimensions of the bond remain unchanged on replacement[59]. For a completely broken bond in the transition complex the kinetic isotopic effect acquires a maximum value of 18. In ordinary chemical reactions, the replacement of hydrogen by deuterium leads to a decrease in the rate of reaction by a factor of 3–8, indicating appreciable deformation of the bond during the reaction[59]. From the above comparison it may be concluded that the "transition state" in a hot reaction has the character of a local collision at the C–H bond in a period of $\sim 10^{-14}$ s, in which the lengths of the C–H and C–D bonds cannot change. Thus the kinetics of hot reactions represent an extreme case of the kinetics of ordinary chemical reactions.

Valuable information on the mechanism of the reactions of hot atoms may be given by experiments to find models for atom–molecule collisions. The first experiments in this direction with tritium atoms heated to 1800° and used to bombard a cyclopropane target[50] showed that the processes of hydrogen replacement take place in a higher energy range than the abstraction processes. This may change our ideas regarding the kinetics of hot atom reactions, particularly the conclusions regarding the mechanism of production of the isotopic effect. An increase in the retarding power of the medium should lead to an increase in the fraction of hydrogen abstraction reactions (the kinetic isotopic effect should increase).

## 2. Reactions of Hot Halogen Atoms

The energy of halogen recoil atoms obtained by an $(n,\gamma)$ reaction varies from several dozen to several hundred eV. Some of the atoms can apparently undergo chemical reaction with the medium on the first collisions. In this connection, the chemical state of the recoil atoms which have undergone the nuclear reaction is of considerable importance. The collection of recoil atoms in the gaseous phase[60] has shown that after an $(n,\gamma)$ reaction the atoms may remain in a metastable state, which leads to charged atoms after an internal conversion process. The process of charge increase takes place after the atom has left the parent molecule. The process is described in more detail as follows. The greater part of the excitation energy of the nucleus after the nuclear reaction is lost by the emission of $\gamma$-quanta (several $\gamma$-quanta with $\sim 1$–3 MeV)¶. The remaining fraction is lost by low-energy transitions accompanied by internal conversion. The lifetime of a level with $E > 1$ MeV is $10^{-14}$ s; the lifetime of transitions with low energies lies in the range $10^{-12}$–$10^{-5}$ s. After the ejection of the $\gamma$-quantum, for example, with $E \sim 1$ MeV, the atom leaves the molecule, and after $10^{-13}$ s it is stopped, after having moved a distance of several molecular diameters. Thus hot reactions initiated by part of the excitation energy of the nucleus after neutron capture take place before the start of the process of avalanche charge increase, as a result of the conversion of soft $\gamma$-quanta. These conclusions are confirmed by many experimental facts, in particular by data on the proportions of charged atoms (indium and manganese) after an $(n,\gamma)$ reaction. These proportions are independent of the original form irradiated by the neutrons and amount to 40–60%. This means that the accumulation of positive charge on the atom takes place in a time interval which is longer than that required for rupture of the bond and several first collisions. Wexler and Davies[62,63] found the proportions of charged atoms after an $(n,\gamma)$ reaction: 25% for $^{82}$Br, 12% for $^{80}$Br, 21% for $^{38}$Cl, and 50% for $^{128}$I. The mean charge of the recoil ions was found to be +10 (for $^{80}$Br). Intensive supercharging of positive $^{80}$Br recoil ions was also observed, the current strength of the resulting negative ions increasing with increase in the density of the medium.

The determination of the fraction of positively charged atoms after radiative neutron capture by the collection of recoil atoms is very imperfect. The probability of energy loss by conversion increases as $z^3$, whereas experiments with different recoil atoms give approximately the same fraction of charged atoms[60].

It follows from the foregoing that the "hot chemistry" of heavy recoil atoms should make allowance for the possibility of twofold introduction of radioactive atoms into the compounds: firstly as a result of recoil from hard capture $\gamma$-quanta, and secondly as a result of the conversion of soft capture $\gamma$-rays and the subsequent processes of charge formation on the atom: intramolecular charge transfer — formation of molecular ion — dissociation of molecular ion — formation of recoil ion — chemical reaction of recoil ion.

Suess[64] and later Libby[65] showed that the rupture of the chemical bond in a diatomic molecule uses up a fraction of the recoil energy which depends on the ratio of the masses of the recoil atom and the second atom. The excitation energy used up in the dissociation is found from the difference between the kinetic energy of the recoil atom and the kinetic energy of movement of the centre of gravity of the molecule:

$$E_{\text{excitation}} = E_m - E_M = p^2/2m - p^2/2(m+x) = E_m \frac{x}{M}, \qquad (26)$$

where $x$ is the mass of the second atom, $M$ the mass of the molecule, $M = m + x$, $m$ the mass of the recoil atom, and $p$

¶ Groshev[61] showed that the proportion of the excitation energy of the nucleus de-excited by photons with $E > 0.5$ times the binding energy of a neutron ($\alpha$) is close to 80–100% only for atoms with magic numbers of neutrons and protons. As a rule, $\alpha$ = 20–30% for heavy atoms, 30% for chlorine, 70% for sulphur, and 60% for phosphorus.

the impulse of the recoil atom. The condition for bond rupture as a result of the recoil effect has the form

$$E_{\text{recoil}}\frac{x}{M} > \nu, \qquad (27)$$

where $\nu$ is the energy of the chemical bond.

Gordus[66] obtained formulae for calculating the condition for ejection of recoil atoms from molecules in terms of the masses of the atoms, the interatomic distances, and the angles between the bonds in polyatomic molecules. In order to obtain approximate data for the case of polyatomic molecules, however, it is possible to use Eqn.(26) and the inequality (27), assuming that $x$ is equal to the mass of the molecular residue. The error amounts to 15–20%. Careful experiments to find the fractions of unbroken bonds in an $(n,\gamma)$ reaction showed that they amount to approximately 0.3–1% and show good agreement with theoretical estimates. It may therefore be assumed that after an $(n,\gamma)$ reaction the chemical bond is broken in almost all cases. Sometimes, however, marked deviations from this relationship are observed. For the rupture of the bond in the HBr molecule, according to Eqn. (27), the recoil bromine atom should have a kinetic energy of not less than 312 eV. From approximate calculation of the spectrum of bromine recoil atoms[67] it follows that 85% of all the bromine atoms have a recoil energy less than the dissociation energy. Suess's first experiments[64,68], however, and later careful experiments carried out in the gaseous phase by other workers[69] showed that only ~10% of the activity of the $^{80}$Br after an $(n,\gamma)$ reaction in the HBr + $C_2H_2$ mixture (with low HBr partial pressure) remains in the form of H$^{80}$Br, whereas we should expect a retention of H$^{80}$Br of the order of 85%. This indicates the high degree of conversion of $\gamma$-rays after the $(n,\gamma)$ reaction, one result of which is the formation of recoil ions which leave the original molecules as a result of coulombic repulsion. The discovery of the existence of recoil ions played an important part in the postulation of ion–molecular hot reactions, thanks to which it has been possible to explain certain facts, in particular the existence of isotopic effects in $(n,\gamma)$ reactions[80]. The formation of positively charged recoil ions does not always explain the experimental data, however. Thus in the isomeric transition, $^{80m}$Br → $^{80}$Br, the internal conversion coefficient is equal to 90–100%, that is, at least 90% of the $^{80}$Br atoms should leave the H$^{80m}$Br molecule as a result of isomeric transition. Experiments[70] showed that the yield of H$^{80}$Br from H$^{80m}$Br amounts to 25%. If in the $(n,\gamma)$ reaction the kinetic energy is insufficient for rupture of the bond in the HBr molecules, and the ejection of bromine atoms can be attributed to the formation of recoil ions as a result of conversion of the capture $\gamma$-rays, how are we to explain the fact that in the case of the isomeric transition in H$^{80m}$Br, where the $\gamma$-rays undergo conversion to the extent of 100%, the proportion of unbroken bonds is greater by a factor of 2.5? One possible explanation may be based on the difference in the magnitude of the charge on the ions after the $(n,\gamma)$ reaction and the isomeric transition (i.t.). In fact, the mean charge of the recoil ions of bromine-80 after the $(n,\gamma)$ reaction was found to be +10, whereas after i.t., according to Cooper's calculations[71], it amounts to +4.7. Calculations carried out by Magee[72] showed that the $HBr^{z+}$ molecules are stable up to $z$ = +4, and this may explain the fact that an appreciable proportion of the activity of $^{80}$Br after i.t. is found in the form of hydrogen bromide.

The mass-spectrometric data confirm the formation of rapidly-moving ions produced by the dissociation of highly charged molecular ions. The kinetic energy of the fragments can be estimated approximately from the difference between the ionisation potentials of the ionised molecule and the fragment ions. Cooper[71] showed that the time taken for the transfer of charge from the $K$-shell to the valency shell is $10^{-12}$ s. In this period, an atom in the molecule undergoes 10–100 vibrations, that is, there is a considerable probability of internal charge transfer with the formation of molecular ions. The relative kinetic energy of $^{80}$Br$^+$ ions from the compound $CH_3{}^{80m}$Br is 10 times greater than that from H$^{80m}$Br (on the basis of an equal distribution of charge throughout the molecule). This may explain the fact that the fraction of unbroken bonds in $CH_3{}^{80m}$Br after i.t. is much smaller than that in H$^{80m}$Br (3–7%).[70]

It may be assumed that the kinetic energy of recoil ions after i.t., and also as a result of the conversion of soft capture $\gamma$-rays, depends on the energy and degree of conversion of the $\gamma$-rays, the ratio of the masses of the recoil atom and the remainder of the molecule, and the values of the ionisation potentials of the molecular ions and fragment ions. In the gaseous phase the fraction of unbroken bonds amounts to several percent but in the liquid phase this fraction reaches about 15% (for example, the yield of $CHBr_2{}^{80}$Br from $CHBr_2{}^{80m}$Br amounted to 13% in the liquid phase in the presence of appreciable quantities of elemental bromine[73]). This can be related to the "cage" effect, which retains the recoil ion in direct proximity to the molecular residue, or to the process of intermolecular charge removal from the molecular ions, facilitating "survival" of the molecule.

Bromine and iodine recoil atoms initiated by different nuclear processes give the same distributions of activity in the products. However, the initial distributions of the atoms, after, for example, an $(n,\gamma)$ reaction and isomeric transition, are different: the $(n,\gamma)$ reaction gives the atom kinetic energy but isomeric transition gives the atom a charge. In the light of the foregoing, it may be assumed that the fact that the atoms show identical behaviour after an $(n,\gamma)$ reaction and i.t. is due to the same factors. One of these is that the conversion of $\gamma$-rays after the $(n,\gamma)$ reaction produces charged recoil atoms whose behaviour will consequently be the same as that of atoms produced in i.t., for which the coefficient of internal conversion is high. Another reason for the identical behaviour of atoms obtained by different nuclear reactions is based on the opposite assumption that the charged atoms are neutralised, as a result of which the recoil atom spectra may be the same in the range of chemical interaction. The first viewpoint leads to the postulate that an important part is played by ion–molecule reactions (see Ref. 80 for more details), whereas the second leads to the hypothesis which gives preference to the part played by kinetic energy in the hot reaction[28,74,75].

There is a third point of view regarding the source of the high activity of hot atoms. It is suggested that, irrespective of the primary processes, the atoms are obtained with an appreciable electronic excitation energy. It is then necessary to speak of the chemistry of "hot orbital electrons"[76].

Finally, a still valid viewpoint is that which concentrates attention on the radical reactions of recoil atoms with fragments formed on the path of movement and as a result of radiative breakdown produced by the Auger electrons after the conversion process[27,77]. A fundamentally new approach to the explanation of results obtained in hot atom

chemistry in organic media was put forward by Shaw[78] whose calculations showed the influence of local pressure, produced by the hot atom in the retardation zone, on the yield of labelled products. Let us examine briefly the experimental data supporting the different views on the mechanism of hot reactions.

(a) Ion-molecular mechanism. It has been established[45-47] that in the reactions of $^{80}Br$ and $^{128}I$ recoil atoms with methane in the gaseous phase in the presence of added inert gases, the yield of labelled products shows good agreement with the equations of Wolfgang's kinetic collision theory (see Section III. 1), confirming the suggestion regarding the reactions of neutral non-excited hot atoms with an excess of kinetic energy. Significant deviation from the equations of the kinetic theory were found in the study of the action of neutrons on an $I_2 + CH_4 +$ + Xe mixture and this was attributed to the transfer of charge from $^{128}I$ atoms (50% of which are obtained in the charged state after an $(n,\gamma)$ reaction) in the $^1D_2$ state to xenon, which thus exhibits a quenching action†.

The reaction of excited iodine recoil ions with xenon may compete to an appreciable extent with the ion-molecular reaction involving the introduction of iodine into methane. From this it was found that the fraction of $^{128}I$ recoil ions after the $(n,\gamma)$ reaction is 23 ± 3%. The fraction corresponding to true hot reactions (suppressed only by the moderators — inert diluents — He, Ne, and Ar) amounts to 18 ± 2%. The remaining 11% of all the reactions of iodine atoms involve interaction between methane and charged $^{128}I$ ions in $p$-states with excitation energy $E < 1.7$ eV, and these are not influenced by the addition of xenon. Study of the hot reactions of $^{80}Br$ recoil atoms in methane under the same conditions showed that only the kinetic energy influences the yield of products, despite the fact that some of the $^{80}Br$ atoms are obtained in the charged state after the $(n,\gamma)$ reaction. In isomeric transition in the $^{80m}BrBr + CH_4$ system, the yield of $CH_3{}^{80}Br$ is less than that in the $(n,\gamma)$ reaction (6.8 ± 0.8% and 12.0 ± 1% respectively)[79]. This result was attributed to the high kinetic energy after the $(n,\gamma)$ reaction. There is another possible explanation, however: if the $^{80}Br$ recoil atoms are formed in a metastable state with sufficiently long lifetime (greater than the lifetime between collisions in the gaseous phase), only some of these atoms, after their first introduction into the methane molecule, will leave the resulting molecule due to the conversion of $\gamma$-rays. These atoms apparently have the same probability of reaction with methane as $^{80}Br$ atoms from $Br^{80m}Br$. We should thus expect that the yield of $CH_3{}^{80}Br$ after the $(n,\gamma)$ reaction should be slightly greater than that for the i.t. process. An analogous process should take place with recoil atoms of the $^{82}Br$ isotope, for which a 6.2-minute isomer has been found‡[77]. This does not solve the problem of the source of the high reactivity of bromine and iodine after a nuclear $(n,\gamma)$ reaction. It is possible that the kinetic energy plays the most important role: on the production of a charge of +5 on the iodine atom in the $CH_3I$ molecule, its kinetic energy after rupture of the C-I bond is ~9 eV,[77] which is, of course, quite sufficient for the replacement of hydrogen in methane. According to calculations, however, after the replacement of hydrogen in methane by the $^{128}I$ atom, the $CH_3{}^{128}I$ molecule will have too much energy to be stabilised (see Filatov[80] for more details). Thus the ion-molecular mechanism of formation of $CH_3{}^{128}I$ in the reactions of $^{128}I$ recoil atoms with methane is to be preferred.

This was confirmed in subsequent studies of the $(n,\gamma)$ reaction in the $I_2 + CH_4$ system containing added alkyl iodides, nitric oxide, and benzene[47]. The yield of $CH_3{}^{128}I$ on irradiation of the gas-phase systems with neutrons decreased rapidly when alkyl iodides were added; this can be attributed to the transfer of charge to RI, which has a lower ionisation potential than iodine, or to the thermal ion-molecular reaction $I^+ + RI \rightarrow I_2^+ + R$, which was also observed in mass-spectrometric studies. Since iodine atoms do not react with nitrogen monoxide, the inhibition of the formation of $CH_3{}^{128}I$ by the addition of NO is due to the transfer of charge to the nitric oxide. The ion-molecular model for the reactions of hot atoms provides an explanation for the low yield (2-4%) of alkyl iodides labelled with $^{128}I$ in the neutron irradiation of the gaseous mixtures $I_2 + C_2H_6$, $I_2 + C_3H_8$, etc. Alkanes, apart from $CH_4$, can remove charge from iodine ions in the $^1D_2$, $^2P_1$, and $^3P_0$ states. In actual fact, the addition of ethane to an $I_2 + CH_4$ mixture inhibits the formation of $CH_3{}^{128}I$.[47]

The hypothesis of ion-molecular reactions of hot atoms has proved useful in the explanation of the results of a study of the chemical consequences of $\beta$-decay in the liquid-phase systems: $^{132}TeCl_4(^{132}Te \xrightarrow{\beta} {}^{132}I) + C_3H_7X + C_6H_6$ and $TeCl_4 + C_3H_7I + C_6H_5I$ (X = I, Br, or Cl). The recoil energy of the iodine atoms obtained by the $\beta$-decay of tellurium is low (0.5 eV) and cannot bring about chemical reactions. Halpern and Sokolovska[81] detected an increase in the specific activity of $C_3H_7{}^{132}I$ in the presence of benzene, which they attributed to the transfer of energy from propyl iodides to the benzene molecules. The formation of propyl iodides, however, was regarded as the reaction of $^{132}I^+$ ions with dipolar $C_3H_7X$ molecules, the yield of the product of replacement of X by $^{132}I$, as a first approximation, being proportional to the dipole moment of $C_3H_7X$. The fact that the spectra of the charged fragments formed in isomeric transition and in irradiation by X-rays with $E = 40$ keV are similar[82] suggests that not only in the chemistry of atoms obtained by i.t., but also in radiation chemistry, we are dealing with hot ions formed by the "coulombic explosion" of highly charged molecular ions.

(b) Kinetic theory of hot reactions of halogen recoil atoms. Some experimental data confirm the idea that before recoil atoms take part in chemical reactions they are neutralised and deactivated. It may thus be suggested that recoil atoms are obtained in the ground state. If we assume that the reactivity of these atoms is determined entirely by their kinetic energy, we can derive equations which permit experimental verification. Examples of such equations for reactions in the gaseous phase are those of Wolfgang, for example, Eqn. (20). Milman[74,75] and Nesmeyanov and coworkers[28] applied these equations to a condensed system. If it is assumed that for condensed systems a good approximation is provided by the elastic-collision model (since the "cage effect" facilitates rapid recombination reactions by radicals in direct proximity to one another), Eqn. (20) becomes

$$R \simeq \frac{e}{v\xi} \ln \frac{E_0}{v} f, \qquad (28)$$

† In the normal state the process of charge transfer is impossible: the ionisation potential of iodine (10.4) is less than that of xenon (12.1). The excitation energy of the $^1D_2$ level (in the ion) is 1.7 eV. The transfer of charge takes place from this level.

‡ Formed in 90% of cases of neutron capture. $E$(i.t.) = keV. Almost all $\gamma$-quanta are converted[27,77].

where $\epsilon$ is the energy of removal from the cell, $E_0$ the initial recoil energy, $\nu = \nu' M/(M-m)$, $\nu'$ is the energy of the C–Br chemical bond, $M$ the mass of the molecule, $m$ the mass of the bromine atom, and $f$, as before, the geometric probability of collision. Eqn. (28) can also be obtained by simple solution of the resonance integral from the theory of neutron retardation, assuming the mechanism of elastic transfer of energy on collision[28].

For a mixture of substances

$$R \simeq f \frac{\varepsilon}{\nu\xi} \ln \frac{E_0}{\nu} = \frac{N\sigma}{\Sigma N\sigma} \frac{\varepsilon}{\nu\xi} \ln \frac{E_0}{\nu}, \qquad (29)$$

where $N$ is the mole fraction of the original compound in the mixture with the second component. It follows from Eqn. (29) that the yield of labelled compound formed by elastic collision is linearly dependent on the mole fraction multiplied by the factor $1/\xi$. In fact, on dilution of $C_2H_5Br$ with chloromethanes, the observed values for the yield of $C_2H_5{}^{82}Br$ on irradiation of the mixtures with neutrons showed good agreement with the results obtained by calculation using formula (29):

$$R = \frac{\varepsilon}{\nu} \ln \frac{E_0}{\nu} \frac{1}{\xi} f = \text{const} \frac{4r_{Br}^2 N}{4r_{Br}^2 N + (1-N)(r_{Br}+r_{Cl})^2 n\xi_{Cl}},$$

where $\sigma$ is the collision cross-section, $\xi_{Cl}$ the logarithmic decrement for the bromine–chlorine collision, $r_{Br}$ and $r_{Cl}$ are the covalent radii of bromine and chlorine, and $n$ is the number of chlorine atoms in the chloromethane molecule. The dependence of $R$ on $f/\xi$ was found to be linear, in complete agreement with the mechanism of elastic transfer of energy[28]. Shaw and coworkers[83] showed that the results of the chemical reactions of hot bromine atoms in the liquid phase in the $RBr + Br_2$ system can be interpreted in terms of a model which assumes that the reactions involve elastic collisions.

To describe the replacement of hydrogen atoms by the hot atoms of heavy elements, it is possible to use an inelastic-collision model which assumes that the yield depends on the fraction of the energy transferred on inelastic collision through the molecule as a whole, $M/(M+m)$.[28] The threshold minimum value of the kinetic energy of the bromine recoil atom, at which replacement of hydrogen is still possible, is estimated at 6 eV. Difficulties are encountered in the estimation of the upper energy limit of the recoil atom for the replacement of a hydrogen atom in molecules. It may be estimated only approximately at ~10 eV. The minimum kinetic energy necessary to bring about reactions of elastic collision is equal to 12 eV for $C_2H_5Br$. On the basis of these considerations, it is possible to construct an approximate curve for the cross-sections of elastic and inelastic collisions leading to hot and epithermal replacement of atoms by hot $^{82}Br$ atoms (Fig. 1). Experiments on the study of the reactions of halogen recoil atoms are now being carried out with allowance for the secondary ionisation of the labelled compound formed in the first stage of the hot reaction. $^{18}F$ atoms obtained by the photonuclear $(\gamma,n)$ reaction have excitation levels of 1.13 MeV and 0.94 MeV, with lifetimes $\sim 10^{-10}$ s.[84] Since change in pressure in the $CF_4$–inert gas system did not lead to a different distribution of $^{18}F$ activity, the $^{18}F$ atoms are formed after the $(\gamma,n)$ reaction in the ground state.

Since the energy of recoil $^{18}F$ atoms after the $(\gamma,n)$ reaction amounts to $\sim 10^5$ eV, they may be ionised in the retardation process and thus still enter the range of chemical interaction in the charged state. A special study has been made of this question[84]. From the values of the energy

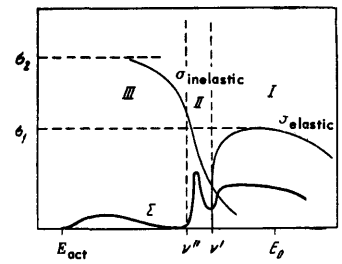



Fig. 1. Probability of chemical reactions of bromine recoil atoms with alkyl bromide molecules. $\sigma_{elastic}$ is the cross-section for elastic collision, $\sigma_{inelastic}$ the cross-section for inelastic collision, $p(E)$ the probability of reactions on one collision, and $\Sigma$ the cross-section for the hot reaction, equal to

$$p_{elastic}\sigma_{elastic} + p_{inelastic}\sigma_{inelastic},$$

($p_{elastic} = \epsilon/\nu$). In range I the reaction due to elastic transfer of energy takes place:

$$Br^* + C_2H_5Br \rightarrow [C_2H_5 + Br + Br^*]_{cell} \rightarrow C_2H_5Br^*.$$

In range II inelastic collision with the molecule as a whole leads to replacement of hydrogen:

$$Br^* + C_2H_5Br \rightarrow \left[C_2H_5\begin{matrix}Br\\ Br^*\end{matrix}\right]_{complex^*} \rightarrow C_2H_4BrBr^*.$$

In range III the reaction of "ordinary" chemistry takes place:

$$Br^* + C_2H_5Br \rightarrow C_2H_4Br + HBr^*.$$

It is possible that the paths of the cross-sections overlap in ranges II and III, and that the reactions of abstraction and replacement of hydrogen are competing reactions, differing only in the values of the probabilities

$$Br^* + C_2H_5Br \rightarrow \left[C_2H_5\begin{matrix}Br\\ Br\end{matrix}\right] \begin{matrix}\nearrow C_2H_4Br + HBr^*\\ \searrow C_2H_5Br^* + H\end{matrix}.$$

of the fluorine atoms at which the ionisation processes take place to the maximum extent, calculated from the formula

$$E = {}^1/_2 m \left(\frac{\Delta E\, a}{h}\right)^2 = 2700\,(\Delta E)^2 \text{ eV}\,\S,$$

it follows that the ionisation processes reach a maximum at energies greater than the neutralisation energies, and that at $E < 10^2$ all the atoms are neutral. The results of the chemical action of hot fluorine atoms in the $CF_4$–inert gases–radical acceptors system, treated from the viewpoint of Wolfgang's kinetic theory, showed[84] that the loss of energy for the collision of fluorine with atoms and molecules is greater than the loss calculated assuming elastic transfer of energy. The fraction of the kinetic energy lost when fluorine collides with argon should be 0.7. Experiment gives 0.94. Comparison of experiment with calculation for collision with a $CF_4$ molecule gives an even greater discrepancy: calculation gives the value $\xi = 0.36$, whereas experiment gives $1.47 \pm 0.28$ (relative to the loss of energy on collisions between fluorine and helium). The probability of chemical interaction between fluorine and $CF_4$ is small: the integral probability of formation of $CF_3{}^{18}F$

§ $\Delta E$ is the ionisation potential, $a$ the dimensions of the atom, $7 \times 10^{-8}$ cm, and $m$ the mass of the fluorine atom.

is smaller by a factor of 16 than the mean loss of energy on collision with $CF_4$ without the formation of a chemical bond. The probability of replacement of two fluorine atoms with the formation of the radical $CF_2{}^{18}F$ is the same as the probability of the replacement of one atom with the formation of $CF_3{}^{18}F$, and this cannot be explained from the energetic viewpoint, since the replacement of two atoms requires the expenditure of a further 4 eV of energy.

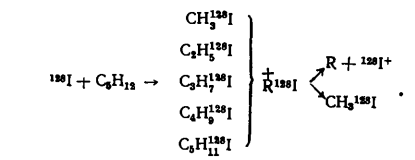
A considerable proportion of the studies which have now been carried out show that the equations of Wolfgang's kinetic theory assist in understanding the processes of energy loss during the retardation of hot atoms and give numerical values for the proportion of the energy lost on collisions with molecules. The retarding powers of different molecules can be compared and are found to be different even for a homologous series of substances. The equations of the kinetic theory can be used to calculate the integral probabilities of the chemical reactions of hot atoms and these are found to be greater by several orders of magnitude than those for ordinary thermal reactions. The next step in the development of reaction mechanism theory may be the determination of the analytical form of the function $p(E)$ — the probability of chemical reaction on one collision — and comparison of calculations with experiment. It is possible that valuable information on the "chemical reaction excitation function" will be provided by studies of the interaction of atoms with molecules in intersecting molecular beams.

(c) Radiative mechanism. The broad spectrum of products formed in the reactions of halogen recoil atoms enabled Willard and coworkers[85,86] to postulate that "nesters of radicals" are formed in the hot atom retardation of radicals" are formed in the hot atom retardation leads to the formation of labelled products. This approach, however, cannot explain a number of facts, including the appreciable yield of labelled products when the experiments are carried out in the gaseous phase. Thus iodine recoil atoms in methane give a 50% yield of $CH_3{}^{128}I$, bromine recoil atoms give ~14% $CH_3{}^{80}Br$, chlorine gives 27%, and tritium gives ~30% $CH_3T$. At the same time there are certain data which can be explained only from the radiative viewpoint of "random fragmentation" of molecules to form radicals. For example, it was found that the yield of $C_2H_5{}^{128}I$ after an $(n,\gamma)$ reaction in a 1.4% solution of $C_2H_5I$ in pentane amounts to 41%,[27] whereas neutron irradiation of a mixture of $I_2$ (0.25 M) with pentane gives a $C_2H_5{}^{128}I$ yield of only 18%. These data can be explained using an "autoradiative model": the distance between the $C_2H_5I$ molecules in the solution is less than the zone corresponding to breakdown brought about by the conversion electrons of soft neutron-capture $\gamma$-rays.

The energies of the electrons emitted by $^{128}I$ are different. A conversion $K$-electron apparently has an energy of several dozen keV, some of the electrons have an energy equal to the $K-L$ transition without the binding energy of the $L$-electron, that is, approximately 20 keV, and some of the electrons are emitted with an energy of several keV. The electrons bring about radiative breakdown (ionisation and excitation) among the molecules lying close to the $^{128}I$ recoil atom which has undergone retardation. The linear transfer of energy by electrons with energies (keV) of 0.1, 1, 10, and 20 is equal to (eV per Å) 3.3, 1.2, 0.23, and 0.13.[27]

Thus the $^{128}I$ recoil atom which has left the mother molecule after the emission of capture $\gamma$-quanta is found, after retardation, in the centre of the zone of breakdown produced by the conversion electrons and characteristic X-rays. The repeatedly drawn-out iodine atoms are rapidly neutralised and subsequently recombine with the surrounding radicals (including radicals of the mother compound) formed as a result of the action of Auger electrons.

The process of $^{128}I$ marking is possibly more complex than is generally assumed. Allowance must be made for the twofold introduction of iodine atoms into the organic compounds: the iodine recoil atoms first replace hydrogen atoms and groups of atoms in pentane, after which conversion takes place with the formation of iodine recoil ions, which again take part in reaction. A scheme for reaction (5) in accordance with this suggestion is given below:



The $^{128}I$ ions may again take part in the ion–molecular reaction $^{128}I^+ + C_5H_{12} \rightarrow R^{128}I^+$, whose activation energy is 10–20 kcal lower than that of the corresponding reaction with neutral atoms.

It is at present impossible to analyse the processes of charge transfer in a condensed system. Theoretical calculation of the rate of dissociation of the linear chain of $H_2^+$ molecules, assuming the existence of intermolecular interaction, showed[87] that dissociation into atoms does not take place if the intermolecular bond is sufficiently strong. From this it follows that the intermediate molecular ions $R^{128}I^+$ may determine the direction of the subsequent reactions of $^{128}I$ atoms.

(d) Thermodynamic conception of hot reactions in condensed systems. A new approach to the study of the mechanism of hot reactions was developed by Shaw[78]. The equation for the yield of a hot reaction (28) contains the quantity $\epsilon$ — the energy of removal from the reaction cell (the energy of formation of a "hole" in the liquid, which a diffusing atom may enter). The magnitude of $\epsilon$ can be estimated from photochemical data (0.05 eV). The ratio $\epsilon/\nu$ amounts to ~0.01. If the absolute calculated yield of a hot reaction is to agree with experiment, it is necessary to assume a considerable number of collisions in the range of chemical interaction (~100) but this cannot be justified. It is suggested[78] that $\epsilon = \Delta E + p\Delta v$, where $\Delta E$ is the heat of volatilisation (formation of a "hole"), and $p\Delta v$ the work done against hydrostatic pressure in the formation of a "hole" with volume $\Delta v$. For most liquids, for example, $C_2H_5Br$, $p\Delta v = 8 \times \times 10^{-5}$ eV ($p$ = 1 atm, $\Delta v$ = 125 Å$^3$). If an atom with appreciable energy moves in the liquid, the result may be the formation of a zone with increased temperature. If the rate of formation of the zone is high, no significant change in the volume of the zone takes place during the retardation of the hot atom, so that we can examine a thermodynamic parameter $(\partial p/\partial T)v$, which, according to direct experiments[88], is found to be equal to 11.5 atm deg$^{-1}$ for ethyl bromide under normal conditions[78]. The loss of energy by hot bromine atoms was calculated by Shaw on the basis of the model of Capron and Oshima (the method

of Capron and Oshima was described by Nesmeyanov and Borisov[4]). It is suggested that the liberated energy is used up in the formation of a bubble of gas in the liquid and that this rapidly brings about retardation of the hot atom. Calculations show that after a period of $\sim 10^{-12}$ s the pressure in the bubble reaches several thousand kg cm$^{-2}$, and this alters appreciably the stability of the cell $\epsilon$. At the same time, substitution of the ratio $\epsilon/\nu$ in formula (28) gives a result which agrees with experiment. Change in temperature during the hot reaction in ethyl bromide is reflected in the magnitude of the pressure: the latter increases with decrease in temperature. An analysis carried out by Shaw shows that the magnitude of the pressure depends to a marked extent on the volume of the hot zone: the pressure increases with decrease in the volume. It may thus be assumed that the introduction of chemically inert retarding agents should increase the yield of mother compound, since in this case the kinetic energy of the hot atom decreases so that the volume of the breakdown zone also decreases.

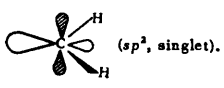
Milman[89] recently observed a relationship between the change in the yield of labelled dibromoethane after an $(n,\gamma)$ reaction with the points of phase transformation and the change in specific heat and dielectric constant with change in temperature. This indicates a close relationship between the chemical effects of nuclear changes and the physicochemical structure of solids and certain of their properties to which attention has not been paid up to the present.

Thus several approaches have been made to the study of the mechanism of the hot reactions of atoms initiated by nuclear changes. Each approach explains only some of the experimental data, indicating that the mechanism of hot processes is complex and that it is possible to construct a theory showing satisfactory agreement with experiment only by making certain simplications and assumptions which are justified in individual specific cases.

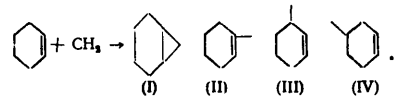
### 3. Reactions of Hot Carbon Atoms

Unlike halogen and tritium recoil atoms, which react with molecules in the ground states, the determination of the state of carbon (including its chemical form) is more complex. The ground state of the carbon atom is a triplet state ($^3P$): $|1s^2 2s^2 2p^2|$ ↑↓ ↑↓ ↑ ↑. Conversion into other states involves a considerable expenditure of energy, thus $sp^3$ hybridisation requires 80–100 kcal. This expenditure is compensated by the energy liberated when carbon forms bonds in the $sp^3$ state. When hot carbon atoms are formed by the reactions $^{14}N(n,p)^{14}C$, $^{12}C(p,pn)^{11}C$, or $^{12}C(n,2n)^{11}C$, however, the state transition $^3P \rightarrow sp^3$ is brought about by the high kinetic energy accompanying the nuclear reaction.

Some information on the reactivity of a hot carbon atom can be obtained from photochemistry. Experiments on the photolysis of diazomethane have shown the existence of a hot $CH_2$ fragment in a ground singlet state with one free orbital and one hybridised orbital[90]:

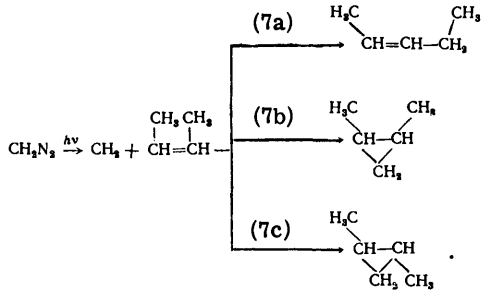

($sp^2$, singlet).

On collision with the atoms of the medium, this hot fragment undergoes a singlet–triplet transition[91,92]. The following products are obtained by the photolysis of diazomethane in cyclohexene solution:

(6) 
(I) (II) (III) (IV)

The yields of the products (II), (III), and (IV) are in the ratio 2 : 4 : 4, in complete agreement with the statistical introduction of $CH_2$ at the C–H bond. The yield of norcarane (I) is much greater than that of the others[92]. The addition of $CH_2$ across a double bond can take place only if the $CH_2$ is in the triplet state, since the first excited state of the double bond — the biradical — is a triplet[93]. The formation of norcarane can be explained if we assume a change in multiplicity on the retardation of hot $CH_2$.

The reactions of hot $CH_2$ in the gaseous phase confirm the singlet–triplet transition. The photolysis of diazomethane in a medium of *cis*-but-2-ene gives the following products:

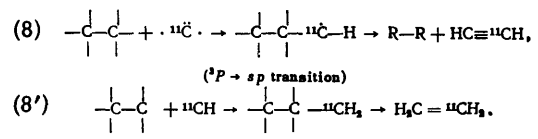



The addition of argon leads to a decrease in the yield of *cis*-pent-2-ene, formed by "insertion" at the C–H bond. The yield of reaction (7b) decreases and that of reaction (7c) increases but the sum of the yields of *cis*- and *trans*-dimethylcyclopropane remains unchanged. Collision with argon is accompanied by the singlet–triplet transition, which then brings about addition at the double bond. The isomerisation in the reactions of hot $CH_2$ with *cis*-but-2-ene is due to the fact that the products of reactions (7b) and (7c) are formed in the triplet state, for which transition to the ground singlet state is forbidden. There is a definite probability of rotation about the bond within the time corresponding to the transition, equal to $10^{-8}$–$10^{-7}$ s. The triplet state of the hot $CH_2$ obtained after several collisions is confirmed by experiments with the addition of oxygen. The ground state of oxygen is a triplet state and when added in small quantities it reacts effectively with the triplet $CH_2$ and the products of the addition of $CH_2$ across the double bond.

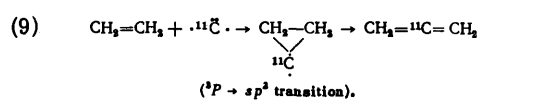
The reactions of hot carbon atoms are now being studied using the isotope $^{11}C$ obtained from carbon by $(n,2n)$, $(p,pn)$, and $(\gamma,n)$ reactions, from nitrogen by a $(p,\alpha)$ reaction, from oxygen by a $(p,pn\alpha)$ reaction, and by the reaction of neutron removal when thin targets are bombarded with $^{12}C^+$ ions.

$^{11}C$ recoil atoms, in reactions with saturated and unsaturated hydrocarbons, cyclopropane, or ethylene oxide, give labelled acetylene as chief product (~30% yield)[31,94,95]. In the reactions of $^{11}C$ recoil atoms with pentane, the chief products are acetylene (22%), ethylene (11%), butane (7%), and n-hexane (26%). If the "insertion" mechanism is

correct, the following reactions should take place in this case:



In the case of unsaturated compounds, considerable yields are obtained of alkenes containing one more carbon atom, for example, the yield of allene from ethylene amounts to 18%:

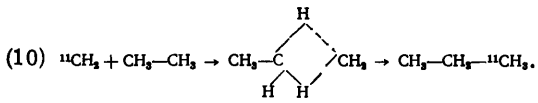


The intramolecular distribution of $^{11}C$ in allene is now being studied in order to prove the mechanism of addition across the double bond[95].

The addition of retarding agents (nitrogen) did not lead to a decrease in the yield of products. This means that the reactivity of the hot carbon atoms is not due to their kinetic energy. The yield of mother compound in the reactions of hot carbon atoms is extremely low (1.5–2%) and this is not surprising, since elastic collision reactions can hardly compete with the insertion processes. The formation of ethylene from saturated compounds apparently takes place by the insertion of a CH fragment at the C–H bond with subsequent rupture of the C–C bond (reaction 8′).

The low yield of cyclic hydrocarbons in the reactions of carbon atoms with unsaturated compounds (3%)[94,95] is due to the insertion of hot $CH_2$ at the double bond in the same way as in the reaction initiated by light. In this case, oxygen also inhibits the yield of cyclic products[31].

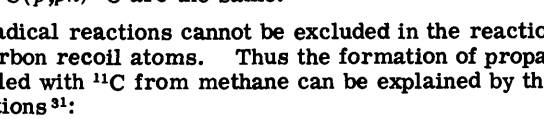
Hot $CH_2$ are formed by the retardation of carbon recoil atoms in hydrogen-containing media. The increase in chain length is due to insertion at the C–H bond:



The formation of n-hexane from pentane takes place in the same way.

Change in phase state did not lead to any significant redistribution of the activity of $^{11}C$ in the products[96]. It was found that the primary products formed by insertion at C–H and C–C bonds are excited[96]. The excitation energy is apparently high, since in the condensed phase the yield of the products of the decomposition of the primary excited labelled molecules does not decrease to zero. The yields of the reactions initiated by the nuclear changes $^{12}C(n,2n)^{11}C$ and $^{12}C(p,pn)^{11}C$ are the same.

Radical reactions cannot be excluded in the reactions of carbon recoil atoms. Thus the formation of propane labelled with $^{11}C$ from methane can be explained by the reactions[31]:



The yield of propane increases with increase in the radiation dose, confirming the radical mechanism, but the yield of ethane does not increase with increase in the dose, contradicting this suggestion.

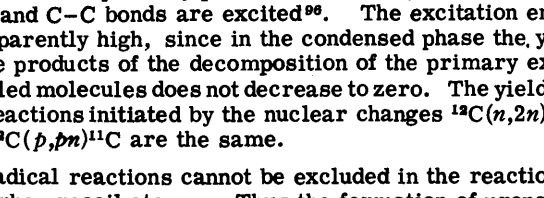
Studies which have been carried out have shown that carbon recoil atoms take part in chemical reactions with molecules in the states C ($^3P$), CH ($sp$), and $CH_2$ ($sp^2$).

The formation of $CH_2$ does not depend on the nature of the compound; the reactions of hot carbon atoms always lead to the formation of the same proportion of $^{11}CH_2$ fragments, which undergo insertion reactions in accordance with simple statistics. Kinetic energy plays no significant part in the reactions of hot carbon atoms. The reactions of hot carbon atoms can be represented schematically as follows. Insertion reactions take place irrespective of the nature of the fragment: the insertion of a carbon atom at the C–H bond gives decomposition products, chiefly acetylene; the introduction of the CH methine group at the C–H bond leads to decomposition to ethylene or the formation of an alkene with one carbon atom more than the original molecule; the insertion of $CH_2$ at C–H and C=C bonds gives hydrocarbons with one atom more than the original molecule. The excitation energy after the insertion process is high, leading to rupture of the nearest C–C bonds. The $CH_3$ radical is apparently not formed in the retardation of a hot carbon atom. This is confirmed by the fact that no labelled methane molecules were found in the products of the stabilisation of hot $^{14}C$ atoms[97]. It is true that study of the process $^{14}N(n,p)^{14}C$ is not a sufficiently reliable method for studying the mechanism of the reactions of hot carbon atoms: the appreciable irradiation times required to obtain sufficiently high activities (200–400 h) lead to appreciable radiative decomposition not only of the original products, but also of the products of the hot reactions. Irradiation for short periods in the $NH_3 + CH_4$ system gives acetylene and ethylene, whose yields decrease with increase in the duration of irradiation[98], confirming the above model for the hot reactions of carbon atoms.

## IV. EXCITATION ENERGY TRANSFER IN REACTIONS OF HOT ATOMS AND PARAMETERS DETERMINING THE COURSE OF HOT REACTIONS

### 1. Energy Transfer on Simple Collision

In hot atom chemistry it is an experimentally established fact that the primary labelled products are in an excited state. Thus in the reactions of tritium recoil atoms with cyclopropane and cyclobutane, decomposition of the primary labelled compound is possible[32,33]:



Since change in pressure in the range 0.1–1 atm leads to an increase in the yield of labelled mother molecules, the lifetime of the excited states is estimated at $\geq 10^{-9}$ s. On going to the condensed phase, where the frequency of collision is greater by a factor of $10^3$, there is a considerable phase effect for these reactions (Table 5).

TABLE 5. Yield of tritium-labelled products obtained by reaction in cyclobutane in the gaseous $^3He(n, p)T$ and liquid $^6Li(n, \alpha)T$ phases (yield of $\square_T$ + + $C_2H_3T$ taken as 100%).

| Conditions | Products | | | | | |
|---|---|---|---|---|---|---|
| | $\square_T$ | $C_2H_3T$ | HT | $n\text{-}C_4H_9T$ | $CH_3T$ | $C_3H_6T$ |
| 9.4 cm□ 2.3 cm $O_2$ 1.4 cm $^3He$ | 50 | 50 | 151 | 3 | 0.6 | 0.2 |
| LiF + □ (liquid) | 82 | 19 | 211 | 10 | 5 | 9.7 |

Analysis of the data given in Table 5 indicates that in the reactions of tritium recoil atoms with cyclobutane, intermediate molecules in two different states are formed: with a lifetime $>10^{-9}$ s (the yield of the reaction depends on the pressure) and with a lifetime $<5\times10^{-12}$ s (since the change to the liquid phase did not block completely the decomposition of the cyclobutane molecule). The first type of state is a triplet state and the second is a singlet state. The fact that the triplet–singlet transition is forbidden is responsible for the long lifetime of the excited states, and increase in pressure decreases the probability of breakdown of the labelled excited molecules. Since the change to the liquid phase does not reduce the decomposition to zero, however, it must be assumed that there exist highly excited molecules with a short lifetime ($<5\times10^{-12}$ s, singlet), shorter than the time interval between two collisions in the liquid phase.

The removal of the excitation energy apparently takes place from the vibrational levels after the intramolecular conversion of the electronic excitation.

## 2. Parameters Determining the Course of a Hot Reaction. The Question of the Existence of a Mechanism for the Specific Transfer of Excitation Energy

Nesmeyanov and coworkers [28-30,52,99,100] suggested the existence of an excitation energy transfer depending not so much on the number of collisions as on the nature of the colliding molecules (specific transfer of energy). The deviation from additivity shown by the tritium-labelled products in the binary mixtures: benzene–cyclohexane [100], benzene–pyridine, and pyridine–cyclohexane [30], or by bromine-labelled products in the ethyl bromide–benzene [28] and methylene bromide–benzene [52] systems and by compounds labelled with $^{14}C$ in the aniline–indole system [29], can be attributed to the transfer of energy from the excited labelled molecules to molecules of an energy "acceptor", analogous to that assumed in radiation chemistry. The analogous relationship for the yields of labelled products observed for the aniline–ethanol (acetone) and acetone–water systems [101] has been examined from other angles, namely from the viewpoint that the yields of the reactions are dependent on the probability of primary interaction and the change in the spectrum of retarded atoms. This viewpoint is also similar to the concept developed in radiation chemistry. Typical curves for the yields of labelled products in binary mixtures of substances are given in Fig. 2.

The yield of labelled product when hot reactions are carried out in a mixture consisting of two components can

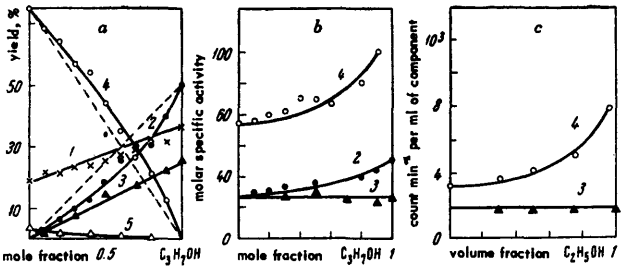



Fig. 2. Radiochemical yields and specific activities of tritium-labelled substances in the $C_6H_6$–$C_3H_7OH$ binary system: *a*) radiochemical yields: HT (1), $C_3H_7OH(T)$ (2), $C_3H_6TOH$ (3), $C_6H_5T$ (4), and cyclohexene(T) (5) for irradiation of the system: 20 mg $Li_2CO_3$ + 0.02 ml of $C_3H_7OH$ + $C_6H_6$ mixtures by a $10^{11}$ n × × $cm^{-2}$ $s^{-1}$ neutron beam for 6 h at 40°. The total activity recorded was independent of composition [42]; *b*) molar specific activity of components [42] in the $C_6H_6$–$C_3H_7OH$ binary system; *c*) absolute specific activities of the components of a binary mixture of aniline (4) and ethanol (3). The irradiation was carried out in monitored neutron beams [101].

be found by the Wolfgang–Estrup method [37] (see III. 1) or by solving the resonance integral of the theory of neutron retardation in an absorbing medium [28,38].

If we take

$$\int_{E_1}^{E_2}\frac{p_i(E)}{E}\,dE=\overline{p_i(E)}\ln\frac{E_2}{E_1}$$

[see Eqns. (20) and (22)], we have, with an accuracy up to the constant factors

$$R_{1i}\simeq\left\{\frac{f_1}{\xi}\overline{p_i(E)}-\frac{f_1}{\xi^2}-\overline{p_i(E)}\,[\overline{f_1p_1(E)+f_2p_2(E)}]\right\}\text{const}, \qquad (30)$$

where $R_{1i}=I_{1i}/\Sigma I$, $I_{1i}$ is the activity of the $i$-labelled product from the first component of the mixture, $\Sigma I$ the activity of all the labelled products in the system, $f_1$ the geometric probability of collision with the first component of the mixture, $\overline{p_i(E)}$ the mean probability of chemical reaction on collision with the formation of the $i$-labelled product from the first component, $\overline{p_1(E)}$ the mean probability of reaction on collision with the formation of all labelled products from the first component, and $\overline{p_2(E)}$ the corresponding probability for the second component. The geometric probability of collision is determined from the relationship

$$f_1=N_1\sigma_1n_1\gamma_1/(N_1\sigma_1n_1\gamma_1+N_2\sigma_2n_2\gamma_2)\quad\begin{matrix}z_1=\sigma_1n_1\gamma_1\\ z_2=\sigma_2n_2\gamma_2\end{matrix}, \qquad (31)$$

where $N_1$ and $N_2$ are the mole fractions of the first and second components of the binary mixture, $\sigma_1$ and $\sigma_2$ the collision micro-cross-sections, $n_1$ and $n_2$ the number of reactive points in the molecule at which chemical reactions are possible on collision, and $\gamma_1$ and $\gamma_2$ the steric-hindrance coefficients for attack. The logarithmic decrement for a mixture of substances can be calculated from formula (12).

Eqn. (30) was obtained [28,38,102] on the basis of the regular features observed in a study of the thermalisation of neutrons when capture processes are taking place, and is applicable if the following conditions are satisfied: (1) the

hot atoms are retarded on atoms of similar mass, or else $E < \xi\, {}^3E_0$, where $E_0$ is the initial recoil energy; (2) the function for excitation of chemical reactions, $p(E)$, has resonance character; (3) collision between an atom and a molecule is accompanied either by chemical reaction or by scattering with the loss of energy; (4) a hot atom spectrum corresponding to asymptotic collision density $1/\xi E$ can be established; (5) the mean proportion of the energy loss is independent of the energy; and (6) the collision micro-cross-section and steric-hindrance coefficient are independent of the energy. The first four conditions are evidently satisfied in the reactions of hot atoms, and the fifth and sixth conditions can be taken as extremely rough approximations necessary for the analysis of Eqn. (30).

Moreover, we assume that the mean loss of energy is independent of composition (this may be satisfied in particular cases). This facilitates the analysis of Eqn. (30).

Analysis of Eqn. (30) leads to the following conclusions[102]: (1) if $\overline{p_1(E)} > \overline{p_2(E)}$ and $z_1 > z_2$, we find that $d^2R_{1i}/dN_1^2 < 0$ and that the dependence of $R_{1i}$ on $N_1$ deviates from linearity in a positive direction; (2) if $\overline{p_1(E)} < \overline{p_2(E)}$ and $z_1 < z_2$, we find that $d^2R/dN^2 > 0$, and the dependence of $R_1$ on $N_1$ shows a deviation downwards towards the $N_1$ axis.

The derivative $d^2R_1/dN_1^2$ does not change sign throughout the whole range of concentrations $N_1$ from 0 to 1, that is, the dependence of $R_1$ on $N_1$ deviates from linearity either upwards or downwards, if $\overline{p_1(E)} > \overline{p_2(E)}$ and $z_1 > z_2$, or $\overline{p_1(E)} < \overline{p_2(E)}$ and $z_1 < z_2$¶. From this analysis it follows that the yields of the labelled products of hot reactions in a binary mixture of substances is non-linearly dependent on concentration and that the dependence may become linear only when $\overline{p_1(E)} = \overline{p_2(E)}$ and $z_1 = z_2$. From this it follows that the explanation of the deviations from additivity shown by the yields of labelled products from the viewpoint of the influence of intermolecular transfer of energy is not unambiguous, since even if the loss of energy does not change with change in concentration, the yield of a hot reaction may be non-linearly dependent on concentration because of differences in the probabilities of chemical interaction. If the retarding power of the medium also changes with change in composition, this will introduce an additional change in the yield of the reactions. The rates of change in $R/N$ at small and large values of $N$ differ by a factor of $(z_1/z_2)^2$. This means that in addition to the ratio between the probabilities of the hot reactions, the yields of labelled products are influenced to a significant extent by such parameters as the collision micro-cross-sections, the number of reactive points in the molecules, and the steric-hindrance coefficients for attack.

Solution of Eqn. (30) for small values of $N$ leads to formulae of the following type[102]:

$$\frac{R_{1i}^1}{R_{1i}^0}\frac{R_{2i}^1}{R_{2i}^0} N_1 N_2 \simeq 1, \qquad (32)$$

$$\frac{R_{1i}^1}{R_{1i}^0} N_1 = \frac{\xi_2}{\xi_1}\frac{z_2}{z_1}, \qquad (33)$$

where $R_{1i}^1$ and $R_{2i}^1$ are the yields of the labelled first and second components with the condition that their concentrations are equal to 1 (that is, the yields of labelled components from the pure substances), and $R_{1i}^0$ and $R_{2i}^0$ the yields of the first and second labelled components when their concentrations are low (that is $R_{1i}$ when $N_1 \simeq 0.1$, and $R_{2i}$ when $N_2 \simeq 0.1$). Eqn. (32) is confirmed by the experimental data for seven binary systems studied. Significant deviation was found only for the $C_6H_{12}$–$C_6H_6$ and $C_6H_6$–$C_5H_5N$ systems, possibly due to the high probability of the reactions of thermal tritium atoms with benzene and pyridine, one result of which is the formation of a polymer whose activity was not recorded in the experiments[103] (see Section II. 2).

In fact, Rowland and coworkers[104] found that the yield of polymer labelled with tritium in the benzene + + cyclohexane system amounted to 30–40%, depending on the duration of irradiation. It is assumed that the labelled polymer is formed through cyclohexadienyl radicals, whose production was noted earlier[99].

Eqn. (33) can be used to find the ratios $z_1\xi_1/z_2\xi_2$. This ratio is equal to 0.7 for the alcohol–benzene system and 0.5 for the alcohol–cyclohexane system. Thus the analogous ratio for the cyclohexane–benzene system can be found by calculation: $0.7/0.5 = 1.4$, which agrees exactly with the value found directly from experimental data on the yields of labelled compounds from a cyclohexane–benzene mixture. This indicates the possibility of using this method to treat the experimental results of studies of the yields of hot reactions in binary mixtures in the condensed phase.

Recently Rowland and coworkers[105] calculated the dependence of $R_1$ on $N_1$ by a Monte Carlo method for a number of binary mixtures in the gaseous phase. It was found that the dependence of $R_1$ on $N_1$ is determined by $p_1(E)$ and the ratios between $\sigma_1$ and $\sigma_2$, and $\xi_1$ and $\xi_2$, that is, the kinetics of hot reactions are determined by factors such as the probability of reaction, the retardation parameter, and the collision micro-cross-section.

This has a clear physical significance. Let us examine in turn the influence of the parameters determining the formation of the products in hot reactions.

### 3. The Influence of the Probability of Chemical Reaction on the Yield of the Products of Hot Reactions in a Binary Mixture of Substances

In the range $E \ll E_0$ (more accurately, $E < \xi\, {}^3E_0$) the hot atom spectrum is determined by the expression $1/\xi E$ (Fig. 3). If it is assumed that the probabilities of chemical reaction with the first and second components in the binary mixture of substances are determined in the range $E_2$–$E_1$ and depend in resonance fashion on energy (Fig. 3), the spectrum of hot atoms entering the range corresponding to determination of the function $p_{1i}(E)$ "loses" a fraction proportional to $\overline{f_1p_1(E)} + \overline{f_2p_2(E)} - \overline{p(E)}$ is subsequently denoted $p$. The fraction of hot atoms which can react with the first component with the formation of an $i$-labelled product (with probability $p_{1i}$) is equal to $1 - (f_1p_1 + f_2p_2)$. Since the probability of formation of an $i$-labelled product in the absence of competing processes is proportional to $f_1p_{1i}$, the yield $R_{1i} \simeq f_1p_{1i} \times (1 - f_1p_1 - f_2p_2)$. From this it follows that with increase in the concentration of the second component in the binary mixture of substances, the hot atom spectrum will show ever-increasing quantities of relatively low-energy atoms at the expense of "removal" of the high-energy fraction of the spectrum in the range $E_2$–$E_1'$. The effect of "selective" action of the hot atoms leads to a non-linear concentration dependence for the yields of the labelled products of the hot reactions.

¶ See Nesmeyanov and Filatov[102] for the detailed analysis.

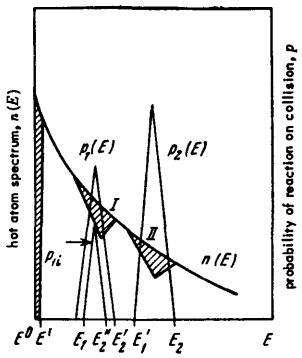



Fig. 3. Dependence of the hot atom spectrum on the probability of chemical reactions in binary mixtures of substances. $p_{1i}(E)$ is the probability of chemical reaction with the first component with the formation of the $i$-labelled product, $p_1(E)$ the same for the formation of all labelled products, and $p_2(E)$ the probability of reaction with the second component with the formation of all labelled products. The hatched regions (I and II) are the parts of the hot atom spectrum leaving the "game" as a result of chemical reactions. The fraction of hot atoms (II) is proportional to $f_2\overline{p_2(E)}$ and the fraction (I) is proportional to $f_1\overline{p_1(E)}$. The fraction of atoms $1/\xi E\{1 - [f_1p_1 + f_2p_2]\}$ (without allowance for the change in the density of collisions with change in concentration) falls in the energy range $(E_2''-E_1)$ of the function $p_{1i}(E)$. In the range of the spectrum $(E'-E^0)$ the atoms are captured by acceptors of radicals and thermal atoms $E_2 \simeq 10$ eV, $E_1 \simeq 1$ eV, $E^0 \simeq 0.03$ eV.

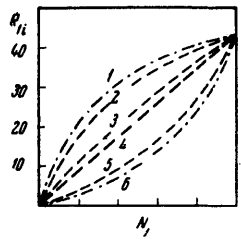



Fig. 4. Yield of labelled first component, formed by hot reactions in a binary mixture of substances, according to the kinetic equation (30), with the conditions that:

1) $p_1 > p_2$, $z_1 > z_2$; 2) $p_1 = p_2$, $z_1 > z_2$;
3) $p_1 > p_2$, $z_1 = z_2$; 4) $p_1 = p_2$, $z_1 = z_2$;
5) $p_1 > p_2$, $z_1 < z_2$; 6) $p_1 = p_2$, $z_1 < z_2$,

where $p_1$ is the probability of reaction of the hot atom on collision with the first component of the binary mixture; $p_2$ the same for the second component; $z_1$ and $z_2$ the steric parameters; $z_1 = n_1\sigma_1\gamma_1$ for the first component and $z_2 = n_2\sigma_2\gamma_2$ for the second component. $R_{1i}$ is the yield of labelled first component, and $N_1$ the mole fraction. The following values were selected for the calculation (1, 3, and 5): $p_1 = 0.3$, $p_2 = 0.2$, $z_1 = 0.3$, $z_2 = 0.1$, $p_{1i} = 0.1$, $\xi = 0.6$, and const = 5. For 2, 4, and 6: $p_1 = p_2 = 0.3$. In 3 and 4, $z_1 = z_2 = 0.3$. For $z_1 < z_2$ we took $z_1 = 0.1$ and $z_2 = 0.3$. The choice of the values of $p$, $z$, and $\xi$ is not critical. The shape of the dependence of $R_1$ on $N_1$ does not depend on the values of $p_1$, $z_1$, and $p_2$, $z_2$, but only on the relationships between $p_{1i}$, $p_1$, $z_1$ and $p_2$, $z_2$.

It is suggested[28,38,101,102] that the existence of this effect, which has been called the "integral effect", explains the *increase in specific activity of any component of the mixture with decrease in its concentration* and also the appearance of an isotopic effect in the reactions of hot tritium atoms in substances such as $CH_2D_2$, where the mean loss of energy has no influence on the result (see Section III. 1). On the other hand, since $f_1 = N_1\sigma_1n_1\gamma_1/\Sigma N\sigma n\gamma$ [see formula (31)], the rate of change in $R_{1i}$ with change in $N_1$ (and the rate of change in specific activity with change in composition) is determined by the parameters $\sigma$, $n$, and $\gamma$ (see Fig. 4).

## 4. The Influence of the Retarding Power of the Medium on the Yield of the Products of Hot Reactions

According to the kinetic equation (30), for smaller losses of energy, the hot atoms have a higher possibility of taking part in reactions, since there is an increase in the number of collisions in the energy range where $p_{1i} > 0$. On the other hand, if the probabilities of the reactions with the components are different (see Fig. 3), for low fractions of the kinetic energy lost the preferred product will be that for which the probability of formation is displaced towards higher energies (products with $p_2$). If appreciable proportions of the energy are lost on collision, the hot atom falls into the low energy range in the first collisions and then the $1i$-product will be formed with high probability. This "retardation effect" may lead to an increase in the specific activity of the component on dilution with a second substance[48]. This also follows from the relationship obtained by substituting, in place of $f/\xi$ in Eqn. (3C), the following expression:

$$f/\xi = N_1z_1/[N_1(z_1\xi_1 - z_2\xi_2) + z_2\xi_2] \qquad (34)$$

($\xi_1$ and $\xi_2$ are the mean logarithmic losses of energy on collision with the first and second components respectively)

$$R_{1i} = \frac{N_1z_1}{(N_1z_1\xi_1 + N_2z_2\xi_2)}\overline{p_{1i}(E)} - \frac{N_1z_1}{(N_1z_1\xi_1 + N_2z_2\xi_2)^2}\overline{p_{1i}(E)}\,[N_2z_1\overline{p_1(E)} + N_2z_2\overline{p_2(E)}]. \qquad (35)$$

The dependence of $R_{1i}$ on $N_1$ is non-linear.

The arguments given in Sections IV. 3 and IV. 4 are valid with the assumption that $z$ and $\xi$ are independent of $E$. If this is not the case, the analysis of the kinetic equation is more difficult.

## 5. The Loss of Energy by Hot Atoms in the Range of Chemical Interaction

As noted above, the loss of energy by a hot tritium atom on collision with a methane molecule is greater than that for collision with deuterium, despite the more favourable ratios of the masses of the tritium and deuterium for the transfer of kinetic energy. Chemical interaction apparently takes place on collision between the hot atom and a molecule even if it does not lead to stabilisation of the atom in

any chemical form, that is, "non-reactive" collisions take place with a high cross-section. This process may be called the "chemical scattering" of energy (inelastic collisions). Thus $\xi$ cannot be calculated rigorously from the ratio of the masses and dimensions of the atoms alone. The mean loss of energy on collision should be related to the collision cross-section in the range of chemical interaction energies and should depend on the energy.

According to the theory of neutron retardation, the number of collisions for retardation from $E_2$ and $E_1$ is determined by expressions (13). The loss of energy along an infinitely small section of the retardation path can be expressed by the general equation:

$$-dE/dx = LEn\sigma_p, \tag{36}$$

where $L$ is the number of molecules in unit volume, $n$ the number of scattering centres, and $\sigma_p$ the micro-cross-section of "chemical scattering". From this,

$$x = \ln\left(\frac{E_2}{E_1}\right)\Big/Ln\sigma_p. \tag{37}$$

Dividing (37) by the diameter of the molecule $\rho$, we obtain the number of collisions with molecul s in the retardation path from $E_2$ to $E_1$ (range in fractions of the molecular diameters):

$$k = \frac{\ln(E_2/E_1)}{Ln\sigma_p}\frac{1}{\rho}. \tag{38}$$

Equating (38) and (13), we obtain for $\xi$ the expression

$$\xi = Ln\sigma_p\rho. \tag{39}$$

The quantity $\xi$ should be dimensionless, as can be readily verified from (39). In the case of a binary mixture of substances we must substitute in formula (39) the "mean dimensions of the molecules" $\overline{\rho} = N_1\rho_1 + N_2\rho_2$, and the product $Ln\sigma_p$ should be replaced by the sum for both components

$$\xi = (L_1n_1\sigma_{1p} + L_2n_2\sigma_{2p})(N_1\rho_1 + N_2\rho_2). \tag{40}$$

Expression (40) gives the relationship between $\xi$ and $\sigma_p$.

This analysis shows the complexity of the processes accompanying the retardation and chemical interaction of hot atoms.

Under real conditions, some part is apparently played by several factors: the change in $\xi$ with change in composition produces a change in the density of collisions in the energy range where the probability of reaction is not equal to zero; a difference in the reaction probabilities and the steric parameters of the components of the binary mixtures leads to a change in the spectral distribution of the hot atoms with respect to energies. This change is greater, the greater the difference in the values of the probabilities and the factors $z = n\sigma\gamma$.

The fraction of the energy lost on collisions by the hot atoms $\xi$ is determined by the scattering micro-cross-sections. Since the micro-cross-section increases in the range of chemical interaction energies, the fraction of energy lost also increases.

Thus the independent quantities in formula (30) are $p(E)$, $\sigma(E)$, and, in implicit form, $\sigma_p(E)$. The functions $p(E)$, $\sigma(E)$, and $\sigma_p(E)$ alter the spectrum and density of collisions of the hot atoms, leading to a change in the yields of the hot reactions which is not proportional to the concentration of the original substances. The analytical expression for these functions, which for a given substance depend only on $E$, is unknown. At present, therefore, we cannot calculate the absolute yield of a hot reaction.

The foregoing does not exclude the possibility that transfer of excitation energy from labelled "newly-formed" molecules influences the yield of the products of hot reactions. Qualitative hypothetical conclusions regarding the existence of this mechanism[30,100] have obtained more rigorous proof. It has been shown[102] that the dependence of the change in the yield of labelled first component ($\Delta R_1$) on the addition of a second component — a hypothetical excitation energy acceptor — is linearly determined by the parameter $N_2^3$. Since $N_2^3 = 1/r_2$, where $r_2$ is the distance between the molecules of the excitation energy acceptor, the observed relationship $\Delta R_1 = \text{const} \times N_2^3$ indicates the existence of linear energy transfer throughout the molecules of the acceptor. The part of excitation energy acceptor is played by alcohol molecules in the $C_6H_6 + C_3H_7OH$ and $C_6H_{12} + C_3H_7OH$ systems and by benzene molecules in the $C_6H_{12} + C_6H_6$ system.

The experimental data show that the relationship $\Delta R_1 = CN_2^3$ applies satisfactorily for $N_2 > 0.6$ M. This indicates that the excited molecule of the first component should be surrounded by not less than six molecules of the excitation energy acceptor if the "protection" mechanism is to be effective. It is suggested[102] that at high concentrations of the energy acceptor the chief part is played by energy transfer influencing the rate of deactivation of the excited freshly-formed molecule, whereas at low concentrations the mechanism of "selective" action of the hot atoms predominates.

It may thus be assumed that at present the following parameters and processes determining the kinetics of hot reactions are known: the probability of reaction on collision, the micro-cross-sections of collision and scattering, and, possibly, the transfer of energy from "freshly-formed" labelled molecules.

## 6. The Possibility of Transfer of Hot Atoms in High-Excitation Reactions

The phenomenon of hydrogen atom transfer was observed in the nineteen-thirties[7] for exchange reactions of the type:

(14) $$H + CH_4 \rightarrow CH_3{-}H{-}H,$$

(15) $$CH_3{-}H{-}H + D \rightarrow HD + CH_4.$$

The methane molecules are hydrogen atom carriers which "catalyse" the process of deuterohydrogen formation. The activation energy of reaction (14) amounts to 10 kcal and the dissociation energy of the "fifth" hydrogen atom is ~17 kcal, that is, the compound $CH_4$–H is fairly stable.

In view of the existence of the processes of charge and excitation energy transfer, and also the above process, it may be assumed that there is a possibility of hot atom transfer from some molecules to others, for example, in the cyclohexane–benzene system after collision between tritium and a benzene molecule — the "catalytic" marking of cyclohexane: $C_6H_5$-T + $C_6H_{12} \rightarrow C_6H_{11}T + C_6H_7$ (compare Section II. 2).

In the RH + ROH system, the alcohol molecules apparently act as tritium atom carriers.

From this viewpoint it is possible to explain the change in the specific activity of certain substances in a mixture

with additives capable of transferring hot atoms. At present, however, we have no proof that such "catalytic" processes take place in hot atom chemistry.

## 7. The Stereochemistry of Hot Reactions and the Elementary Act of the Establishment of a Bond

It follows from formula (24) that the three-dimensional structure of molecules should influence primarily the replacement of atoms, since this takes place with attack by the hot atom at large angles to the direction of the bond formed by the atom being replaced. In fact, the agreement between the experimental results and calculated data assuming that the steric hindrance for attack $\Omega = 0.45$ in the replacement of a primary atom shows that steric factors play a decisive part in the competing reactions of abstraction and replacement. In attack at large angles to the bond direction, the rotational levels of the molecule are apparently excited. In this connection the mass of the molecule should apparently influence the establishment of a chemical bond following the transfer of energy. This can be readily followed by analysing the yields of the products formed by rupture of the C–C bond in different hydrocarbons. It is found that the tritium recoil atom reacts with the lighter residue of the molecule. Thus in the reaction

$$(16)\qquad T + CH_3{-}CF_3 \rightarrow \begin{cases} CH_3T \\ CF_3T \end{cases},$$

the ratio of the yields $CH_3T/CF_3T$ amounted to 15, whereas in the reaction

$$(17)\ T + CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \rightarrow \begin{cases} CH_3T + R \\ CH_3{-}CH_2{-}CH_2{-}CH_2T + CH_3^{\cdot} \end{cases},$$

the ratio $CH_3T/CH_3CH_2CH_2CH_2T$ was found to be 2.8 (Table 6). For chlorinated, brominated, and fluorinated methanes, it was also found that the effect of replacement of an atom was preferred to a greater extent, the smaller the mass of the fragment with which the hot atom reacts ("the inertial effect")[106,107].

The period of rotation through an angle $\theta$ is related to the moment of inertia ($I$) by the relationship

$$\tau \simeq 2\theta\sqrt{I/2E}. \qquad (41)$$

Calculation[106] shows that the time required for the rotation of $CH_2F$ through an angle of 1 radian amounts to $\sim 5 \times \times 10^{-14}$ s if the recoil atom communicated several electron volts of kinetic energy to the $CH_2F_2$ molecule on collision at the C–F bond. This time interval is greater than the duration of the interaction between the hot atom and the C–F bond ($10^{-14}$ s). In fact, the yield of the products obtained by the replacement of fluorine by tritium atoms in $CH_2F_2$ amounted to fractions of 1%, whereas as a result of the ease of rotation of the methyl group about the centre of inertia in $CH_3F$ the yield of $CH_3T$ amounted to 4.4%.

TABLE 6. Inertial effect in the reactions of hot tritium atoms[106].

| Substance | Ratio of yield of $CH_3T$ to the yield of $R_{n-1}H_{2n-1}T$ per C–$CH_3$ bond |
|---|---|
| $C_2H_6$ | 2.7* |
| $n\text{-}C_4H_{10}$ | 1.8 |
| $n\text{-}C_5H_{12}$ | 2.8 |
| $iso\text{-}C_5H_{10}$ | 4.7 |
| $neo\text{-}C_5H_{12}$ | 8.7 |
| $n\text{-}C_6H_{14}$ | 2.2 |
| For $CH_3{-}CF_3$ | Ratio $\frac{CH_3T}{CF_3T} \simeq 15$ |

* For example, for $C_3H_8$: $CH_3T/C_2H_5T = \frac{11.0}{4.0} = 2.7$.

In the calculation it is also necessary to allow for the values of the collision cross-sections, the energy of the bonds, and the possibility of removal of the excitation energy. In the series $CH_3F$, $CH_3Cl$, and $CH_3Br$, the yield of $CH_3T$ increases systematically (4.4%, 7.1%, and 12.0%) in accordance with the increasing cross-sections of collision for tritium with the atoms on going from fluorine ($0.88 \times 10^{-16}$ cm²) to chlorine ($1.6 \times 10^{-16}$ cm²) and bromine ($1.96 \times 10^{-16}$ cm²)† – the energy of the C–X bond (X = halogen) also decreases in the above series of compounds, so that the conclusion regarding the influence of collision cross-section is ambiguous; the results show better agreement with experiment, however, for the former model. In the liquid phase the freedom of rotation of the molecules is limited. From the viewpoint of the "inertial effect", the yield of replacement products should decrease, but this is not observed (Table 7): the yield of the chlorine-replacement product increases for both $CH_3Cl$ and $CH_2Cl_2$. In the liquid phase there is apparently a sharp increase in the survival of labelled molecules as a result of the transfer of energy on collision.

The transfer of energy (non-specific) here is facilitated by the fact that the rotational energy, which is essentially kinetic, is readily converted into energy of translational movement. The rate of removal of the excitation energy is equal to the number of collisions between the atoms and molecules:

$$z = 2/\sqrt{\pi}\,\sigma\, v N_1 N_2 q, \qquad (42)$$

where $\sigma$ is the collision cross-section for the excited molecule, $v$ the velocity of the particles, $N_1$ and $N_2$ are their concentrations, and $q$ is the probability of the process,

TABLE 7. Relative yields of tritium-labelled molecules as a result of the reactions of hot tritium atoms with chloromethanes*.[108]

A

| Substance | Yield of products | | |
|---|---|---|---|
| | $CH_3T$ | $CH_2TCl$ | $CH_2TI$ |
| $CH_3Cl$ 9.1 cm, gas | 27.8 | 30.4 | 40.9 |
| Liquid | 45 | 65 | — |

B

| Substance | Yield of products | | | |
|---|---|---|---|---|
| | $CH_2TCl$ | $CHTCl_2$ | $CH_2TI$ | $CHTCII$ |
| $CH_2Cl_2$ 8.1 cm, gas | 6.9 | 13.9 | 15.3 | 6.4 |
| Liquid | 37 | 44 | — | — |

* Yield of HT taken as 100%; $^3$He pressure 1.5 cm; on irradiation in the gaseous phase the ampoules contained $I_2$.

† The covalent radii were used for the calculation[108].

equal to unity for the conversion of energy of rotation into translational energy and equal to $\sim 10^{-4}$ for the conversion of vibrational energy into translational energy.

Thus for attack at large angles to the bond direction, the rotational levels are excited. The removal of excitation energy takes place effectively on each collision with another molecule, so that increase in pressure leads to an increase in the yield of replacement product. In the case of attack along the bond, the vibrational levels of the molecule are excited. The probability of conversion of vibrational energy into translational energy is smaller by a factor of $10^4$ than that for the conversion of rotational energy into translational energy. Thus the yield of abstraction products formed as a result of this attack depends little on pressure, as confirmed by experiment[33].

It is undoubtedly true that in the establishment of a chemical bond the electronic levels of the molecule are also excited. The lifetime of excited electronic states amounts to $10^{-12}$–$10^{-13}$ s. This increases to $10^{-9}$–$10^{-7}$ s if a change in multiplicity takes place. In a period of $\sim 10^{-8}$ s the molecule is able to undergo approximately $10^5$ vibrations and approximately $10^3$ rotations. If the internal conversion of electronic excitation takes place readily, there is a definite probability of energy transfer on collision with surrounding molecules (non-specific transfer of energy). Certain substances, for example, benzene, are able to remove excitation energy directly from electronic levels (specific transfer of energy).

In the gaseous phase the time interval between two collisions is inversely proportional to pressure and is equal to $\sim 10^{-7}\, p^{-1}$ s, where $p$ is the pressure in mmHg. At a pressure of 100 mmHg the lifetime of an excited molecule should be greater than $10^{-8}$ s if deactivation is to take place on collision. In a liquid, the number of collisions per second amounts to $\sim 5 \times 10^{12}$, so that transfer of energy on collision is possible even if short-lived states are excited. The question of the specific transfer of excitation energy in reactions of hot atoms remains open. At present the main task is to establish precise experimental facts indicating that such processes take place.

The next step in the further development of the theory of the elementary acts of chemical reactions at high energies is possibly a quantum-mechanical approach, which here is facilitated by the fact that the reactions of hot atoms take place on local collision in a limited part of the molecule, so that the remaining part of the molecule can be regarded as not taking part in the primary act of establishment of the chemical bond. The first steps in this direction have already been taken[109].


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# THE USE OF ELECTRON PARAMAGNETIC RESONANCE FOR THE STUDY OF CATALYSTS

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## I. INTRODUCTION

The essential features of the EPR method (electron paramagnetic resonance) have been described in detail in many monographs and reviews[1-6].

The efficiency of this method in the study of catalysts is because in most cases the catalysts are paramagnetic. The nature of the paramagnetic centres may be different but they are all, in the final analysis, produced by unpaired electrons, which give EPR signals. The intensity and shape of the lines in the EPR spectrum can give information on the concentration and state of the paramagnetic centres, with which the catalytic activity of the contacts is usually associated (at any rate in reactions taking place by a radical mechanism). Here it must be borne in mind that both the bulk properties and the surface properties are reflected in the EPR. It is known that the paramagnetism of catalysts, which are most frequently studied in the isolated state at room temperature, does not reflect completely the paramagnetic state of the contacts during catalysis. Moreover, new paramagnetic centres may be produced during catalysis, so that in the comparison of the dynamic paramagnetism of the contacts with their catalytic activity, allowance must be made for the fact that the correlations will be justifiable only if the above features are taken into account.

In a number of studies it has been shown that the irradiation of catalysts by $\gamma$-rays, a neutron beam, etc., alters their catalytic activity[7]. Other work, often carried out with the same materials, has established that this irradiation generally leads to the production, in the catalyst, of defects which can be detected using the EPR method. It is convenient to compare the data obtained by different authors on the change in catalytic activity after irradiation on the one hand with the parameters of the EPR signals of the same catalyst on the other. This is particularly necessary since a simultaneous comparison of these two parameters has been made in very few studies.

In the discussion of the factual material, we have used the classification of catalytic reactions proposed by Polyakin[8], who divides all catalytic reactions into three main types: reactions involving the pairing and unpairing of electrons; reactions taking place with electron transfer (oxidation); and reactions involving the donation and withdrawal of an electron pair (acid–base reactions).

## II. REACTIONS INVOLVING THE PAIRING AND UNPAIRING OF ELECTRONS

Reactions of this type which have been studied by the EPR method include deuterium exchange in molecular hydrogen, hydrogenation, dehydrogenation, and radical polymerisation†. For these reactions to take place, it is usually necessary that the catalyst surface have paramagnetic centres ("free valencies"[12]) or, at least, that such centres be readily produced under the catalysis conditions by the influence of heat and the reaction mixture. The interaction between the surface paramagnetic centres in this case is not significant. Since the completion of the catalytic act in this type of process does not require the transfer of electrons, dielectric substances (for example, $SiO_2$ or $Al_2O_3$) with paramagnetic centres on their surface may also act as catalysts here. If the catalytic act takes place on those paramagnetic centres which are detected by the EPR method, we should expect that the intensity of these signals and the catalytic activity should change in the same sense.

### 1. Deuterium Exchange in Molecular Hydrogen

The reaction $H_2 + D_2 \rightleftharpoons 2HD$ takes place at a satisfactory rate on a number of catalysts. In recent years it has been studied on silica gel and on alumina as a model reaction for determining the influence of the irradiation of these oxides on their catalytic activity.

It has been established[13] that thoroughly dehydrated and ignited (8 h at 200–300°C in a vacuum) silica gel containing less than 0.1% Fe and Al, after irradiation at room temperature by $\gamma$-rays from $^{60}Co$ (5–10 Mrad), gives a relatively weak EPR signal [a quintet with $g$-factor equal to the $g$-factor of diphenylpicrylhydrazyl (DPPH) and splitting 22 G]. It is suggested that the observed paramagnetic centre is formed by the removal of a hydrogen atom from a surface hydroxyl group and that the hyperfine structure (HFS) is due to the interaction of the unpaired electron with the protons of neighbouring OH-groups or adsorbed water molecules. It is considered that the increased catalytic activity of irradiated silica gel in the isotopic exchange $H_2 + D_2 \rightleftharpoons 2HD$ may be associated with these paramagnetic centres. It is also suggested that the EPR spectrum after irradiation does not reveal all the paramagnetic centres produced by irradiation.

Silica gel which has been degassed at 500°C and then irradiated at room temperature with the same dose gives a narrow singlet ($g$-factor = 2.0004). In Molin and Voevodskii's opinion[14], shared by Kazanskii, this signal is due to electrons trapped in oxygen vacancies of the lattice. Kohn[15] also studied the paramagnetic resonance absorption of silica gel which had been degassed at ~500°C and then irradiated at 50°C by $\gamma$-radiation from $^{60}Co$ (dose $10^{19}$ eV$\times$ $\times g^{-1}$) or by X-rays with an energy of 50 keV. The work was carried out with silica gel in which the concentration of impurities (Fe, Al, Mg) did not exceed 0.1–0.01%. Kohn, like Kazanskii, detected an EPR signal (singlet) stable at room temperature (in a vacuum). Kohn also attributed the signal to the trapping of electrons in the oxygen vacancies of the lattice, but whereas Kazanskii and coworkers identified the paramagnetic centres observed in the EPR spectrum with the colour centres of the silica gel (the so-called $F$-centres), Kohn showed that the $F$-centres, which are also produced after irradiation, are not associated with the paramagnetic centres. Similarly the $F$-centres are not associated with the catalytic activity with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$. In actual fact, as noted by

† The $o$-$H_2 \rightleftharpoons p$-$H_2$ process is not considered, since it takes place on all paramagnetic substances[9-11].

Taylor and Kohn[16-18], the main bulk of the hydrogen is chemisorbed on the *F*-centres so strongly that these centres cannot react further with hydrogen. Only ~ 5% of the sorbed hydrogen is capable of undergoing exchange with gaseous $H_2$ or of removal by evacuation at room temperature. Calculations show that this quantity of mobile hydrogen would be sufficient to ensure the increased catalytic activity of the irradiated silica gel. According to Taylor and Kohn's data[17], however, the rate of the exchange of this mobile fraction of the sorbed hydrogen is not sufficiently high for the exchange to be a stage in the catalytic process $H_2 + D_2 \rightleftharpoons 2HD$.

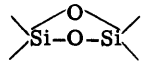
In Kazanskii's experiments, the EPR line did not become broader when oxygen was admitted, and from this it was concluded that the signal is due to bulk defects. Kohn, however, found that this signal disappears when oxygen is added ("the oxygen effect"). The accumulated data suggest that some of the paramagnetic centres are also present on the surface of the contact.

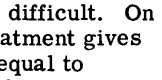
Kohn and Taylor[19] studied the change in the catalytic activity of silica gel which had been degassed at 450–600°C and subjected to $\gamma$-irradiation with a dose of approximately $10^{19}$ eV $g^{-1}$ (concentration of Fe, Al, and Mg impurities less than 0.1–0.01%) with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$ at room temperature (static method), and established that after irradiation the silica gel is 100–2000 times more active than before irradiation. At the same time, the activation energy is reduced from 9 kcal × × $mole^{-1}$ to 2 kcal $mole^{-1}$. From this it might be concluded that the increase in the catalytic activity of the silica gel after irradiation is associated with the generation of the defects responsible for the appearance of the narrow EPR signal. In a recent paper, however, Taylor[18], referring to Kohn's results[20], points out that when the silica gel is heated at a temperature close to its melting point, its catalytic activity approaches that of the irradiated contact. The heating was carried out[20] for 16 h at 920°C. After this treatment, the rate constant for the reaction $H_2 + D_2 \rightleftharpoons 2HD$ on commercial silica gel, even at -78°C, was equal to $5 \times 10^{-7}$ $min^{-1}$ $m^{-2}$ — for comparison it should be noted that the rate constant for the reaction $H_2 + D_2 \rightleftharpoons$ $\rightleftharpoons 2HD$ at room temperature on an analogous silica gel specimen after irradiation with $\gamma$-rays from $^{60}Co$ (activity 600 c for 1 min at 35°C) is equal to $5.5 \times 10^{-5}$ $min^{-1}$ $m^{-2}$. Unfortunately, Kohn does not give the value of the rate constant at room temperature for silica gel which had been heated at 920°C, and this makes comparison difficult. On other modifications of $SiO_2$, this thermal treatment gives an even greater effect: the rate constant is equal to $10^{-3}$ $min^{-1}$ $m^{-2}$ on quartz, and $10^{-4}$ $min^{-1}$ $m^{-2}$ on quartz glass and cristobalite (these substances have a surface area of approximately 6–8 $m^2$ $g^{-1}$).

Kohn[20] also showed that the catalytic activity of silica gels is directly proportional to the concentration of aluminium present. After degassing at high temperature followed by irradiation (35°C, 600 c, $^{60}Co$ $\gamma$-radiation, 1 min), the rate constant at 25° on silica gel shown by spectroscopic analysis to contain no aluminium, was equal to $3.7 \times 10^{-6}$ $min^{-1}$ $m^{-2}$, whereas for silica gel specimens containing 0.01% $Al^{3+}$, 0.1% $Al^{3+}$, and 0.5% $Al^{3+}$, the values ($min^{-1}$ $m^{-2}$) were $3.5 \times 10^{-5}$, $5.5 \times 10^{-5}$, and $1.6 \times 10^{-4}$ respectively. An analogous direct relationship between the activity and the aluminium content is observed for silica gel specimens degassed at 500° and 625°C, but in this case the absolute values of the rate constants are smaller by 1–2 orders of magnitude. (An increase in the catalytic activity of silica gel after the introduction of additional quantities of Al was established by Kohn and Taylor[17]). It may also be noted that silica gel with maximum purity, even after extensive irradiation ($6 \times 10^{20}$ eV $g^{-1}$), adsorbs very little hydrogen, the quantity adsorbed being smaller by a factor of ~ 100 than the quantity adsorbed by irradiated commercial silica gel[16,17].

On the basis of these facts, Kohn[20] suggests that the increased catalytic activity of irradiated silica gel is due to a complex consisting of adsorbed hydrogen and a positive hole, trapped on an aluminium atom. Kohn himself, however, considers that this suggestion is only a rough approximation, since it does not explain a number of facts: the increase in activity after irradiation by ultraviolet light[16,17] or by $\gamma$-rays followed by ultraviolet light[16,17], or the poisoning of the catalyst by dry oxygen[21].

The facts indicate that the catalytically active centre in silica gel contains aluminium. In Kohn and Taylor's opinion[17], it cannot be assumed that the aluminium impurity in the silica gel forms a $\gamma$-$Al_2O_3$ phase and that it is the presence of this phase which determines the catalytic activity of the silica gel. This cannot be assumed chiefly because pure $\gamma$-$Al_2O_3$, ignited at 520°C, shows almost no change in activity after irradiation, whereas the catalytic activity of silica gel containing aluminium impurity and heated at the same temperature, increases after irradiation by a factor of 100–2000, as already noted. Kohn and Taylor[17] conclude that the aluminium must be introduced into the silica gel structure. At the same time it is undoubtedly true that heating (degassing) the silica gel increases its activity, the values of the catalytic activity after high-temperature treatment and irradiation being of the same order of magnitude. On this basis, Taylor[18] suggested that the observed changes in catalytic activity are more probably associated with the sorbed molecules (that is, with the removal of water or with the interaction of radiation with the complex catalyst — "poison"), than with the actual solid.

It is generally assumed[22] that the thermal dehydration of silica gel leads to the formation of so-called "siloxane bridges"  on its surface.

It may be suggested that the catalytically active centres of silica gel with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$ are alumosiloxane "bridges"  , formed during the thermal or radiation dehydration of the contact. Hydrogen is probably activated on these strained energy-rich structures.

The ability of these "bridges" to activate hydrogen should naturally decrease with decrease in the temperature of catalysis. At the temperature of liquid nitrogen, these "bridges" are apparently almost inert with respect to this reaction. At the same time, the $\gamma$-irradiation of previously calcined silica gel at the temperature of liquid nitrogen will probably activate these "bridges", making them able to activate hydrogen even at -196°C. At low catalysis temperatures therefore, we should expect that previously calcined silica gel specimens will have a much lower catalytic activity than contacts which have been calcined and then irradiated. The difference in the catalytic activity of silica gel after thermal treatment, and also after thermal treatment followed by irradiation (at the

temperature of liquid nitrogen) should increase with decrease in the temperature of catalysis. This is probably the reason for the observed marked difference in the catalytic activity of silica gel at -196°C after thermal treatment on the one hand and after irradiation at the temperature of liquid nitrogen on the other hand. In fact, for example, the rate constant for deuterium exchange on silica gel containing 0.01% aluminium, after irradiation for 16 h at -196°C, is greater than $3 \times 10^{-4}$ $min^{-1}$ $m^{-2}$ (at -196°C), whereas the rate constant for the same silica gel specimen after heating at 900°C amounts to less than $3 \times 10^{-7}$ $min^{-1}$ $m^{-2}$.

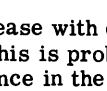
The suggestion regarding the possible part played by alumosiloxane "bridges" as active centres for the reaction $H_2 + D_2 \rightleftharpoons 2HD$ on the surface of a silica gel catalyst cannot be taken as proved. It is definitely established, however, that the higher the calcining temperature, that is, the more complete the dehydration of the silica gel, the higher the catalytic activity with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$. After thermal treatment the silica gel does not show EPR signals, so that the catalysis here is not associated with paramagnetic centres.

Analogous relationships are observed for the catalysis of the reaction $H_2 + D_2 \rightleftharpoons 2HD$ on alumina. Here also it has been established that the higher the temperature of preliminary heating (activation) of the catalyst in a vacuum, the less marked the effect of subsequent irradiation[18,23-25] (the irradiation was carried out in a vacuum for 3 min at -78°C from a $^{60}Co$ source at a rate equal to $2 \times 10^{17}$ eV × × $g^{-1}$ $min^{-1}$; the catalytic activity was also measured at -78°C). For a catalyst previously heated at 650°C, however, the activity decreased by almost one-half after irradiation. The lower the temperature of preliminary heating of the catalyst, the more rapid the decrease in the catalytic activity induced by the irradiation: the time taken amounted to 2-4 d (at room temperature) for a catalyst heated at 400°C, and to several hours, even at -78°C[23] ("annealing") for a catalyst heated at 200°. At the same time, alumina gives an intense EPR signal after irradiation (both after irradiation at the temperature of liquid nitrogen in a vacuum[26] and after irradiation by $^{60}Co$ $\gamma$-rays with an energy of 1.25 MeV at room temperature[25]).

Kazanskii[26] observed a correlation between the decrease in the intensity of one of the components of the complex EPR signal observed at -196°C and the decrease after annealing in the induced catalytic activity of catalysts previously heated at 200-500°C. On this basis it was suggested that "the additional activity of the irradiated alumina gel and the labile EPR signal are produced by the same centre".[1] It is quite probable that the irradiation of $\gamma$-$Al_2O_3$ previously heated at 650°C also leads to the appearance of EPR signals. At the same time, the catalytic activity of $\gamma$-$Al_2O_3$ decreases after this thermal treatment, as already noted. There are thus grounds for assuming that the above suggestion is erroneous.

Taylor[18] considers that the increase in catalytic activity after irradiation is associated with the removal of sorbed molecules of "poisons" (for example, water) from the surface, not only for silica gel but also for all non-metallic catalysts. This applies particularly to $\gamma$-$Al_2O_3$. Kolbanovskii and coworkers[25] also point out that the activation of $\gamma$-$Al_2O_3$ is most probably due to the removal of sufficient quantities of water from the catalyst.

It may be assumed that dehydration of the alumina gel surface leads to the formation of aloxane "bridges"



(-Al<O>Al-), which can probably act as active centres for the reaction $H_2 + D_2 \rightleftharpoons 2HD$. This assumption makes it possible to explain the regularities observed. In fact, if the preliminary heating of $\gamma$-$Al_2O_3$ is carried out at an insufficiently high temperature, this leads to the formation, on the surface of the catalyst, of a certain quantity of aloxane "bridges" and thus to the production of a definite stable catalytic activity. If this catalyst is then irradiated at low temperature (-78° or -196°C), new aloxane "bridges" are formed, accompanied by the liberation of water. In the process, the catalytic activity evidently increases. It must be assumed, however, that under these conditions the water remains in the catalyst. The aloxane "bridges" are probably less stable than alumosiloxane bridges. (For an approximate estimate of the bond strength, we may note that the energy of rupture of the Al-O- bond at 298°C is 116 kcal $mole^{-1}$, whereas that of the Si-O- bond is 193 kcal $mole^{-1}$;[27] the rate of rehydration of calcined alumina gel is greater than that of calcined alumina-silica and, more particularly, silica gel[28]). It may therefore be assumed that the aloxane "bridges" will react more readily than alumosiloxane bridges with the water remaining in the catalyst, particularly with increase in temperature (the so-called "low-temperature annealing"). If, however, the heating is continued until the water is almost completely removed and formation of the aloxane "bridges" on the surface takes place to the maximum extent, subsequent irradiation can only break down these bridges and thus decrease the catalytic activity. This interpretation explains why the effect of irradiation is greater, the lower the temperature of preliminary heating of the catalyst. On the other hand, it also explains why the irradiation of alumina gel specimens heated at 650°C leads to a decrease in catalytic activity. The phenomenon of the "annealing" of the induced catalytic activity is also explained.

It follows that the increase sometimes observed in the catalytic activity with respect to deuterium exchange in molecular hydrogen on silica gel and alumina gel after irradiation is not due to defects giving an EPR signal. The fact, observed in a number of instances, that the intensity of the signal and the catalytic activity change in the same sense, does not reflect their correlation as cause and effect but merely indicates that both these parameters are determined by the same factor (in this case radiation dehydration). It is not excluded, however, that some paramagnetic centres produced during irradiation may catalyse the isotopic exchange.

A parallelism between the intensity of the signal and the catalytic activity with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$ is not observed on sugar carbons[29]. The maximal activity is shown by carbon heated at 905°C, for which the intensity of the EPR signal is a minimum. The maximal intensity (and minimal width) is shown by the EPR signal for carbon heated at 607°C. In Turkevich and Laroche's opinion, the high activity of carbon heated above 607°C is because treatment of the carbon in this way produces antiferromagnetic regions on which hydrogen is readily chemisorbed. Activation of hydrogen in the catalysis of the reaction $H_2 + D_2 \rightleftharpoons 2HD$ also apparently takes place on these regions.

The intensity of the EPR signal induced by irradiation is found to change in the same sense as the activity with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$ for two catalysts: ZnO and $TiO_2$ (anatase). Thus Kohn and Taylor[30] showed that after irradiation with $^{60}Co$ $\gamma$-rays ($10^{18}$-$10^{29}$ eV $g^{-1}$,

at -78°C) the activity of pure zinc oxide for this reaction increases by a factor of 3–10, the time required for the induced activity to decrease by half being greater than one month. Terenin and coworkers[31] detected the gradual appearance of two EPR signals after the irradiation of zinc oxide with ultraviolet light (and even with visible light) at 77°K, in air: one signal had $g$-factor 1.964 and line width $\Delta H$ = 4.5 G, and the second had $g$-factor 2.018 and $\Delta H$ = = 3.0 G. Analogous signals gradually appeared after irradiation in a vacuum at the same temperature.

Schneider[32] also detected an EPR signal with a $g$-factor 1.657 and $\Delta H$ = 4.6 G after the irradiation of zinc oxide with ultraviolet light in a vacuum at room temperature.

Terenin[31] suggests that the singlet with $g$-factor 1.914 is produced by centres freed from oxygen during photodesorption — unpaired electrons in donor levels — and that the singlet with $g$-factor 2.018 is due to chemisorbed oxygen atoms. The intensity of these signals decreases rapidly when irradiation is stopped.

It can be seen that soft irradiation which does not lead to the displacement of atoms in the lattice, on the one hand increases the catalytic activity of ZnO in the reaction $H_2 + D_2 \rightleftharpoons 2HD$, and on the other induces EPR signals in the catalyst.

Mishchenko and coworkers[33] established that changes in the same sense are shown by the intensity of the EPR signal induced in titanium dioxide (anatase) by $\gamma$-irradiation with $^{60}Co$ (at -196°C in a vacuum, integral dose $1.7 \times 10^7$ r) and its catalytic activity in deuterium exchange in molecular hydrogen at -196°C. An interesting feature is that Kohn and Taylor[30] detected an increase in the catalytic activity of $TiO_2$ (rutile) with respect to this reaction, only after treatment by irradiation in a reactor. Here, however, the catalysis was carried out at -78°C, that is, a significantly higher temperature.

The above examination suggests that in pure ZnO and $TiO_2$ (anatase) the centres responsible for the EPR signals are simultaneously the centres for the activation of hydrogen in the reaction $H_2 + D_2 \rightleftharpoons 2HD$.

## 2. Hydrogenation–Dehydrogenation Reactions

A number of recent papers have compared the paramagnetic properties, influence of irradiation, and catalytic activity for platinum and palladium catalysts deposited on various carriers, and also for other catalysts, with respect to hydrogenation–dehydrogenation reactions.

(a) Hydrogenation reactions. Nicolau and coworkers[34] studied the hydrogenation of $p$-nitroanisole and crotonic acid on a catalyst consisting of 5% Pt on diamagnetic carbon, and showed that this catalyst gives a narrow EPR signal (singlet with $\Delta H$ = 2–5.4 G). Nicolau and coworkers[35] had previously established that this signal is due to the introduction of the electrons of the platinum into a so-called "pseudo-sandwich" complex with carbon. It was shown that not all of the electrons of the platinum enter complexes of this type, since the observed intensity of the signal is smaller than the calculated value by approximately four orders of magnitude.

Specimens of the catalyst were heated in air in the range 50–500°C. It was found that the higher the temperature of preliminary annealing, the lower the intensity of the EPR signal and the catalytic activity. After heating at 500°C, both quantities decrease to zero. Distinct changes in the same sense are thus shown by the catalytic activity with respect to the hydrogenation of these compounds and the concentration of unpaired electrons bound in the "pseudo-sandwich" complexes. In the hydrogenation of nitrobenzene and $p$-nitrotoluene on catalysts consisting of Ni on zeolite, 1% Pt on active carbon, and 5% Pd on carbon black, Graham[36] observed an increase in the activity of the catalysts after irradiation by X-rays, $\beta$-rays, deuterons, or neutrons. He found that the lower the melting point of the metal catalyst, the more ready its activation during irradiation and the more rapid the decrease in this induced catalytic activity. In Graham's opinion, the generation of active centres involves the creation of defects on the surface, and the decrease in catalytic activity is due to their elimination by surface diffusion and annealing. It is quite probable that under appropriate conditions these defects may be revealed in the EPR spectrum, although Graham unfortunately did not carry out these measurements.

At the same time, Minachev[37] did not observe an increase in the catalytic activity of a catalyst consisting of 0.5% Pt on alumina–silica with respect to the hydrogenation of cyclohexane, after irradiation of the contact with $^{60}Co$ $\gamma$-rays (energy of $\gamma$-quanta 0.6 MeV).

A parallelism between the appearance of a narrow EPR signal and catalytic activity with respect to hydrogenation is also observed for titanium dioxide.

According to the data of Gray and coworkers[38], $TiO_2$ with maximum purity does not catalyse the hydrogenation of benzene, and Chester[39] reports that thoroughly oxidised titanium dioxide does not give an EPR signal. $TiO_2$ which has been partly reduced by hydrogen is a satisfactory catalyst for the Fischer–Tropsch synthesis[38]. At 4.2–2.16°K, this catalyst gives an EPR spectrum consisting of 2–4 lines ($\Delta H$ = 18–30 G).[39] With increase in temperature the signal is converted into an asymmetric singlet. (It should be noted that Nicolau also detected a narrow singlet in $TiO_2$ at room temperature[40].) The nature of this signal is not clear. In Chester's opinion[39] the signal may be due to $Ti^{3+}$ ions in the interstices or at lattice sites in the Ti lattice, perturbed by adjacent oxygen vacancies. It may also be due to electrons (trapped spontaneously) in the interstices. It is not excluded that the signal is given by certain unidentified centres produced as a result of the introduction of hydrogen (but not H and OH). In any case, the signal from a catalyst with oxygen content reduced as a result of heating in a vacuum is quite different.

It was pointed out above that the catalytic activity of pure zinc oxide with respect to the reaction $H_2 + D_2 \rightleftharpoons 2HD$ increases after irradiation. At the same time, previously irradiated zinc oxide ($^{60}Co$ source, $6–10 \times 10^3$ r $min^{-1}$ in a vacuum at 15° ± 5°) shows a lower catalytic activity in the hydrogenation of ethylene at 0° than a non-irradiated specimen[41]. The probable reason for this is that the activation of the ethylene necessary for its hydrogenation does not take place on the hydrogen-activation centres induced by irradiation and revealed in the EPR spectrum.

The irradiation of zinc oxide during catalysis ($^{60}Co$ source, $2.5 \times 10^{19}$ eV $g^{-1}$ $h^{-1}$) increases its catalytic activity with respect to the synthesis of methanol from hydrogen and carbon monoxide[42]: the effect was maximal at the lowest catalysis temperature (201°C) — catalytic activity increased by a factor of 4–5.

Kohn and Taylor[17] tried to hydrogenate ethylene on irradiated industrial silica gel. Moderate activity was

detected. For example, after irradiation (1 g silica gel, dose rate $2 \times 10^{17}$ eV $g^{-1}$ $min^{-1}$) all the ethylene was hydrogenated in 4 d at room temperature (the catalytic activity was measured by a static method in a system with a volume of 30 $cm^3$, and the molar ratio of hydrogen and ethylene in the mixture was 2 : 1). There is no sense in relating this induced catalytic activity to the EPR signal induced by irradiation and observed at room temperature. It is known[43] that ethyl radicals adsorbed on the surface of irradiated silica gel are destroyed even at -70°C.

The intensity of the narrow EPR signal and the catalytic activity do not always change in the same sense. An important part is played by the chemical character of the paramagnetic centre. The intensity of the EPR signals and the catalytic activity will change in the same sense only when the paramagnetic centres are chemically capable of catalysing the hydrogenation (or dehydrogenation) of a given substance. In addition to the examples examined above where a change in the same sense does not take place, no parallelism is observed between the intensity of the narrow and broad signals for alumina–chromium oxide catalysts and their activity with respect to the hydrogenation of ethylene. The maximal activity with respect to this reaction was shown by chromium oxide which had been heated to 700°C and exhibited antiferromagnetic properties[44]. The intensity of the EPR signals of this catalyst was low, however, and its width was approximately 500 G.

(b) Dehydrogenation reactions. In the dehydrogenation of cyclohexane on silica gel, alumina, alumina–silica catalyst, $ZrO_2$, MgO, ZnO, or NiO irradiated with electrons (energy 0.8 MeV) or with $^{60}Co$ $\gamma$-radiation (dose rate 400 r $s^{-1}$), a correlation was observed between the appearance of the EPR signal and the induced catalytic activity[45]. The irradiation was carried out in ampoules containing the catalyst and cyclohexane (the ampoules were first evacuated and heated at 400°C). After this treatment, a signal due to the $C_6H_7^{\cdot}$ radical was detected in $SiO_2$, $Al_2O_3$, and $Al_2O_3$–$SiO_2$, unidentified weak signals were detected in $ZrO_2$ and MgO, and no EPR signal was detected in ZnO or NiO. From this it was concluded that $SiO_2$, $Al_2O_3$, and $Al_2O_3$–$SiO_2$ exhibit maximal catalytic activity and $ZrO_2$ lower catalytic activity, and that in ZnO and NiO there is almost no induced catalytic activity. At the same time, as the authors of the paper point out, NiO and ZnO have a high "thermal" catalytic activity (at 300°C) with respect to the dehydrogenation of cyclohexane, whereas the other oxides examined above do not catalyse this reaction at all at the same temperature.

Nicolau[46] showed that platinum, deposited on a carrier containing diamagnetic carbon (the carrier was first immersed in sugar solution and then heated for 1 h at 800°C), brings about intensive catalysis of the dehydrocyclisation of 1,1,3-trimethylcyclopentane, whereas the catalytic activity of $Pt/Al_2O_3$ and $Pt/SiO_2$ is smaller by a factor of 3.5–9. The catalytic activity of the $Pt/C + Al_2O_3$ catalyst is higher than that of $Pt/C + SiO_2$. It is significant that only catalysts containing carbon give EPR signals (concentration of paramagnetic centres $9 \times 10^{18}$ spin $g^{-1}$, $\Delta H$ = 10 G and $2.3 \times 10^{16}$ spin $g^{-1}$, $\Delta H$ = 12 G respectively). It can be seen that here also the intensity of the narrow EPR signal and the catalytic activity with respect to the dehydrogenation change in the same sense.

Summarising the results for hydrogenation–dehydrogenation reactions, it may be noted that in most cases a parallelism is observed between the intensity of the narrow EPR signals and the catalytic activity. We would emphasise again, however, that a significant part is played by the chemical character of the centre responsible for the appearance of the signal. Thus the centres responsible for the catalysis of the dehydrogenation of cyclohexane on $SiO_2$, $Al_2O_3$, and $Al_2O_3$–$SiO_2$ are evidently not identical to the centres which are responsible for the catalysis of $H_2 + D_2 \rightleftharpoons 2HD$. In actual fact, it was shown that the reaction $H_2 + D_2 \rightleftharpoons 2HD$ takes place on previously calcined silica gel and alumina gel which give no EPR signal, whereas the dehydrogenation of cyclohexane does not take place on these catalysts even at high temperature. Hydrogen and cyclohexane are apparently activated on different centres in these catalysts.

As already noted, irradiated zinc oxide is inactive with respect to the dehydrogenation of cyclohexane but effectively catalyses deuterium-exchange in molecular hydrogen (see above). In this case also the hydrogen-activation centres produced during irradiation are probably not capable of activating cyclohexane (the statement that here there is a rapid decrease in the intensity of the EPR signals of zinc oxide[45] is apparently without foundation, since the entire catalyst–hydrocarbon system is subjected to irradiation).

### 3. The Radical Polymerisation of Ethylene

The polymerisation of ethylene is catalysed by a number of catalysts containing transition metal ions[47]. Some of these catalysts have recently been studied by the EPR method. Chromium oxide catalysts have been studied in most detail in this connection. These catalysts are usually prepared by impregnating carriers (alumina or alumina–silica) with chromic acid solution with subsequent activation.

Sometimes the catalyst was activated by heating for 4 h at 350°C, followed by reduction with hydrogen at the same temperature[48,49]; sometimes the catalyst was activated by heating in air at 500°C for 4 h [50] or at 350°C [51], or in a vacuum at 350°C for 4 h [51], or at 400°C for 3 h [52]; sometimes the catalyst was treated with organic solvents[53,54]. O'Reilly and MacIver[55] prepared an alumina–chromium oxide catalyst by impregnating $\gamma$-$Al_2O_3$ with chromium nitrate, followed by roasting and reduction at 500°C. Some reduced specimens were activated by heating at 500°C. An analogous catalyst can also be obtained by coprecipitating chromium and aluminium nitrates, followed by roasting at 500–1400°C. In this work[56] some specimens were reduced by hydrogen at 500°C.

The concentration of chromium in the catalysts was varied from 0.5 wt.% to ~67 wt.%, calculated as $Cr_2O_3$. Usually, however, the total chromium concentration amounted to 2.5–3 wt.%, and then, after activation by heating in air or in a vacuum, the catalysts prepared by the impregnation method gave an EPR spectrum at room temperature containing signals of two types: a broad line ($\Delta H$ = 500–1300 G, $g$-factor 1.97–1.98) and a narrow line ($\Delta H$ = 16.7–50 G, $g$-factor 1.97–1.99)[2,48,49,51–53,55]. In a reduced alumina–chromium oxide catalyst prepared by the impregnation method (in this case the chromium concentration calculated as $Cr_2O_3$ was varied from 0.078 wt.% to 10.1 wt.%), O'Reilly and MacIver[55] detected an additional asymmetric signal, whose parameters were not given (it is merely stated that at a frequency of 9.5 Gc $s^{-1}$ this signal has a maximum close to 1500 G). The intensity of

this signal is a maximum at low chromium concentrations and changes little on oxidation. Moreover, the quantity of chromium responsible for this signal is independent of temperature in the range from -195° to +162°C.

The EPR spectrum of a coprecipitated alumina–chromium oxide catalyst[56] at $Cr_2O_3$ concentrations of 8.05–66.4 wt.%, in addition to a broad absorption line, shows another signal with parameters: $\Delta H$ = 200–750 G, $g$-factor 1.975 ± 0.01. After heating at 500–900°C, specimens with a low $Cr_2O_3$ concentration (8.05 wt.%) show only the broadest line, whereas specimens with a high $Cr_2O_3$ concentration (66.4 wt.%) show only the narrower absorption line ($\Delta H$ = 200–750 G). After roasting at 1400°C, however, at all $Cr_2O_3$ concentrations, only this last signal is observed.

Let us now consider how different authors explain the origin of the observed EPR signals. It is suggested[1,48,49,51,53] that the broad signal of the impregnated contacts is due to $Cr_2O_3$ microcrystallites. O'Reilly and MacIver[55] consider that the state of $\alpha$-$Cr_2O_3$ responsible for the broad signal corresponds more closely to $Cr_2O_3$ gel, which is paramagnetic at room temperature ($\alpha$-$Cr_2O_3$ is antiferromagnetic and has a Curie point of +30°C.[57]) In the coprecipitated catalyst, the broad signal is again, in the opinion of MacIver and coworkers[56], due to $Cr_2O_3$ microcrystallites, amorphous towards X-rays. The narrower signal ($\Delta H$ = = 200–750 G), observed only for the coprecipitated contact, is given by a solid solution of $Cr_2O_3$ in $Al_2O_3$.[56]

Finally, in the opinion of MacIver and coworkers[55,56], the asymmetric signal on both types of catalyst is due to $Cr^{3+}$ ions which are interacting weakly with one another and are situated in the lattice sites of the carrier, both on the $Al_2O_3$ surface and close to the surface.

As will be shown later, however, the narrow EPR signal is of the greatest interest from the viewpoint of the catalytic properties of deposited chromium oxide contacts, so that we shall examine its nature in more detail.

The narrow line is symmetrical on alumina gel and asymmetrical on $Al_2O_3$–$SiO_2$.[51] O'Reilly[2], and also Kossee and van Reijen[53], consider that the narrow line is due to $Cr^{5+}$ ions. O'Reilly considers that this line cannot be due to diluted $Cr^{3+}$ or $Cr^{4+}$ ions, since then the spectra should have shown a fine structure, but this was not observed. Kossee and van Reijen[53], who observed only a narrow signal with careful reduction (by boiling in organic solvents) of $CrO_3$ deposited on alumina, established that these specimens have a magnetic moment which is very close to the value corresponding to the spin of one unpaired electron. These authors therefore conclude that the narrow signal is due to quinquevalent chromium ions. Kazanskii and coworkers[51], in their latest work, also concluded that this signal is due to $Cr^{5+}$ ions. They consider, with some justification, that O'Reilly's proof is inadequate, and give additional data in support of this conclusion. A constant value for the $g$-factor at different frequencies (3.2 cm and 21.8 cm) can be observed only if the narrow signal is due to $Cr^{5+}$ ions. If the signal were due to $Cr^{4+}$ or $Cr^{3+}$ ions, the value of the $g$-factor should have increased on going from high to low magnetic fields. The detection of HFS [hyperfine structure (Ed. of Translation)] for the narrow signal on an alumina–silica catalyst[58] is also a weighty argument in support of the suggestion that the narrow line is due to $Cr^{5+}$ ions. In actual fact, the HFS indicates the absence of strong exchange interaction, so that the fine structure, if it had been observed (in this case, if the signal had been due to $Cr^{3+}$ or $Cr^{4+}$ ions), should have been clearly defined.

Further support for this conclusion regarding the origin of the narrow line in the EPR spectrum of the chromium oxide catalyst for the polymerisation of ethylene is provided by the fact, established by a number of authors, that the narrow signal is not shown by the catalysts after intensive reduction by hydrogen[50,51,55] and that this signal appears after contacts which have been previously completely reduced are oxidised[51,55]. Moreover, the narrow signal is never observed from activated $CrO_3$ in the absence of carrier, so that stabilisation of the $Cr^{5+}$ ions takes place on the surface of the carrier[51,52].

Evidence that the $Cr^{5+}$ ions are situated on the surface of the carrier is provided by the oxygen effect (for the narrow EPR signal) detected by Kazanskii and coworkers[51]. Moreover, Nicolau and Thom[59] established that at constant surface area of the carrier ($\gamma$-$Al_2O_3$) the intensity of the narrow signal remains constant with change in the chromium concentration from 1 wt.% to 20 wt.%. In their opinion, this indicates that the paramagnetic centres responsible for the signal are situated chiefly on the surface of the catalyst. There is no agreement regarding the state in which the $Cr^{5+}$ ions are present on the surface of the chromium oxide catalyst. O'Reilly[60], on the basis of the fact that the width of the narrow line remains constant with change in the concentration of chromium in the alumina–chromium oxide catalyst, suggests that the $Cr^{5+}$ ions form a phase. Kazanskii and coworkers[51] agree with this conclusion and support it with the fact that the value of the Weiss constant which they calculated for the alumina–chromium oxide catalyst is +25, that is, it is greater than zero. This means that exchange interaction takes place between the $Cr^{5+}$ ions, which therefore form a phase[51].

MacIver[55] states that $Cr^{5+}$ ions are $Cr^{6+}$ ions on which an electron is "trapped". For coprecipitated alumina–chromium oxide catalysts[56] he gives some evidence that the $Cr^{6+}$ ions are present in small $Cr_2O_3$ crystals on the surface of the carrier. The maximum intensity of the narrow signal is observed at a chromium concentration of 4.55 wt.%, which corresponds to the maximal $Cr_2O_3$ surface area. The intensity of the signal decreases at a chromium concentration greater than 7.6 wt.% $Cr_2O_3$, that is, in the range where an appreciable increase in the dimensions of the $Cr_2O_3$ granules takes place. MacIver and coworkers also established that the asymmetric signal attributed to isolated $Cr^{3+}$ ions remains unchanged under conditions in which reduction of $Cr^{5+}$ ions takes place. In their opinion, both facts indicate that the $Cr^{5+}$ ions are situated on the catalyst surface not in isolation but in small $Cr_2O_3$ crystallites. We have already noted, however, that the narrow signal has never been observed from activated $CrO_3$ in the absence of a carrier. In our opinion, this fact can be reconciled with MacIver's suggestion that the $Cr^{5+}$ ions are situated on the $Cr_2O_3$ surface only if it is assumed that the $Cr^{5+}$ ions are distributed on the interface between the $Cr_2O_3$ microcrystallites and the carrier.

Comparison of the results of statistical calculations with experimental data, in particular with data on the EPR of alumina–chromium oxide catalysts, established[56] good agreement between experiment and calculation for a model with random distribution of isolated $Cr^{5+}$ ions on the surface.

Thus MacIver's results, contrary to O'Reilly and Kazanskii's suggestion, indicate that $Cr^{5+}$ ions do not form a phase on the surface of the alumina.

As already noted[58], $Cr^{5+}$ ions on the surface of an alumina–silica carrier do not give an HFS and thus do not form a phase; the signal is anisotropic. To explain these facts it was postulated[58] that $Cr^{5+}$ ions are introduced into the alumina–silica support, in other words, that replacement of some of the $Si^{4+}$ ions by $Cr^{5+}$ ions takes place in the tetrahedra of the surface layer of the alumina–silica. The quinquevalent chromium ions form a surface compound with the alumina–silica support[54]. The quantity of $Cr^{5+}$ ions formed in an alumina–silica catalyst after its activation is small[52] and amounts to 3–4%; 85–88% of the chromium remains in the form of $Cr^{6+}$ ions.

It can thus be seen that on an alumina–silica carrier the quinquevalent chromium ions are present in the form of a dilute solid solution on the surface, whereas on alumina, in the opinion of some authors, they form a phase, while in the opinion of others a phase is not formed. The evidence in support of the suggestion that a $Cr^{5+}$ phase is not formed on the surface of an alumina–chromium oxide catalyst is more convincing.

The $Cr^{5+}$ ions may, in fact, be distributed on the surface sufficiently closely for the observed exchange interaction to take place between them[51] but at the same time at such a distance from one another that no formation of a phase takes place at this stage. The $Cr^{5+}$ ions may, for example, form a sufficiently "concentrated" two-dimensional surface solution. It is evident, moreover, that even if the appearance of HFS indicates unambigously that the $Cr^{5+}$ ions are present in the form of a dilute solid solution, the absence of HFS cannot be taken as proof that these ions form a phase.

Let us examine the relationship between the EPR signals of deposited chromium oxide catalysts and their catalytic activity with respect to the polymerisation of ethylene[53].

Kossee and van Reijen[53] were the first to suggest that the $Cr^{4+}$ or $Cr^{5+}$ ions, which give a narrow EPR signal, are the active centres of the catalyst. Recent experimental results indicate a correlation between the intensity of the narrow EPR signal of original chromium oxide–alumina–silica catalysts and their catalytic activity with respect to the polymerisation of ethylene. Kazanskii and coworkers[52] showed that the maximal catalytic activity is given by catalysts containing 2.5–4 wt.% of chromium. These are the catalysts which give the most intense narrow EPR signal (we are speaking of the original catalysts). Antuf'ev and coworkers[61] also established that the catalytic activity and intensity of the narrow EPR signal change in the same sense. In the opinion of these authors, $Cr^{5+}$ ions are the active component of chromium catalysts for the polymerisation of ethylene. This conclusion is confirmed by data on the chemisorption of the reaction components on the catalyst. Recent work by Kazanskii and coworkers[58] has shown that the $Cr^{5+}$ ions are the centres for the chemisorption of ethylene on the one hand and of water vapour — a poison which inhibits polymerisation — on the other.

It is significant that in the works cited the catalytic activity was compared with the intensity of the narrow signal of the original activated catalysts. At the same time, it can be seen from published data[52] that the intensity of the narrow signal has decreased by approximately one-half 3 h after the start of the reaction, reaching a steady value for the given experimental conditions.

It has been established that sexivalent chromium ions do not take part in the catalysis of the polymerisation of ethylene: disappearance of $Cr^{6+}$ ions from the catalyst produces almost no change in its activity[52,61]. Similarly, intermediate oxides are not the active component: their presence in the catalyst has no influence on the catalytic activity of the catalyst[52]. A catalyst without carrier, containing after activation only $Cr_2O_3$, is inactive with respect to the polymerisation of ethylene[52,61], so that chromium sesquioxide is also inert with respect to this reaction. In accordance with this, catalysts in which the narrow EPR signal disappears after reduction by hydrogen are catalytically inert[50].

The EPR method has recently been used to study deposited molybdenum catalysts for the polymerisation of ethylene[62]. It was suggested that in this case the catalytically active component consists of quinquivalent molybdenum ions formed during the reduction of the catalysts. It should be noted that here also, as in the study of the chromium catalysts, the EPR measurements were made before catalysis. During catalysis, further reduction of the catalysts takes place, but according to the published data this additional reduction is not extensive.

The formation of $Mo^{5+}$ ions is related to the reaction of the molybdenum oxides with the carrier, in the course of which these ions are stabilised. It is pointed out that the nature of the carrier has a significant influence on the shape of the absorption line: thus on alumina gel the signal (molybdenum concentration 8 wt.%) is symmetrical ($g$-factor = 1.933, $\Delta H$ = 80 G) but on an alumina–silica carrier the signal is asymmetric ($\Delta H$ = 60 G, $g_{\parallel}$ = 1.879, $g_{\perp}$ = 1.933). Asymmetric signals are also formed in catalysts based on $ZrO_2$ and $ZrO_2.SiO_2$.

In the case of alumina–molybdenum oxide and molybdenum oxide–alumina–silica catalysts, the catalytic activity of the catalysts and the intensity of the original EPR signal change in the same sense. Both quantities reach a maximum at a concentration of 20% $MoO_3$ in the catalysts.

The correlation between the intensity of the narrow EPR signal and catalytic activity was observed not only in the case of chromium and molybdenum catalysts but also in the polymerisation of ethylene on a Ziegler catalyst [$TiCl_4$ + $Al(C_2H_5)_2Cl$].[63]

The course of the reaction between $TiCl_4$ and $Al(C_2H_5)_2Cl$ was followed continuously: the reaction mixture — $TiCl_4$ + + $Al(C_2H_5)_2Cl$ in heptane at room temperature — was circulated through the resonator. After some time, a narrow EPR signal (singlet) was detected. It was established that in this system, reduction of $TiCl_4$ to $TiCl_3$ takes place and part of the $TiCl_3$ is precipitated. This precipitate does not give an EPR signal at room temperature. The authors tried to attribute this to the possible dimerisation of $TiCl_3$ in the solid phase but it is not excluded that the absence of resonance absorption by the precipitate at room temperature may also be due to the too-rapid spin–lattice relaxation of the $Ti^{3+}$ ions. In this connection a recent paper devoted to the study of an analogous system is of interest[64]; it was established that the precipitate formed 0.5 h after the components $TiCl_4$ and $Al(C_2H_5)_2Cl$ were mixed contains no aluminium, has the composition $Ti(C_2H_5)Cl_3$, and gives no EPR signal at room temperature. At the same time, the precipitate removed 4 h after the components were mixed has the overall formula $Ti_3Cl_6Al(C_2H_5)$, contains $Ti^{3+}$, and gives an EPR signal at room temperature.

It is pointed out that "the curves giving the time dependence of the rate of polymerisation of ethylene and the time dependence of the concentration of unpaired electrons have identical shapes". The addition of 10% of water or oxygen (relative to the aluminium) increases the intensity of the signal by a factor of approximately 2. According to the data given in a patent[65], to which the authors refer, the same quantities of water and oxygen bring about maximal increase in the yield of polymer.

The nature of the signal was examined in subsequent work. A study of the $TiCl_4 + Al(C_2H_5)Cl_2$ system in heptane[66] ($[TiCl_4] = 0.108$ M, $[Al(C_2H_5)Cl_2] = 0.055$ M) established that here also an EPR signal (singlet) appears some time after the components are mixed (at room temperature). The intensity of this signal corresponds to approximately 2% of the concentration of alkylaluminium chloride. This signal consists of two superimposed singlets: a symmetrical singlet with $\Delta H = 22$ G and $g$-factor 1.925, and a weaker asymmetric signal with $\Delta H$ approximately 10 G and $g$-factor 1.933. After the components are mixed, the intensity of the signal increases, at first very rapidly, and then, after the precipitation of $TiCl_3$, which in this case gives an EPR signal, very slightly. After examining possible mechanisms, the authors concluded that the observed EPR signals are due to $Ti^{3+}$ ions which are formed as a result of complex formation by $TiCl_4$ with the alkylaluminium halides and reduction of the $TiCl_4$ in this complex to $Ti^{3+}$. The greater the strength of the alkylaluminium halide as a Lewis acid — the acid strength increases in the order $Al(C_2H_5)_2Cl$, $Al(C_2H_5)Cl_2$, $AlCl_3$ — the greater the concentration of this soluble complex and the greater the intensity of the EPR signal.

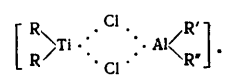
The symmetrical signal is assigned to the complex $(TiCl_3)_2.[Al(C_2H_5)Cl_2]$ and the asymmetric signal to the complex $TiCl_3.[Al(C_2H_5)Cl_2]$, obtained by the decomposition of the first complex, particularly when the ratio Al/Ti is less than unity. In a study of the closely related systems[67]

$(C_5H_5)_2TiCl_2 + Al(CH_3)_3$ [I]; $(C_5H_5)_2TiCl_2 + Al(CH_3)_2Cl$ [II];
$(C_5H_5)_2Ti(CH_3)Cl + Al(CH_3)Cl_2$ [III];
$(C_5H_5)_2TiCl_2 + Al(CH_3)Cl_2$ [IV];
$(C_5H_5)_2Ti(CH_3)Cl + AlCl_3$ [V],

however, it was shown that the analytically determined $Ti^{3+}$ ion concentration is equal to the concentration of unpaired electrons given by measurement of the signal intensity; experimental proof is thus obtained that in these systems the EPR signal is due to $Ti^{3+}$ ions. At a high concentration of the complex (not less than $1 \times 10^{-1}$ M) the spectrum shows a singlet, but at a low concentration (less than $1 \times 10^{-2}$ M) an HFS is observed (HFS in analogous systems at low concentrations of the complex was previously observed by Shilov and coworkers[68] and Maki and Rendall[69]). The conversion of the HFS into a singlet at increased concentration of the complex is accompanied by an opposite decrease in the width of the line.

An interesting phenomenon is observed in work with dilute solutions of the complex ($\leq 1 \times 10^{-2}$ M). As the Cl atoms on the aluminium are gradually replaced by $CH_3$ groups, the shape of the spectrum changes from one with a distinct HFS through a shape with an indistinct HFS to a broad singlet (the observed HFS, consisting of six components, indicates a high electron density at the aluminium nucleus, for which the spin is equal to 5/2). It may therefore be assumed that the localisation of the unpaired electrons on the aluminium decreases with decrease in the acidity of the complex, that is, the alkyl groups increase the delocalisation of the unpaired electrons in the complex.

From the fact that the $g$-factor is almost constant in the different complexes studied, it is concluded that the electron in the complex is localised to only a slight extent on R, R′, and R″, and that its density is a maximum on Ti, Al, and Cl in



A detailed investigation of the nature of the active component of the Ziegler catalyst is described by Varodi and coworkers[64], who established that the solubility in hydrocarbons shown by the above precipitates separating in the $TiCl_4 + Al(C_2H_5)_2Cl$ system is low but increases by a factor of about 1000 in the presence of $TiCl_4$. Dissolution leads to the formation of a complex of the type $(C_2H_5)TiCl_3 - Al(C_2H_5)Cl$. This complex is found in the filtrate after separation of the precipitate.

A suspension of the precipitate in heptane is catalytically inactive. The system also remains catalytically inert after the addition of $TiCl_4$. The system formed by the precipitate + $Al(C_2H_5)_2Cl$ also has a low activity. The catalytic activity increases sharply by a factor of about 3 only after the precipitate is mixed with a filtrate containing the soluble complex compound. At the same time, the catalytic activity of the filtrate itself is also low.

The catalytic activity is thus shown by the entire precipitate–soluble complex system, the presence of $TiCl_4$ in the system playing a particularly important part and leading to the maximal formation of the soluble complex compound which is the active cocatalyst.

It can be seen that on all three types of ethylene-polymerisation catalyst studied by the EPR method, it has been possible to establish that the catalytically active component of the catalysts contains $M^{n-1}$ ions, where $n$ is the highest valency of the transition metal. This is probably a general feature, although it cannot be explained at present.

## III. REACTIONS INVOLVING ELECTRON TRANSFER

Typical reactions of this group include the decomposition of hydrogen peroxide and dinitrogen oxide, and also oxidation by molecular oxygen. Catalysts for reactions of this type[70] exhibit a high electrical conductivity, which is necessary in order to ensure the possibility of electron transfer, through the catalyst, between the molecules reacting on the catalyst surface (from the molecule being oxidised to oxygen, or from one $H_2O_2$ (or $N_2O$) molecule to another). Paramagnetism (or ferromagnetism) is not, however, a necessary property of catalysts for this group of reactions. In recent years it has indeed been shown that there exists a whole class of catalysts for reactions involving oxidation — semiconductors containing no transition elements — which do not exhibit paramagnetism[71]. There are, moreover, a number of oxidation processes on transition metal oxides (in particular, on vanadium pentoxide), which take place without the reduction of $V_2O_5$, and in which paramagnetic ions (for example, $V^{4+}$ ions) play no significant part[72]. Most oxidations, however, at any rate those involving aromatic substances and alkenes, take place in the steady state on partly reduced oxides, which contain unpaired electrons and are therefore revealed in the EPR spectrum. The study of these spectra may give

some information on the structure and properties of these catalysts. For example, Nicolau and Thom[40] made a comparative study of the EPR spectra of powdered manganese oxides ($MnO_2$ and $Mn_2O_3$) and of the same oxides deposited on $\gamma$-alumina. The conductivity electrons may lead to broadening of the paramagnetic resonance absorption lines for oxide powders which are not in the highest valency state. In actual fact, the width of the absorption spectrum of $MnO_2$ powder amounts to 1600 G (the signal shows HFS containing four components); with $Mn_2O_3$ powder, $\Delta H$ is also equal to 1600 G. Deposition of these oxides on $\gamma$-$Al_2O_3$ leads to a sharp decrease in the width of the EPR signals (for $MnO_2/\gamma$-$Al_2O_3$, $\Delta H$ = 8 G and for $Mn_2O_3/\gamma$-$Al_2O_3$, $\Delta H$ = 5 G), disappearance of the HFS (for $MnO_2$), and a decrease in the intensity of the signals (from $10^{17}$ to $10^{16}$ unpaired electrons per gramme with $MnO_2$, and from $10^{17}$ to $10^{13}$ unpaired electrons per gramme with $Mn_2O_3$). This sharp change in the signal parameters was attributed to the dispersal of the paramagnetic oxides in the form of aggregates (agglomerates) over the $\gamma$-$Al_2O_3$ surface. The decrease in the width of the lines is attributed to the magnetic dilution of $MnO_2$ by the diamagnetic $\gamma$-$Al_2O_3$, and the particularly sharp decrease in the intensity of the signal with $Mn_2O_3$ is attributed primarily to the formation of a covalent bond between the $Al^{3+}$ and $Mn^{3+}$ ions.

A common feature of the signals observed by Nicolau and Thom is their asymmetry. This asymmetry was attributed to the anisotropy of the crystal and also to the influence of active oxygen. Unfortunately, a comparative study of the catalytic properties of different manganese catalysts was not carried out.

### 1. The Decomposition of Hydrogen Peroxide and Dinitrogen Oxide

Many organic polymeric materials have a low electrical conductivity activation energy, that is, they are semiconductors with a narrow forbidden zone. They thus serve as models of a semiconducting oxide. Semiconductors, however, are effective catalysts for the decomposition of hydrogen peroxide. It is thus not surprising that organic semiconductors such as polyacenequinone (PAQ), poly(acrylonitrile) (PAN), copper polyphthalocyanine (CPP), and poly(aminoquinone)s are active catalysts for the decomposition of hydrogen peroxide[73,74]. The decomposition of dinitrogen oxide also takes place on organic semiconductors[74], the maximal activity being shown by PAN, pyrolysed at 350°C in an atmosphere of argon. PAN pyrolysed in air has an extremely low activity with respect to this process. Here, therefore, oxygen has a significant influence on the catalytic properties of this semiconductor. It is probable that as this reaction proceeds, the activity should decrease as a result of the chemisorption of oxygen, which is one of the products of the decomposition of $N_2O$. An interesting feature is that in the decomposition of $H_2O_2$ there is no indication of a difference in the activities of PAN pyrolysed in air or in an atmosphere of argon. $H_2O_2$ is probably sorbed on the surface no less strongly than oxygen, so that the latter cannot displace $H_2O_2$ from the catalyst surface.

The decomposition of $N_2O$ also takes place intensively on poly(isoprenechloranil) (PICA) and poly(benzimidazole) (PBIA). All three polymers PAN, PICA, and PBIA, are semiconductors with a long system of conjugated double bonds and nitrogen atoms with a lone pair of electrons. Phthalocyanines (free phthalocyanine and CPP) and also polyacenequinone have almost no catalytic influence on the decomposition of $N_2O$. This is apparently due to the absence of a long system of conjugated double bonds in the case of phthalocyanines, and in the case of polyacenequinone to the absence of $\dot{N}$ atoms which apparently act as centres for the chemisorption of dinitrogen oxide molecules.

### 2. The Oxidation of Organic Substances

As already noted, the oxidation of hydrocarbons on the oxides of transition metals in their highest valency states is accompanied by partial reduction of the latter. The activity of the catalyst increases in the process and the concentration of paramagnetic centres also increases. Examples of this parallelism are familiar: for example, the maximal catalytic activity with respect to the oxidation of benzene (flow-circulation method) is shown by a vanadium–molybdenum catalyst containing 30% molybdenum, and the same catalyst also shows the maximal intensity and width for the EPR signal (singlet) observed at room temperature ($\Delta H$ = 190 G).[75] At a molybdenum concentration less than 30%, $MoO_3$ forms a solid solution with $V_2O_5$. To preserve electrical neutrality in the system, the $Mo^{6+}$ ions must be converted into $Mo^{5+}$ ions, or some $V^{5+}$ ions must be converted into $V^{4+}$ ions. At an Mo concentration less than 5%, the EPR spectrum of the catalyst shows an anisotropic HFS (two groups of lines with eight components in each, $g_\perp$ = 1.99, $g_\parallel$ = 1.90, $\Delta H_\perp$ = 50 G, $\Delta H_\parallel$ = 145 G), characteristic of the $V^{4+}$ ion.[76] From this it was concluded that the second mechanism is involved, that is, the addition of $Mo^{6+}$ ions to the catalyst leads to the production of $V^{4+}$ ions in an amount which, at an $MoO_3$ concentration $\leq$ 30%, is approximately equal to the quantity of added $Mo^{6+}$ ions. At a higher $MoO_3$ concentration, however, the latter react with $V_2O_5$ to form a chemical compound in which only every fifth vanadium ion is converted into $V^{4+}$. It is considered that the $V^{4+}$ ions act as impurity levels which influence the electronic properties of the semiconductor ($V_2O_5$) and hence its catalytic activity. Ioffe and coworkers[75] consider that the results provide experimental proof of "the general influence of lattice defects on the catalytic properties of semiconducting catalysts".

Ioffe considers that the addition of ions of higher valency, for example, $Mo^{6+}$ ions, to $V_2O_5$ is not necessary for the oxidation of naphthalene or *o*-xylene on $V_2O_5$, because here, as a result of the intensive reduction of the catalyst, there is spontaneous generation of defects (in the form of $V^{4+}$ ions) responsible for the increase in the catalytic activity of the vanadium oxide catalyst[77].

The $V^{4+}$ ions apparently act as centres for the activation of the molecules of the hydrocarbon being oxidised (in particular, benzene[78]). In order to bring about this activation, that is, to displace the electron density from the hydrocarbon to the catalyst, it is necessary to ensure that the Fermi level of the catalyst is sufficiently low-lying[78]. These conditions are satisfied[78] in the oxidation of benzene on a vanadium–molybdenum catalyst, which is a solid solution of $MoO_3$ in $V_2O_5$.

It is probably possible in principle, by introducing sexivalent impurity ions (for example, $Mo^{6+}$), to create such a high concentration of $V^{4+}$ ions in the $V_2O_5$ lattice that the rate of transfer of electrons from the hydrocarbon (benzene or naphthalene) to the catalyst becomes equal to the rate of transfer of electrons from the catalyst to oxygen.

The operation of the catalyst (in the oxidation of the given hydrocarbon) will thus reach a steady state and no change will take place in its chemical and phase composition. The quantity (~30 mole %) of $Mo^{6+}$ ions (and hence the equivalent quantity of $V^{4+}$ ions) which can be introduced into $V_2O_5$ without breaking down its crystal structure is insufficient to bring about this equalisation of the rates of the donor and acceptor stages in the oxidation of aromatic hydrocarbons: this is indicated by the partial reduction of the vanadium–molybdenum catalyst in the oxidation of benzene[79], naphthalene, and xylene[77]. It is for this reason that the catalytic oxidation of benzene, xylene, naphthalene, and, apparently, other aromatic hydrocarbons, takes place in the steady state on lower oxides. The latter are thus the active components of vanadium oxide catalysts for the oxidation of aromatic compounds. This is also indicated by results obtained in a study of the oxidation of naphthalene on "sodium vanadium bronze". This "bronze" has a crystal structure close to that of vanadium pentoxide, exhibits a high electrical conductivity, contains $V^{4+}$ ions[80], and gives an EPR spectrum with a signal analogous to the signal of a partly reduced vanadium oxide catalyst[81] and the optimal vanadium–molybdenum catalyst[75]. Nevertheless, the "sodium vanadium bronze" is quite inactive with respect to the oxidation of naphthalene (under the ordinary conditions of catalysis for this process) until partial reduction takes place with the formation of lower oxide phases on its surface[80]. It was also shown that the active component of the vanadium oxide catalyst is a mixture of the oxides $V_2O_4$ and $V_6O_{13}$, the $V_2O_4$ playing the leading part[82]. Of the two modifications of vanadium(IV) oxide studied — the grey crystalline form and the black form amorphous towards X-rays — the grey has the higher catalytic activity. It is the black modification, however, which exhibits intensive resonance absorption at room temperature (singlet with $\Delta H$ = = 166 G), whereas the grey modification gives no signal under analogous conditions[83]. Finally, Ioffe and coworkers[75] themselves emphasise that the line width of the EPR signal of used vanadium oxide catalysts is almost independent of the chemical composition of the catalyst. This is attributed to the fact that during catalysis, diffusion of $V^{4+}$ ions to the surface of the catalyst takes place, with the formation of lower oxide phases on the surface.

All these facts indicate that the activity of the vanadium oxide catalyst with respect to the oxidation of naphthalene is due not simply to the presence of defects in its structure, even if these defects are $V^{4+}$ ions, but to the formation, on the catalyst surface, of definite chemical compounds $V_2O_4$ and $V_6O_{13}$ for which the "defect character" of the crystal lattice is not significant for catalysis.

It appears from published data that the nature of the EPR signals (singlets) observed at room temperature for vanadium pentoxide, partially reduced vanadium oxide catalyst, vanadium(IV) oxide amorphous towards X-rays, and "vanadium bronze", has not been finally established. Ioffe and coworkers[75] attributed the EPR signal which they observed at room temperature for vanadium–molybdenum catalysts to the presence of $V^{4+}$ ions.

Ragle[84] considers that the EPR signals (singlets) observed at room temperature for commercial vanadium pentoxide, vanadium bronzes, and partly reduced vanadium catalysts, are due to an electron localised close to the vanadium. The absence of HFS is attributed to the mobility of these electrons. An analogous conclusion regarding the nature of the paramagnetic centres in $V_2O_5$ was reached by Ioffe and Patrina[85].

However, this cannot explain the difference in the behaviour of crystalline $V_2O_4$ and the form amorphous towards X-rays. This may be due to differences in the degree of dispersion of these modifications of $V_2O_4$.

Crystalline $V_2O_4$ is antiferromagnetic at room temperature[86]. In amorphous $V_2O_4$, however, because of its high degree of dispersion and the marked departure from ordering in the structure, the antiferromagnetism is probably removed to some extent and this makes it possible to observe EPR signals from $V^{4+}$ ions at room temperature.

This interpretation explains a number of other facts. During catalysis, the surface of the vanadium oxide catalyst disintegrates, becomes amorphous, and almost doubles in area[87]. The disintegration of the catalyst surface is accompanied by an increase in the intensity of the EPR signal; at the same time, the catalyst may not be chemically reduced. For example, the intensity of the signal from $V_2O_5$ after catalysis of the oxidation of phthalic anhydride increases[83] by a factor of approximately 30, but no reduction of the catalyst is observed[88]. Moreover, it was established that the intensity of the EPR signal from amorphous $V_2O_4$ increases after catalysis by a factor of approximately 2, with the simultaneous partial oxidation of the catalyst (the experiments were carried out in gradient-free conditions and measures were taken to eliminate the possible influence of inner-diffusion retardation, which might have led to oxidation of $V_2O_4$ inside the granule[89]). Special experiments showed that the intensity of the $V_2O_5$ signal decreases after remelting: by a factor of 2 for "analytical reagent" grade $V_2O_5$ and by a factor of 5 for "pure" grade $V_2O_5$. At the same time, the concentration of $V^{4+}$ ions in the oxides decreases by factors of only 1.5 and 2 respectively. Thus "annealing" of the defects takes place much more readily than the decrease in the concentration of $V^{4+}$ ions. All these facts can be explained only by relating the EPR signals observed at room temperature to the presence, in the catalyst, of defects (dislocations) which are centres for the localisation of electrons.

The fact that the signal with maximal intensity is observed from amorphous $V_2O_4$ and not from the other oxides studied can be attributed firstly to the fact that only $V_2O_4$ could be obtained in the most highly dispersed state, and secondly to the fact that this oxide contains the maximal number of mobile electrons, of which a definite proportion may be localised on the dislocations in the solid.

It should be emphasised again that the nature of the signals observed at room temperature is the subject of discussion. For us, however, it is significant that the intensity of these signals is not correlated with the activity of the vanadium oxide catalysts with respect to the oxidation of aromatic hydrocarbons.

The EPR method has also been used to study the vanadium–potassium–sulphate–silica gel (VKSS) so-called "complex" catalyst for the oxidation of naphthalene to phthalic anhydride[90]. This catalyst is prepared by impregnating coarsely-porous silica gel with an aqueous solution of vanadyl sulphate and potassium sulphate with subsequent roasting at about 400°C. It was previously considered that this treatment converted the vanadyl sulphate completely into $V_2O_5$ [91,92] and hence that in principle any soluble vanadium salt, for example, ammonium metavanadate, could be used for the preparation of the catalyst. Vanadyl sulphate was convenient simply because it penetrates more evenly into the silica gel and ensures regular formation of $V_2O_5$ throughout the whole volume of the

carrier. According to these ideas, the high selectivity of the oxidation of naphthalene to phthalic anhydride on the VKSS catalyst was due to the particularly favourable distribution of the vanadium oxides in the bulk of the carrier. The vanadyl sulphate was merely the starting material for their formation.

In the study of this type of vanadium catalyst, use was made of the fact that of all the vanadium compounds whose presence might have been expected in the VKSS catalyst — vanadyl sulphate, $V_2O_5$, $V_6O_{13}$, and $V_2O_4$ — only vanadyl sulphate gives an intense EPR signal at room temperature[76,77,83], whereas special experiments established that the vanadium oxides deposited on silica gel are not revealed in the EPR spectrum at room temperature. It was found that the catalyst prepared by impregnating silica gel with an aqueous solution of vanadyl sulphate and potassium sulphate, with composition corresponding to that used in industry, after heating at 400°C exhibits maximal selectivity with respect to phthalic anhydride and gives an EPR spectrum with HFS. The EPR signal is also preserved after the catalysis has been carried out for a prolonged period. Moreover, contacts prepared by impregnating silica gel with vanadyl sulphate solution without potassium sulphate, which after roasting do not give a signal and hence do not contain $VOSO_4$, give an intense broad EPR signal after catalysis of the oxidation of naphthalene for several minutes. The appearance of this signal can be attributed to the regeneration of vanadyl sulphate in the catalyst during catalysis. In fact, during the oxidation of the original vanadyl sulphate to $V_2O_5$ on the catalyst, $SO_3$ is liberated and may be retained by the carrier. In the reduction of $V_2O_5$ during catalysis, the $V_2O_4$ formed reacts with the sorbed $SO_3$ to form vanadyl sulphate.

It was found that a catalyst prepared by impregnating silica gel with a solution of ammonium metavanadate and potassium sulphate, that is, a catalyst not containing vanadyl sulphate and hence not giving an EPR signal at room temperature either before or after catalysis, shows extremely low selectivity. After this catalyst has been treated in $SO_3$ vapour at room temperature, however, it begins to oxidise naphthalene much more selectively, and the concentration of the products of extensive oxidation decreases sharply. This catalyst, like that with composition corresponding to that used in industry, also gives a signal with HFS‡.

The observed facts indicate that the outstanding properties of the VKSS catalyst are due chiefly to the characteristic features of its chemical composition, namely the presence of vanadyl sulphate (which gives an EPR signal detectable at room temperature).

Since in the catalysts examined the vanadyl sulphate gives a signal with HFS, it is present in the catalyst and on its surface in the form of a dilute solid solution. The operation of a VKSS catalyst which has not been heated and which, before and after catalysis, contains an appreciable quantity of the original vanadyl sulphate, revealed in the EPR spectrum by the intense singlet characteristic of the $VOSO_4$ phase, is completely analogous to that of a previously heated catalyst in the catalysis of the oxidation of naphthalene. This can be interpreted in different ways[90]. It is possible that in order to obtain the "optimum" VKSS catalyst, the form in which the $VOSO_4$ is present — as a separate phase or in the form of a dilute solid solution — is not important and that only its presence in the system is important.

It has recently been reported that the oxidation of organic substances can also be catalysed by organic semiconductors. Thus it is stated that tetralin is oxidised by a stream of oxygen bubbles in the presence of poly(acrylonitrile)[74]. It is suggested that the action of the poly(acrylonitrile) involves the catalysis of the decomposition of hydroperoxides formed during the autoxidation of the hydrocarbon.

## IV. REACTIONS INVOLVING THE DONATION AND WITHDRAWAL OF AN ELECTRON PAIR

Catalysts for this type of reaction are protonic or aprotonic acids or bases. Solid aprotonic catalysts generally show neither electrical conductivity nor paramagnetism, so that the possible applications of the EPR method in the study of catalysts of this type are extremely limited. Here also, however, its application may be useful sometimes, for example, in the examination of the influence of irradiation on the catalytic activity of silica gel and alumina–silica catalysts with respect to the reactions of cracking and isomerisation. In particular, Weisz and Swegler[93] established that pure silica gel heated for 16 h at 550°C and then irradiated with fast and slow neutrons (20 h, dose $7.5 \times 10^{18}$ cm$^{-2}$ for each type of neutron) shows no catalytic activity with respect to the cracking of isopropylbenzene (the catalytic activity was measured in a Schwab reactor at 420°C and a pressure of 1 atm). At the same time, the activity with respect to the isomerisation of hex-1-ene to hex-2-ene and hex-3-ene (measured in a flow assembly at 350°C) increases appreciably. Mikovsky and Weisz[94] also showed that irradiation with a large neutron dose ($10^{20}$ cm$^{-2}$) increases the activity of silica gel in the isomerisation of but-1-ene by a factor of approximately 50, but increases the activity of an alumina–silica catalyst by a factor of 1.5–3 (the catalytic activity was measured in a flow microreactor after storage for 6 months to ensure removal of the induced radioactivity). The heat of activation on irradiated alumina–silica is 9.7 kcal mole$^{-1}$, whereas the value for the original catalyst is 11.4 kcal × × mole$^{-1}$. The selectivity of the process remains unchanged after irradiation. It is also noted that the specific surface of the irradiated catalysts is smaller by 10–20% than that of the original catalysts.

Contrary to the results of Weisz, earlier work by Lucchesi and coworkers[95,96] established a decrease in the catalytic activity of an alumina–silica catalyst (87% $SiO_2$), previously heated at 540°C (16 h) and 675°C (3 h), in the isomerisation of the double bond in but-1-ene after electronic irradiation (fast neutron beam $8.9 \times 10^{18}$ cm$^{-2}$, slow neutron beam $6.1 \times 10^{18}$ cm$^{-2}$, $\gamma$-radiation dose $1.2 \times 10^{10}$ r). The catalytic activity measured 30 d after irradiation at 65°C.

We have already pointed out that the irradiation of anhydrous silica gel leads to the generation of an EPR signal which can be related to the appearance of defects in the structure of the catalyst. Panchenkov and coworkers[97] studied the cracking of isopropylbenzene in a flow assembly at 400°C on an irradiated alumina–silica catalyst with

‡ Treatment with $SO_3$ vapour naturally cannot alter the distribution of $V_2O_5$ in the bulk of the carrier, so that the high selectivity with respect to phthalic anhydride shown by the VKSS catalyst cannot be attributed entirely to the difference in the regularity of the distribution of $V_2O_5$ in the bulk of the carrier during its impregnation with vanadyl sulphate and metavanadate.

composition: $Al_2O_3$ 12.8, $SiO_2$ 87.1, $Fe_2O_3$ 0.07%. The catalyst was irradiated with protons (energy 1.5 MeV, intensity of beam 20 μA at the temperature of liquid nitrogen) and γ-rays (dose 48 million r) at room temperature, and it was established that an EPR signal (singlet) appears after irradiation. At the same time, judging from the degree of conversion, the catalytic activity increases by 25–40% after irradiation with protons and by 77–93% after γ-irradiation.

Comparison of the results obtained by Weisz and Panchenkov shows that irradiation generates EPR signals in these catalysts and influences their activity with respect to the reactions of cracking and isomerisation. It is known that γ-$Al_2O_3$, which is a strong aprotonic and weak protonic acid, is a comparatively poor catalyst for the cracking reaction and that alumina–silica and silicon–zirconium catalysts, which are strong protonic and aprotonic acids, are effective catalysts for this reaction[98]. It may thus be concluded that cracking takes place actively on protonated surfaces and much less readily on aprotonic catalysts. This explains the inertness of roasted irradiated silica gel (a weak protonic acid) in the cracking of isopropylbenzene. In actual fact, irradiation creates defects in the lattice (EPR signals) but it cannot create the protonated surface necessary for cracking. The increase in the activity of roasted irradiated $SiO_2$ with respect to the isomerisation of hex-1-ene and but-1-ene can probably be attributed to the fact that this reaction, unlike cracking, also takes place on an aprotonic catalyst such as $SiO_2$. Irradiation, by producing defects in the surface, naturally leads to an increase in the number of aprotonic active centres on unit surface area of the catalyst. Similarly, as we have already seen, irradiation increases the activity of a catalyst with protonic acidity — the alumina–silica catalyst — with respect to the process catalysed by protonic surfaces, that is, the cracking process.

The decomposition of the oxygen-containing compounds formic acid and propan-2-ol involves simultaneous dehydrogenation and dehydration of the starting material. Dehydrogenation is a reaction taking place by a radical mechanism, whereas dehydration involves an acid–base reaction. It is thus natural to expect that the decomposition of the above substances should take place on catalysts of the radical type[99] which exhibit acidic properties simultaneously. For example, dehydration takes place readily on silica gel, which is a relatively strong aprotonic acid. It was shown above that irradiated silica gel gives a strong EPR signal and catalyses the dehydrogenation of cyclohexane. It was thus expected that irradiated silica gel would catalyse the decomposition of the oxygen-containing compounds in two directions — with dehydrogenation and with dehydration. It was in fact shown[100] that irradiated silica gel (Xerogel R) begins to catalyse not only the dehydration of formic acid, but also its dehydrogenation.

Slinkin and coworkers[101] studied the EPR signals of alumina–chromium oxide catalysts with a wide range of compositions (1.5–93 wt.% Cr) after roasting at 450°, 600°, and 1000°C, and after catalysis had been carried out on them. In agreement with data obtained by other authors, it was found that the original catalysts at room temperature show two signals: a narrow signal with $\Delta H$ = 40–55 G, and a broad signal with $\Delta H$ = 1000 G. After catalysis, at a chromium concentration ≤ 14%, the narrow signal ($Cr^{5+}$ ions) disappears. With increase in the roasting temperature, the intensity of the broad line increases and its width decreases to 500 G. It was concluded that the active centres of the catalyst are not $Cr^{5+}$ ions but a number of centres containing $Cr^{6+}$, $Al^{3+}$, and $O^{2-}$ ions. The actual catalytic process studied is not reported, however, and an earlier paper referred to by the authors merely notes that the decomposition of propan-2-ol was studied. It is not clear from the text whether dehydrogenation, or dehydration, or both took place. It may be assumed that both processes should take place on this catalyst, which after catalysis gives an intense EPR signal and which contains a strong aprotonic acid — $Al_2O_3$.

The decomposition of propan-2-ol and cyclohexanol on certain organic semiconductors was recently studied[74]. On three of these — poly(benzimidazole), poly(acrylonitrile), and poly(isoprenebenzoquinone) — decomposition involves dehydration and dehydrogenation simultaneously; dehydration of the alcohols takes place almost exclusively only on the most "acidic" compound — polyacenequinone.


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ALEXANDR NAUMOVICH FRUMKIN

Dear Alexandr Naumovich,

Your pupils, collaborators, and the Editorial Board of the journal "Uspekhi Khimii" convey to you their warm greetings in connection with your jubilee and wish you health and many years of fruitful endeavour.

We have no doubt that the freshness and sharpness of your intellect, your energy, and outstanding capacity for work will ensure that the ideas which you have been developing will further enrich science and its practical applications with new achievements.

We all greatly value the opportunity to work with you, the leading electrochemist in the world, and are ready to assist you in every way in the further development of new and most advanced ideas of our Soviet science.

We wish you many happy days and major creative success.

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# ELECTROCHEMICAL REDUCTION OF OXYGEN

V. S. Bagotskii, L. N. Nekrasov, and N. A. Shumilova

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## 1. INTRODUCTION

Electrochemical (cathodic) reduction of molecular oxygen on various metallic or carbon electrodes has been the subject of numerous experimental studies in recent years. The increased interest in this reaction is due in the first place to its wide occurrence and great practical importance. The electrochemical reduction of oxygen greatly influences metal corrosion processes in aqueous media in the presence of free access of oxygen[1]. In analytical

chemistry this reaction can be used to determine the oxygen dissolved in various solutions, for example in sea water[2]. If cathodic reduction of oxygen could be achieved in practice at a sufficiently high rate and if effective oxygen electrodes could be prepared, this reaction could be used as the cathodic process in many electrochemical manufacturing processes, instead of the reaction involving the evolution of hydrogen; this would result in an appreciable saving of electrical energy. Numerous attempts have also been made to use the electrochemical reduction of oxygen for the industrial preparation of hydrogen peroxide[3].

However, perhaps the greatest interest attaches to the problem of using the electrochemical reduction of molecular oxygen in combination with the electrochemical oxidation of various types of fuel to achieve electrochemical flameless "cold" combustion[4]. This process constitutes the basis of the operation of the so-called fuel cells in which the chemical energy of the fuel is directly converted into electrical energy. Oxygen is the most readily accessible and most convenient oxidising agent for fuel cells and the complete solution of the problem of designing such cells depends greatly on the possibility of making adequately stable and effective electrodes for the reduction of oxygen.

The overall reduction of an oxygen molecule involves the participation of four electrons:

$$\text{in acid solutions } O_2 + 4H^+ + 4e \rightarrow 2H_2O, \quad (1)$$

$$\text{in alkaline solutions } O_2 + 2H_2O + 4e \rightarrow 4OH^-. \quad (1')$$

The equilibrium potentials corresponding to this reaction can be readily calculated by a thermodynamic procedure from the standard free energy of formation of water from gaseous hydrogen and oxygen. At 25° and an oxygen pressure of 1 atm this equilibrium potential is $\varphi_\gamma^{(1)} = +1.229$ V relative to the equilibrium potential of the hydrogen electrode in the same solution[5]. Since the equilibrium potentials of the hydrogen and oxygen electrodes vary in the same way with the pH of the solution, their difference is independent of the composition of the solution. The equilibrium potential of the oxygen electrode measured relative to that of the normal hydrogen electrode (in acid solution at pH 0) is $\varphi^{(1)} = +0.401$ V† in alkaline solution at pH 14 (when the pH is increased by one unit, the potential decreases by 59 mV).

A characteristic feature of the oxygen electrode is that the equilibrium potential calculated by a thermodynamic procedure is never established experimentally. When platinum, carbon, or other inert electrodes are immersed in an electrolyte in contact with gaseous oxygen; a potential $\varphi_\gamma$ between 0.8 and 1.1 V is established, i.e. 0.1–0.4 V less positive than the thermodynamic value. The potential established depends on the preliminary treatment of the electrode. In this respect the oxygen electrode greatly differs from the hydrogen electrode; as is well known, the equilibrium potential of the hydrogen electrode is relatively readily and reproducibly established at platinum and certain other metals. The difficulty in attaining the equilibrium potential of the oxygen electrode has a number of causes, in particular the possibility of the intermediate formation of hydrogen peroxide and the effect of the layers of oxygen adsorbed on the electrode surface. The only paper in which the attainment of an oxygen potential at a platinum electrode close to the equilibrium value is described is that of Bockris and Huq[6]. According to the authors, this result was achieved by very thorough purification of the solution. However, it is not entirely clear how they succeeded in eliminating effects due to the state of the surface and to what extent equilibrium between the oxygen and solution was in fact established on the electrode.

The formation of hydrogen peroxide in the cathodic reduction of oxygen was observed in the previous century, when this reaction began to be studied in connection with the investigation of the Grove oxygen–hydrogen cell[7,8].

Hydrogen peroxide can form as an intermediate in the overall four-electron reaction (1):

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2, \quad (2)$$

$$O_2 + H_2O + 2e \rightarrow HO_2^- + OH^-. \quad (2')$$

Further electrochemical reduction of hydrogen peroxide to water (or hydroxide ions) proceeds according to the equations

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O, \quad (3)$$

$$HO_2^- + H_2O + 2e \rightarrow 3OH^-. \quad (3')$$

The normal equilibrium potentials of reactions (2) and (3) calculated from thermodynamic data are respectively $\varphi^{0(2)} = +0.713$ V and $\varphi^{0(3)} = +1.744$ V (w.r.t. normal hydrogen electrode)[5,9]. It is evident from these values that the potential corresponding to the reduction of peroxide is much more positive than the potential of its formation from oxygen. This means that hydrogen peroxide is thermodynamically more readily reducible than oxygen. Thus hydrogen peroxide is thermodynamically unstable and can appear and accumulate as an intermediate only due to kinetic factors [the low rate but not thermodynamic impossibility of reaction (3)]. As a result, hydrogen peroxide appears under certain conditions, whereas in others it cannot be detected.

The hydrogen peroxide formed by the reduction of oxygen can disappear not only as a result of its further reduction but also as a result of its catalytic decomposition under the influence of the material of the electrode:

$$2H_2O_2 \rightarrow O_2 + 2H_2O, \quad (4)$$

$$2HO_2^- \rightarrow O_2 + 2OH^-. \quad (4')$$

As will be seen below, in many cases catalytic decomposition is the main process preventing the accumulation of hydrogen peroxide.

Reaction (1) can also proceed according to a different mechanism, not associated with the formation of hydrogen peroxide as an intermediate but with the dissociation of oxygen molecules into atoms, which are adsorbed on the electrode surface:

$$O_2 \rightarrow 2O_{ads}, \quad (5)$$

$$O_{ads} + 2H^+ + 2e \rightarrow H_2O, \quad (6)$$

$$O_{ads} + H_2O + 2e \rightarrow 2OH^-. \quad (6')$$

The determination of the actual reaction pathway [via stages (2) and (3) or via stages (5) and (6)] often involves considerable difficulties; the appearance of hydrogen peroxide is a clear demonstration that the first pathway is correct, but its absence cannot be regarded by itself as an unambiguous proof that the second reaction pathway actually obtains.

† Here and henceforth $\varphi_\gamma$ will denote the potential relative to the hydrogen electrode in the same solution and $\varphi$ the potential relative to the fixed potential of a reference electrode (in solution at a specified pH), for example relative to the normal hydrogen electrode (pH 0).

Reactions (2), (3), and (6) are themselves complex and can involve a number of intermediate stages, in each of which one species is added (proton or electron). In contrast to hydrogen peroxide, the intermediate products thus formed are completely unstable and cannot be detected by the usual electrochemical or analytical means. The most likely first stage of reaction (2) is the addition of the first electron:

$$O_2 + e \rightarrow O_2^-. \quad (7)$$

The formation of the molecular $O_2^-$ ion does not require the expenditure of an unduly large amount of energy and this reaction is quite possible. Further reactions of this ion can proceed, for example, as follows:

In acid solutions

$$O_2^- + H^+ \rightarrow HO_2, \quad (8)$$

$$HO_2 + e \rightarrow HO_2^-, \quad (9)$$

$$HO_2^- + H^+ \rightarrow H_2O_2. \quad (10)$$

In alkaline solutions

$$O_2^- + H_2O \rightarrow HO_2 + OH^-, \quad (8')$$

$$HO_2 + e \rightarrow HO_2^-. \quad (9')$$

In the reduction of hydrogen peroxide by reaction (3) the possible first stage is the addition of an electron to a hydrogen peroxide molecule with simultaneous breakdown of the latter into a hydroxide ion and a hydroxyl radical:

$$H_2O_2 + e \rightarrow HO + OH^-. \quad (11)$$

However, it must be stipulated that the nature and fate of the intermediate products of this reaction cannot as yet be exactly established from the available experimental data.

It is thus seen from this by no means complete list of the possible electrochemical and chemical reactions in the system oxygen–hydrogen peroxide–water that this system is extremely complex; this greatly hinders the interpretation of the results of experimental studies. The situation is aggravated by the fact that the reduction of oxygen occurs at potentials at which the formation of adsorption-type or chemically individual oxide layers is possible on the surface of many metals. The variation of the nature and properties of these layers with potential and with experimental conditions (including the previous history of the electrode) has different effects on the possible individual stages and reactions, which makes the problem still more difficult.

In recent years experimental data have been obtained for the reduction of oxygen at a number of electrodes; these make it possible to throw at least some light on the individual aspects of the mechanism of this process. The present review deals with the results obtained for metallic electrodes.

## 2. REDUCTION OF OXYGEN AT A MERCURY ELECTRODE

The mercury electrode has proved very convenient for the investigation of the kinetics of the electrochemical reduction of oxygen and its use has led to the determination of a number of features of this reaction. The detailed investigation of this kind, at a dropping mercury electrode, was made by Heyrovský as early as 1924.[10,11] The convenience of the mercury electrode is due to the high reproducibility of the liquid mercury surface, which can be readily renewed. Furthermore, the fact that the reduction of hydrogen peroxide at the mercury electrode is very slow and occurs only at highly negative potentials is of great importance. This makes it possible to separate clearly the potentials corresponding to the reduction of oxygen and to the reduction of hydrogen peroxide, and to investigate each of these reactions separately.

Fig. 1 shows polarisation curves for the reduction of oxygen in acid (curve *a*) and alkaline (curve *b*) solutions at a dropping mercury electrode. For all the solutions the polarisation curves consist of two waves, of approximately the same height; the first wave corresponds to reaction (2) and the second to reaction (3). The limiting current densities for both waves, $i_{d_1}$ and $i_{d_2}$, correspond to the limiting diffusional flux of oxygen towards the electrode surface, allowing for the participation of two electrons in each reaction per oxygen molecule. When the partial pressure of oxygen $p_{O_2}$ is changed, and hence also the amount of dissolved oxygen, the limiting current shows a corresponding change.

Let us consider in detail the first wave [reaction (2)]. Analysis of the curve obtained in acid solutions shows that the dependence of the current density on the surface concentration of molecular oxygen $[O_2]_S$ and on the potential is of the form[12-14]

$$i = k_1 [O_2]_S \exp[-\alpha F \varphi / RT], \quad (12)$$

where the transfer coefficient $\alpha$ is 0.5. Under conditions far removed from concentration polarisation, i.e. at current densities $i \ll i_{d_1}$, the surface concentration is equal to the bulk concentration of the dissolved oxygen $[O_2]$, while the latter is in turn proportional to the partial pressure of oxygen. In this case

$$i = k_2 p_{O_2} \exp[-\alpha F \varphi / RT], \quad (13)$$

or

$$\varphi = \text{const} - b \log i + b \log p_{O_2}, \quad (14)$$

where

$$b \equiv \frac{RT}{\alpha F} 2.3 \sim 0.11 - 0.12V.$$

Experiment shows[12,15] that in acid solutions the reduction potential $\varphi$ at constant current density is independent of the pH. Fig. 2 shows an example of the variation of the half-wave potential for the first wave with the pH of the solution. Thus the kinetic equations (12) and (13) are

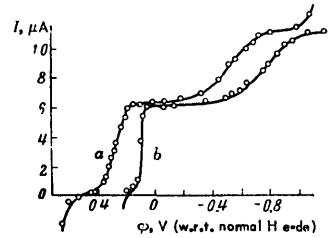



Fig. 1. Polarisation curves for the reduction of oxygen and hydrogen peroxide at a dropping mercury electrode in solutions at different pH:
1) 1.67; 2) 12.5; data of Bagotskii and Yablokova[12].

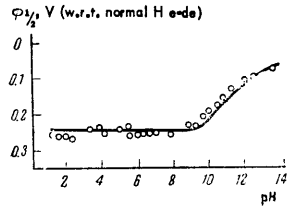



Fig. 2. Dependence of the half-wave potential for the reduction of oxygen on the pH of phosphate buffer:
circles — experimental data; continuous curve — calculated by Eqn. (16); data of Bagotskii and Yablokova [12].

independent of the pH of the solution, which in turn suggests that hydrogen ions do not participate in the slow stage which determines the rate of the overall reaction (2).

The form of the kinetic equation (12) or (13) and the independence of the reaction rate of the pH indicates that the slow stage of process (2) is reaction (7) — the formation of the oxygen molecular ion [12-14,16,17]. A change in kinetics on transition from acid to alkaline solutions is characteristic of the reduction of oxygen to hydrogen peroxide at a mercury electrode. Fig. 1 shows that in alkaline solutions the first wave is much steeper than in acid solutions. The $b$ coefficient of the kinetic equation (14) in alkaline solutions is about 0.03 V, i.e. smaller by a factor of four than in acid solutions. Furthermore, Fig. 2 shows that in alkaline solutions the reduction potential varies with the pH: with other conditions constant (current density, oxygen pressure), the potential decreases by 0.06 V per pH unit in the range between pH 9 and pH 11, and by 0.03 V at pH values greater than 11.

A similar change in the reaction on going from acid to alkaline solutions was also observed in the experiments of Krasil'shchikov [16,18,19] on the reduction of oxygen to hydrogen peroxide at a silver electrode. To explain his results, Krasil'shchikov suggested that in alkaline solutions the slow stage is the reaction involving the addition of a second electron [stage (9)] and not the stage involving the first electron [stage (7)] which determines the rate of the overall reaction in acid solutions. The theory of electrochemical kinetics shows that the $b$ coefficient in the kinetic equation (14) is $2.3\,RT/(1+\alpha)F$, which is equal to 0.04 V with $\alpha = 0.5$, i.e. close to the experimental value. Thus Krasil'shchikov's hypothesis accounts satisfactorily for the values of the kinetic coefficients in alkaline solutions, but the reason for the change in the rate-limiting step on going from acid to alkaline solutions still remains obscure.

Another hypothesis was put forward by Bagotskii et al. [12,14] concerning the mercury electrode. It was shown that in alkaline solutions the equilibrium potential for the system oxygen–hydrogen peroxide is established at the mercury electrode. The dependence of this potential on the concentration of the components (oxygen, hydrogen peroxide, hydroxide ions) is consistent with thermodynamic relations. The tabulated values of the normal equilibrium potential for this system were actually corrected on the basis of experimental measurements [9] ($\varphi^{0(2)} = +0.713$ V instead of +0.684 V given in Latimer's handbook [5]), and hence also the standard free energy of hydrogen peroxide solution ($\Delta G_{H_2O_2} = -32\,900$ cal instead of -31 470 cal).

The attainment of equilibrium between oxygen and hydrogen peroxide at a mercury electrode in alkaline solutions is also confirmed by the measurements of Koryta [20]. The attainment of this equilibrium at a porous carbon electrode was demonstrated as early as 1943 by Berl [21].

Since the potential corresponds to equilibrium, it follows that the polarisation curve in alkaline solutions is determined solely by concentration polarisation, i.e. the rate-limiting process is the diffusion-dependent stage in which the reacting oxygen molecules are brought to the electrode surface and the reaction products — hydrogen peroxide ions or molecules — are removed. On this hypothesis the $b$ coefficient in Eqn. (14) is found to be 0.03 V, which is consistent with experiment. Furthermore, this hypothesis also accounts for the observed dependence on the pH in alkaline solutions: up to pH 11 the equilibrium potential for reaction (2) changes by 0.06 V per unit pH, while at higher pH values the change in potential is smaller by a factor of two due to the ionisation of hydrogen peroxide [reaction (2′)].

On the basis of the above hypotheses, it is easy to explain the change in reaction mechanism on going from acid to alkaline solutions. In acid solutions the rate of reaction is determined by stage (7), while the remaining stages, (8)–(10), proceed fairly rapidly, so that equilibrium is set up between $O_2^-$ ions and the reaction product $H_2O_2$:

$$O_2^- + 2H^+ + e \rightleftarrows H_2O_2. \qquad (15)$$

As the pH increases, other conditions remaining the same, the concentration of $O_2^-$ rises too. This leads to an increase in the rate of the reaction which is the reverse of reaction (7), i.e. the oxidation of molecular oxygen ion $O_2^-$. At a certain pH the rate of the reverse reaction becomes comparable with that of the forward reaction, i.e. the reaction becomes reversible.

On the basis of the above hypotheses, it is possible to derive an overall kinetic equation, which expresses the dependence of the rate of reduction of oxygen on the potential over the entire range of pH: [12]

$$i = \frac{i_{d_1}}{1 + \exp[\alpha F(\varphi - \varphi_{1/2})/RT] + \dfrac{\gamma}{a_H^+ [a_{H^+} + K_d]} \exp[2F(\varphi - \varphi^{0(2)})/RT]}, \qquad (16)$$

where $\varphi_{1/2}$ is the half-wave potential (first wave) in acid solutions, $\gamma$ the solubility of oxygen in the solution, and $K_d$ the dissociation constant of hydrogen peroxide. The only quantities which cannot be determined by independent (non-electrochemical) measurements are the transfer coefficients $\alpha$ and the half-wave potential. Having determined these values from measurements in one solution, it is possible to calculate the complete polarisation curves in other solutions, both acid and alkaline. Polarisation curves calculated in this way for two solutions are compared with experiment in Fig. 3. A similar comparison is made also in Fig. 2 for the dependence of the half-wave potential on the pH. In both cases the agreement between calculation and experiment is satisfactory, which indicates the validity of the initial hypotheses.

A characteristic feature of the next stage of the overall oxygen reduction process — reduction of hydrogen peroxide to water — is a very low slope of the polarographic wave (Fig. 1). The results of kinetic measurements may be represented by the equation [12]

$$\varphi = \text{const} + b \log[H_2O_2]_S - b \log i, \qquad (17)$$

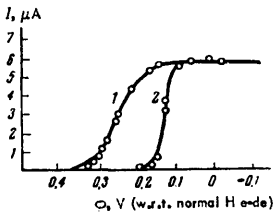



Fig. 3. Polarisation curves for the reduction of oxygen to hydrogen peroxide in solutions at different pH:
1) 3.31; 2) 11.3; circles — experimental data; continuous curve — calculated by Eqn. (16); data of Bagotskii and Yablokova [12].

where the coefficient $b = 2.3RT/\alpha F$ is 0.24–0.26 V, i.e. twice as great as for the first stage. In acid solutions the potential is independent of the pH. At pH > 11 there is a sharp decrease of the potential. This is satisfactorily explained by the hypothesis that only the hydrogen peroxide molecule and not the corresponding ion constitutes the reacting species; at pH > 11 and a constant total concentration of the peroxide, the concentration of the undissociated molecules begins to decrease.

On the basis of these data, the hypothesis was put forward [12] that the slow stage is reaction (11) involving the addition of an electron to a hydrogen peroxide molecule with its simultaneous dissociation into a hydroxide ion and a hydroxyl radical.

When a hydrogen peroxide solution is in contact with a mercury electrode, there is some, although not very rapid, catalytic decomposition of the peroxide. Comparison of the measured rate of the catalytic decomposition with the rates of the electrochemical reduction of hydrogen peroxide at the given potential [reaction (3)] and its electrochemical oxidation [the reverse reaction (2)] shows [22] that, at least in dilute solutions, these rates agree closely. Hence it follows that the catalytic decomposition of hydrogen peroxide on mercury may be regarded as coupled electrochemical oxidation and reduction (dismutation) of hydrogen peroxide, both processes occurring simultaneously. In more concentrated solutions the rate of catalytic decomposition of the peroxide is tens of times greater than the calculated value, which shows that in such solutions a non-electrochemical mechanism of the catalytic breakdown obtains (possibly a chain mechanism involving the migration of active intermediate products from the surface of the mercury electrode into the bulk of the solution).

## 3. REDUCTION OF OXYGEN ON PLATINUM AND PLATINUM GROUP METALS

In the study of the electrochemical reduction of molecular oxygen on platinum, and in general on solid electrodes, it is necessary to overcome considerable difficulties arising in the first place from the inhomogeneity of the surface of such electrodes and the effect on the kinetics of the process of the physicochemical properties of the electrode surface, which vary with potential, time, adsorption of various components of the solution, etc.

Among the large number of experimental findings concerning the ionisation of oxygen on smooth platinum in acid and alkaline solutions, the following may be regarded as established (although their interpretation is not the same in different investigations):

a. In contrast to the mercury electrode, only one oxygen reduction wave is observed at an activated smooth platinum electrode, and according to the majority of measurements the overall process involves the addition of four electrons. The appearance of a second wave, noted, for example, by Shepelin et al. [23], is probably associated with the low activity of the electrode under the experimental conditions.

b. The half-wave potential for the reduction of dissolved oxygen is close to the reduction potential of surface platinum oxides at any pH of the solution [24-27].

c. An increase in the pH of the solution by one unit causes a decrease of the oxygen reduction half-wave potential by 0.06 V. [24,28]

d. Hydrogen peroxide is formed in the reaction.

e. The kinetics of the process are appreciably affected by the degree of oxidation of the electrode surface. Surface platinum oxides have been found to both inhibit [27,29] and accelerate [24,30] the ionisation of oxygen. The dual effect of the oxidation of electrode surface on the reaction kinetics has been investigated by Müller and coworkers [31,32] and by Khrushcheva et al. [33]

Various hypotheses have been put forward concerning the mechanism of the cathodic reduction of oxygen, which may be reduced to three principal reaction mechanisms.

1. According to Krasil'shchikov and Andreeva [28], the rate-limiting stage in the process is the interaction of hydrogen atoms adsorbed on the platinum surface with molecules of dissolved oxygen. The characteristic feature of this mechanism is that it assumes the presence of adsorbed hydrogen at potentials more positive by 0.9 V than that of the reversible hydrogen electrode, which is contradicted by the results of the investigation of the surface properties of platinum [34,35], including the measurements made by Vielstich [27] by the triangular pulse method in the presence of oxygen in the solution.

2. In view of the similarity of the potentials for the reduction of oxygen and the surface platinum oxides, Sawyer and coworkers [24,36] put forward a mechanism based on the hypothesis of the electrical reduction of the oxides and their subsequent regeneration as a result of the chemical interaction of oxygen with the surface of the metal:

$$Pt(OH)_2 + 2e \rightarrow Pt + 2OH^-, \quad (18)$$

$$Pt + H_2O + \frac{1}{2}O_2 \rightarrow Pt(OH)_2. \quad (19)$$

Giner [25] and Lingane [26] have expressed similar views. According to Sawyer, two-electron reduction of oxygen to hydrogen peroxide [reaction (2)] takes place on electrodes free from chemisorbed oxygen.

3. Some investigators [21-33,37-41] have been developing the view that the electrochemical reduction of oxygen on platinum proceeds in two consecutive stages with the formation of hydrogen peroxide as an intermediate. In contrast to the reaction at the mercury electrode, hydrogen peroxide is reduced (or decomposes) at potentials corresponding to its formation, so that as a rule two separate waves are not observed. The main results of these studies are presented below.

Nekrasov and Müller [37] were the first to study the ionisation of oxygen by the method of the rotating disc electrode

with a ring, proposed by Frumkin and Nekrasov[42]. The rotating disc electrode with a ring consists of a single mechanical system comprising two electrodes — a disc and a ring — which are electrically independent. The use of this electrode yielded significant new information about the mechanism of the process which would be difficult to obtain in other ways. With this method the formation of hydrogen peroxide could be controlled directly during the reaction at the disc (smooth platinum) by oxidising at the platinised platinum ring electrode the part of the peroxide which failed to react at the disc electrode and was brought to the surface of the ring by the flow of liquid. Thereby it was possible to separate the various stages of the process and to study each of them individually.

The process in alkaline solutions was studied in greatest detail. It was found that, at fairly high rates of rotation of the electrode (for example, in excess of 700 rev $min^{-1}$), the polarisation curves for the reduction of oxygen at a smooth platinum disc electrode show a clear current maximum at a disc electrode potential $\varphi_r^{(d)} = 0.5$ V after which the current fell to a minimum at a potential of ~0.1 V (Fig. 4, curves *1–3*). Measurements at the disc electrode led to the detection of the formation of hydrogen peroxide over the entire range of oxygen reduction potentials at the disc electrode, the yield of the peroxide increasing with potential up to the value corresponding to the minimum on the cathodic curve for the disc electrode (Fig. 4, curves 1*a*–3*a*). Only at disc electrode potentials more negative than this does the observed amount of hydrogen peroxide decrease.

This form of the curves was explained by a fall of the rate of reduction of hydrogen peroxide at the smooth platinum disc electrode as the surface platinum oxides became reduced. The minimum rate of reduction is reached at a potential of 0.1 V, after which it again increases. A method has been suggested[37] for the treatment of the experimental results by plotting the so-called "corrected" polarisation curves: the current, calculated on the basis of the theory of the disc electrode with a ring[43,44], corresponding to the reduction of that part of the hydrogen peroxide which fails to react on the surface of the disc and is carried away by the liquid stream, is added to the current measured at the disc electrode. Thus the "corrected" current corresponds to the complete reduction (to water or hydroxide ions) of all the oxygen participating in the first stage of the process; the rate in this stage is equal to half the "corrected" current. The "corrected" curves (Fig. 4, curves *1′–3′*) show distinct limiting diffusion current plateaus. This result leads to the conclusion that at potentials more negative than 0.5 V, the cathodic reduction of oxygen to hydrogen peroxide is diffusion-dependent and the rate of the overall reaction is determined by the rate of reduction of hydrogen peroxide. On the other hand, in the region of the rise of the polarisation curve (at $\varphi_r > 0.6$ V) the first stage of the process becomes irreversible.

The fact that the mechanism of the reduction of oxygen involves a number of consecutive stages with intermediate formation of hydrogen peroxide is confirmed by the similarity of the polarisation curves for the reduction of oxygen and of hydrogen peroxide added to the solution. Additional evidence in favour of this hypothesis is the closeness of the values (when $\varphi_r < 0.5$ V) of the rate constant for the reduction of hydrogen peroxide calculated by the formula of Levich and Ivanov[43] on the basis of measurements with a ring-type disc electrode, and the values of the rate constant for the overall four-electron oxygen reduction process found by an independent method[32].

Study of the effect of surface platinum oxides on the electrochemical reduction of oxygen in an alkaline solution[31,32] showed that preliminary oxidation of the electrode retards the reduction of oxygen to hydrogen peroxide, and shifts the half-wave potential for the first stage of the process towards negative values (Fig. 5, curves *a* and *b*). The reduction of oxygen and the surface oxides in the same potential ranges can be explained by the fact that oxygen can be reduced only when the surface is already partially free from surface oxides, as pointed out by Vielstich[27].

The surface oxides have the opposite effect on the second stage of the process. Fig. 5 shows that, when $\varphi_r < 0.5$ V, i.e. in the potential range where the reaction kinetics are determined only by the rate of reduction of hydrogen peroxide, the current at an electrode subjected to preliminary oxidation (curve *1*) is appreciably higher than at an electrode

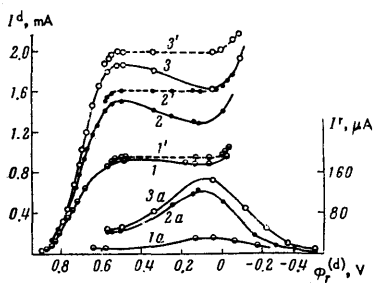



Fig. 4. Polarisation curves for the reduction of oxygen at a platinum disc electrode in 0.125 *N* KOH for different values of *m*:
1) 1040 rev $min^{-1}$; 2) 2950 rev $min^{-1}$; 3) 4560 rev × × $min^{-1}$; 1′)–3′) currents corrected for the amount of hydrogen peroxide evolved; 1*a*)–3*a*) variation of the limiting current for the oxidation of hydrogen peroxide at the ring ($I^r$) with the potential of the disc electrode; data of Nekrasov and Müller[37].

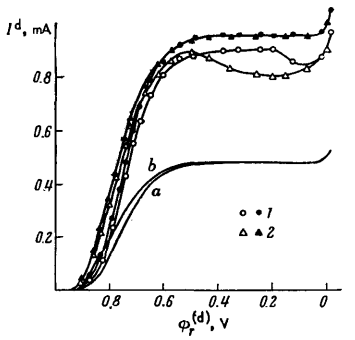



Fig. 5. Polarisation curves for the reduction of oxygen at oxidised (curve 1) and reduced (curve 2) electrodes; filled symbols — polarisation curves corrected for the amount of hydrogen peroxide evolved; *a*) and *b*) calculated polarisation curves for the reduction of oxygen to hydrogen peroxide at oxidised and reduced electrodes respectively; data of Müller and Nekrasov[31].

subjected to preliminary reduction (curve 2). The accelerating effect of surface oxides on the second reaction stage is associated with the fact that their presence ensures the occurrence of the catalytic breakdown of hydrogen peroxide on the surface of the platinum electrode. A possible mechanism for this process was put forward by Haber and Grinberg[45]:

$$Pt + HO_2^- \rightarrow PtO + OH^-, \quad (20)$$

$$PtO + HO_2^- \rightarrow Pt + O_2 + OH^- \text{ etc.} \quad (21)$$

Molecular oxygen, which is more readily reduced electrochemically than hydrogen peroxide itself, is formed during the catalytic decomposition. Direct electrochemical reduction of the peroxide has an effect on the reaction kinetics only at sufficiently negative potentials.

The occurrence of the catalytic breakdown of hydrogen peroxide on platinum and its retardation at more negative potentials was observed experimentally in alkaline and acid solutions by the method based on a rotating disc electrode with a ring[31,32,46]. The acceleration of the catalytic breakdown of hydrogen peroxide by surface platinum oxides was also observed by Bianchi et al.[47]

The doubly charged cations $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$ have an appreciable effect on the reduction of oxygen on platinum. This was noted for the first time in the work of Kozawa[48], who observed a lowering of the current yield of hydrogen peroxide in the presence of alkaline earth metal cations. The studies of Müller and Sobol'[40], who used the method of the rotating disc electrode with a ring, showed that the effect of the above cations is similar to that of oxygen chemisorbed on the electrode surface: their presence in solution retards the first stage of the reaction and accelerates the second stage (Fig. 6). The effect of the cations increases in the series $Ca^{2+} < Sr^{2+} < Ba^{2+}$.

The effect of cations on the electrochemical reduction of oxygen can be explained on the hypothesis that they are adsorbed on the electrode surface which results in strengthening of the bond between adsorbed oxygen and platinum. The adsorption measurements of Balashova and Kulezneva[49] confirmed the specific adsorption of $Ca^{2+}$ and $Ba^{2+}$ cations on platinum in alkaline solutions, the extent of adsorption increasing on going from $Ca^{2+}$ to $Ba^{2+}$.

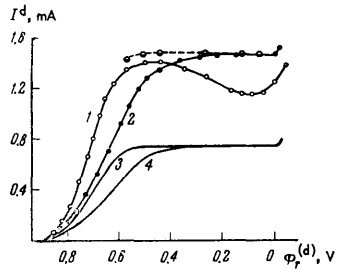



Fig. 6. Polarisation curves for the reduction of oxygen at a smooth platinum disc electrode in 0.125 *N* KOH:
1) without added doubly charged cations; 2) in the presence of $10^{-3}$ M $Ba^{2+}$; calculated polarisation curves for the first stage: 3) without added cations; 4) in the presence of $Ba^{2+}$ cations; the dashed line represents curve 1 corrected for the unreacted hydrogen peroxide; data of Müller and Sobol'[40].

The application of the method of the rotating disc electrode with a ring in the investigation of the ionisation of oxygen in acid solutions[33,38,39,46] made it possible to demonstrate the formation of hydrogen peroxide in the reduction of oxygen at a disc electrode, to observe its catalytic decomposition, and to elucidate the effect of surface platinum oxides on the first and second stages of the process. It was found that reduction of the electrode surface increases the yield of hydrogen peroxide to 70–90%. On the basis of these results, it was concluded that the mechanism of the process in acid solutions is qualitatively similar to that in alkaline solutions.

An important feature of the cathodic reduction of oxygen in acid solutions, which makes a quantitative treatment of the results difficult, is the time variation of the activity of the smooth platinum electrode, which may be due to the deactivating effect of the adsorption of anions. Polarisation measurements in solutions of various acids showed the occurrence of a pronounced shift of the half-wave potential for the reduction of oxygen towards negative values in the series $HClO_4 < H_2SO_4 < HCl < HBr$, i.e. the shift increasing with the adsorbability of the anions; this was also noted by other workers[48,50,51].

Calculation of the rate constants for the first and second stages of the reaction in 1 *N* $H_2SO_4$ on the basis of the polarisation curve measured under nearly steady-state conditions showed that in this case both reactions are inhibited, and at sufficiently positive potentials (oxidised electrode) the rate of the overall process is determined mainly by the rate of formation of hydrogen peroxide; on displacement of the potential towards negative values (reduced electrode) it is determined by the rate of reduction of hydrogen peroxide[38,39].

Interesting data on the effect of the state of electrode surface on the first and second stages of the ionisation of oxygen and also on the mechanism of the reduction of the surface oxides were obtained by the use of a rotating disc electrode with a ring, potential pulses of various amplitudes being applied to the disc. The apparatus constructed for this purpose[52] provided both periodic and single triangular and trapezoidal potential pulses, the rate of change of the applied potential ranging from 0.001 V $s^{-1}$ to 2000 V $s^{-1}$, the amplitude of the trapezoidal pulse being ±2.2 V, and the period corresponding to the upper horizontal section of the trapezium, i.e. the pause between the pulses, varying from $4 \times 10^{-5}$ to 35 s. The application of trapezoidal pulses in the investigation of the mechanism of electrode reactions makes it possible to follow not only the changes in the properties of the electrode surface but also to investigate the effect of the time during which the electrode is kept at a specified potential and the reversibility of the phenomena. Independent variation of the parameters of the trapezoidal pulses, i.e. pulse amplitude, duration of the period at a constant potential, and the rate of increase and fall of the potential increases the scope of the technique.

To investigate the effect of the state of the surface on the kinetics of the ionisation of oxygen, pulses of different amplitude are applied to the disc electrode; this produces electrodes with different degrees of oxidation. This method was used to study the effect of the degree of oxidation of the platinum electrode and the rate of reduction of

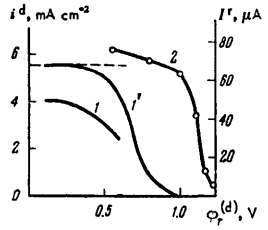



Fig. 7. Polarisation curves for the reduction of molecular oxygen in 1 *N* sulphuric acid at a rate of rotation of 2250 rev min$^{-1}$ with application of potential pulses of different amplitudes:
1) 0.1–0.6 V; 1') 0.1–1.2 V; 2) variation of the current at the ring with the amplitude of the potential pulse; data of Frumkin et al.[41]

oxygen. Fig. 7 shows the variation of the current at a ring electrode with the amplitude of triangular potential pulses applied to the platinum disc in an acid medium. It is evident that, as the amplitude increases in the anodic sense, i.e. as the degree of oxidation of the electrode increases, the current observed at the ring diminishes. On the other hand, the limiting current at the disc is higher when the anodic value of the pulse amplitude is greater, as can be seen from a comparison of the curves in Fig. 7. Thus experimental data show that the amount of hydrogen peroxide removed from the bulk of the solution falls and suggest that the second stage of the ionisation of oxygen is accelerated by surface platinum oxides.

This method also revealed the inhibiting effect of the oxides on the first stage of the ionisation of oxygen in acid solutions. Without the pulse method, the study of this effect is difficult because the adsorption of anions has a strong influence on the kinetics of the process in an acid medium.

A combination of the methods based on the rotating disc electrode with a ring and on triangular potential pulses made it possible to investigate the mechanism of the reduction of surface platinum oxides. In a number of studies it was noted that the oxidation of the electrode surface during anodic polarisation requires a greater amount of electricity than its reduction. Vetter and Berndt[53] and then Dietz and Göhr[54] explained this phenomenon by the reduction of surface platinum oxides to hydrogen peroxide. If this explanation is correct, then calculation shows that, on applying potential pulses at a high rate to the disc, in an atmosphere of nitrogen, hydrogen peroxide should be detected at the disc. Actually, when potential pulses were applied to the disc at a rate of 100 V s$^{-1}$, the limiting value of the cathodic amplitude being 0.1 V and the anodic value varying from 0.7 to 1.5 V, in an atmosphere of nitrogen in both acid and alkaline media, hydrogen peroxide was not detected. In control experiments with potential pulses applied at the same rate in an atmosphere of oxygen, where hydrogen peroxide is formed on ionisation of dissolved oxygen, the latter was detected at the ring. Thus it can be regarded as demonstrated that the reduction of oxygen chemisorbed on the surface of the platinum electrode does not result in the formation of hydrogen peroxide.

Investigation of the effect of the state of the electrode surface on the kinetics of the ionisation of oxygen includes the study of the problem of the variation of the nature of the bond between adsorbed oxygen and the electrode surface (in particular its strengthening) or the variation of the structure of the adsorbed layers of oxygen. In the experiments on these processes by the method of trapezoidal potential pulses the $i$–$\varphi$ curves shown in Fig. 8 were obtained[52]. These curves were measured with trapezoidal potential pulses applied to the electrode at a rate of change of potential of 100 V s$^{-1}$, at amplitudes between 0.01 and 1.5 V, the electrode being maintained at a potential of 1.5 V (horizontal part of the trapezium) for various times.

Fig. 8 shows that the total amount of electricity consumed during the anodic half-period of the pulse ($Q_a$) remains virtually constant regardless of the period during which the electrode is kept at a potential of 1.5 V. $Q_c$, the amount of electricity consumed during the cathodic half-period, remains virtually constant for $10^{-3}$ s, since this is commensurate with the duration of the entire potential pulse. A significant change is observed in the range 0.001–0.1 s, which is probably associated with the accumulation of oxygen during the period at the constant potential $\varphi$ = 1.5 V. The simultaneous shift of the oxygen desorption potential towards cathodic values indicates an increase in the irreversibility of the desorption process. This observation may be explained, on the one hand, by increased coverage of the electrode surface with oxygen and, on the other hand, by a strengthening of the bond between oxygen and the surface of the platinum.

In the experiments described above the electrodes used were "reduced" or "oxidised" electrochemically, i.e. by cathodic or anodic polarisation. However, although during cathodic polarisation the bulk of adsorbed oxygen atoms or surface oxides are removed, complete reduction of the surface nevertheless does not take place. Complete removal of oxygen from the surface may be achieved by reducing it with gaseous hydrogen at 400° with subsequent degassing in a vacuum at 1000°. This method of purification of the surface for electrochemical measurements was proposed by Burshtein and coworkers[55–57].

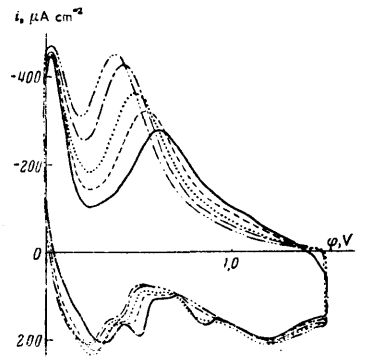



Fig. 8. $i$–$\varphi$ curves with application of potential pulses at a rate of 100 V s$^{-1}$, the potential being varied from -0.01 to 1.5 V and the electrode being maintained at $\varphi$ = 1.5 V for different periods:
1) 40 μs; 2) 10 ms; 3) 100 ms; 4) 1 s; 5) 5 s; data of Alekseev et al.[52]

In the work of Bagotskii et al.[58,60] this procedure was used to study the state of oxygen on the surface under various experimental conditions and also in experiments designed to elucidate the effect of adsorbed oxygen on the electrochemical reactions in the system oxygen–hydrogen peroxide. The data obtained showed that, when anodic charging curves are measured at thoroughly degassed platinum, the deposition of the first portion of adsorbed oxygen occurs at more cathodic potentials than in the case of a platinum surface treated in the usual way (starting with potentials $\varphi_r$ = 0.2–0.3 V). The main bulk of oxygen adsorbed exists in three forms at potentials of 0.6–0.8, 0.95–1.0, and 1.4–1.5 V respectively (Fig. 9). Thus oxygen may be present on the surface of the platinum electrode in various forms, which differ from one another in bond energy and relative stability.

The anodic and cathodic charging curves show appreciable hysteresis even at very low current densities. During the time corresponding to the cathodic section of the curve only 20% of adsorbed oxygen is removed by the time the initial potential is restored. After switching off the cathodic current, the potential again shifts towards positive values and on repeated reduction a similar amount of oxygen is again eliminated. If after removal of only part of the deposited oxygen, the anodic charging curve is again measured, an additional quantity of oxygen may be adsorbed, virtually equal to the initial amount. This type of irreversibility of the process indicates gradual penetration of oxygen into the bulk of the metal after its adsorption. The rate of penetration of oxygen into platinum (and its removal in the reverse process) depends on the potential and temperature. On degassed platinum this penetration effect is much more pronounced than on cathodically reduced platinum, in which atomic layers in the bulk of the metal are probably occupied by sorbed gases. These results, showing the penetration of anodically adsorbed oxygen into the bulk of smooth platinum, are consistent with data obtained earlier[61–63] under different experimental conditions (at higher temperatures or at higher anodic polarisations). When traces of molecular oxygen are introduced into a cell with thoroughly degassed platinum, the electrode assumes a potential $\varphi_r$ = 0.70–0.72 V, which is steadily maintained for a long time. Experiment shows[60] that equilibrium corresponding to reaction (2) is then established on the platinum electrode between oxygen and hydrogen peroxide (some of which is formed immediately after introduction of oxygen, when the electrode potential is more negative than 0.7 V). In contrast to the mercury electrode and other electrodes, the equilibrium on degassed platinum is established not only in alkaline, but also in acid solutions. However, when considerable amounts of oxygen are introduced, and also after weak anodic polarisation, the equilibrium breaks down. These data again show the strong effect of adsorbed oxygen on the mechanism of electrochemical reactions in the system oxygen–hydrogen peroxide.

Little work has been done on the study of the mechanism of the cathodic reduction of oxygen on other metals of the platinum group — palladium and rhodium. The measurements made at a palladium disc electrode with a ring[64] indicate considerable similarity in the electrochemical behaviour of palladium and platinum in the cathodic reduction of oxygen both in acid and alkaline solutions. In both cases formation of hydrogen peroxide is observed and therefore the reaction proceeds in two consecutive stages; the oxidation of the surface of the palladium electrode retards the first stage of the process and accelerates the second; the occurrence of the catalytic breakdown of hydrogen peroxide on the surface of the electrode has been established. The differences that exist are principally quantitative. In particular, it was found that both stages are faster on palladium than on platinum. The greater activity of palladium compared with platinum was also observed in other experiments[65–67].

Application of the method of the rotating disc electrode with a ring in the investigation of the ionisation of oxygen in alkaline solutions on the rhodium electrode[68] showed that this process also proceeds in two consecutive stages with the intermediate formation of hydrogen peroxide. However, it was shown that the process on rhodium is significantly different from that on platinum and palladium. Thus the polarisation curves for the ionisation of oxygen on the rhodium electrode (Fig. 10, curves *1–3*) do not show the fall of current characteristic of palladium and platinum (Fig. 4, curves *1–3*). The relative yield of hydrogen peroxide (the ratio of the current at the ring to half the "corrected" current at the disc) continuously decreases as cathodic polarisation is increased, whereas on platinum and palladium the yield passes through a maximum. Study

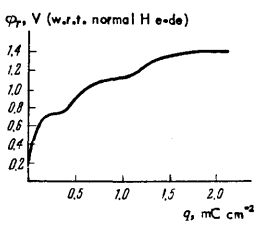



Fig. 9. Anodic charging curve for a degassed platinum electrode in 1 *N* $H_2SO_4$ at 25°; data of Luk'yanycheva and coworkers[58,59].

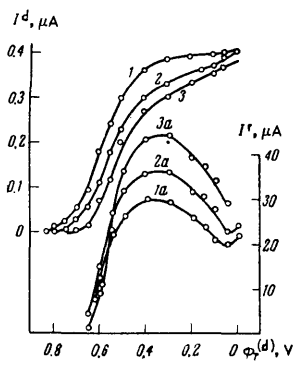



Fig. 10. Polarisation curves ($I^d$) for the ionisation of oxygen in 0.1 *N* KOH (curves 1–3) and the corresponding variation of the current at the ring ($I^r$) with the potential of the disc (curves 1*a*–3*a*) at $m$ = = 2250 rev $min^{-1}$ at reduced (curve 1), standard-activated (curve 2), and oxidised (curve 3) rhodium electrodes; data of Nekrasov et al.[68]

of the kinetics of the ionisation of oxygen as a function of the degree of oxidation of the electrode established that, as the latter increases, the half-wave potential of the polarisation curve shifts towards negative values (Fig. 10, curves *1–3*). At the same time there is an increase in the amount of hydrogen peroxide detected at the ring (Fig. 10, curves 1*a*–3*a*). In other words, an increase in the degree of surface oxidation of the rhodium electrode retards both the first and the second stages of the process.

Analysis of the experimental data leads to the conclusion that, in contrast to platinum and palladium, the second stage in the ionisation of oxygen on rhodium is electrochemical. Appreciable catalytic breakdown of hydrogen peroxide on this metal was not observed under the conditions of the experiment. Thus the results obtained for the rhodium electrode confirm the view expressed above that the acceleration of the second stage of the process on platinum and palladium by surface oxides is associated with the occurrence of the catalytic breakdown of hydrogen peroxide.

## 4. REDUCTION OF OXYGEN AT A SILVER ELECTRODE

The cathodic reduction of oxygen on silver has been investigated to a lesser extent than the reduction on mercury or platinum. In a number of experiments on the ionisation of oxygen on silver[16,69-71] it was shown that this process also is accompanied by the formation of hydrogen peroxide as an intermediate. However, the two-step polarisation curve characteristic of the mercury electrode is not as a rule observed. As with platinum, only one reduction wave is obtained in the case of silver, with a more or less distinct limiting current plateau, whose height varies between values corresponding to two-electron and four-electron processes.

As noted above, Krasil'shchikov[16,18,19] believes that in acid and neutral solutions the mechanism of the ionisation of oxygen on silver is similar to that for the process on mercury. In an acid medium the *b* coefficient is close to 0.116 and the stage involving the addition of the first electron is rate-limiting. As the alkalinity of the solution increases, the *b* coefficient falls and in fairly concentrated solutions (about 1 *N*) it is 0.04 V. In Krasil'shchikov's view, under these conditions the most likely rate-determining stage is the one involving the addition of the second electron.

On the other hand, Akopyan[72] suggested that the reduction of oxygen to hydrogen peroxide in alkaline solutions on silver is reversible (as on mercury).

In a few individual cases two polarographic waves were observed in the reduction of oxygen on silver. Such curves were obtained by Palous and Bouvet[69] for sintered silver electrodes with circulating electrolyte and for flat silver electrodes subjected to different types of treatment. Mazitov et al.[71] obtained polarograms consisting of two waves for silver electrodes which had been subjected to preliminary heat treatment in a gas flame.

Many workers believe that both two-electron [reaction (2′)] and four-electron [reaction (1′)] processes occur in the ionisation of oxygen on silver. Thus Kabanov and Siver[73], who studied the ionisation of oxygen at a silver disc electrode in a weakly acid medium, found that the reduction of oxygen at an air-oxidised electrode involves two electrons, whereas the reduction at a reduced electrode involves three electrons over the entire range of angular velocities of the electrode during the reaction, which in the authors' view can be explained by supposing that the relative contributions of the two-electron and four-electron processes are in the proportions 1 : 1.

Delahay[74], who studied the reduction of oxygen on various metals by an analytical method, also concluded that the total number of electrons involved in the ionisation of oxygen on silver changes. He established that the number of electrons participating in the ionisation on silver in a neutral solution changes from three to four in the potential range 0.05–0.0 V. He explained this result by an increase in the rate of ionisation of hydrogen peroxide with increase in electrode polarisation.

Recently, data have been obtained in a number of studies[69,71] showing that the kinetics of the ionisation of oxygen depend on the state of the electrode surface, on the preliminary activation of the electrode, and on the presence of oxides or chemisorbed oxygen on the surface. Zhutaeva et al.[75] studied the ionisation of oxygen on silver by the method of the rotating disc electrode with a ring and also its combination with the triangular pulse method. They showed that the ionisation curve (Fig. 11, curve *1′*) does not have a distinct limiting current plateau and in the potential range between 0.4 and -0.1 V there is an approximately linear increase in current with potential. The overall number of electrons participating in the reaction in this potential range increases from 3 to 3.9–4.

Over the entire range of the rotation rates of the electrode (600–5000 rev min$^{-1}$) there is a discrepancy between the experimental current $I^d_{exp}$ and the diffusion current for the four-electron process $I^d_{theor}$, the discrepancy increasing with the rate of rotation of the electrode. Over the entire range of oxygen ionisation potentials an anodic current due to the oxidation of hydrogen peroxide is observed at the ring, which indicates the formation of hydrogen peroxide as an intermediate. When the polarisation curve for the ionisation of oxygen is "corrected" for the amount of unreacted hydrogen peroxide, curve *1′* (Fig. 11) with a limiting diffusion current plateau is obtained. This shows that the observed discrepancies between the experimental current and the diffusion current are due to the low rate of reduction of hydrogen peroxide.

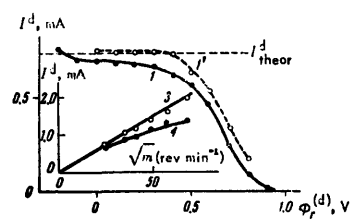



Fig. 11. 1) Polarisation curve for the reduction of oxygen at a silver disc electrode at a rate of rotation of the latter of 600 rev min$^{-1}$; 1′) currents corrected for the amount of unreacted hydrogen peroxide; 3) and 4) variation of the current at the disc electrode with $\sqrt{m}$ [3) limiting diffusion current; 4) current at $\varphi$ = 0.3 V]; open circles — corrected currents; data of Zhutaeva et al.[75]

The dependence of the currents at the ring electrode and also of the relative yield of hydrogen peroxide on the potential of the disc is presented in Fig. 12, which shows that, at a potential of 0.85 V in 1 *N* KOH, a 100% yield of hydrogen peroxide is observed, and therefore under these conditions the ionisation of oxygen proceeds by reaction (2′) with participation of two electrons. At less positive potentials there is at first a sharp and then a gradual decrease in the amount of hydrogen peroxide removed into the bulk of the solution. This is accompanied by an increase in the average number of electrons involved in the reaction. At a potential $\varphi_r$ of about 0.0 V the current corresponding to the four-electron process is attained. When the concentration of the KOH solution is varied, the region of the 100% yield of hydrogen peroxide also shifts; thus in 1 *N* KOH solution this yield is observed in the range of potentials $\varphi_r$ between 0.9 and 0.8 V, while in the solution at pH 7.2 it occurs over a wider range of potentials, $\varphi_r$ = = 1.2–0.8 V.

The polarisation curves for the ionisation of oxygen on silver show hysteresis, i.e. the reverse, anodic curves are displaced towards higher current densities. Comparison of the results obtained with a ring electrode with these data shows that the increase in current at the disc for the anodic curve is accompanied by a reduction in the amount of hydrogen peroxide detected at the ring. The observed acceleration of the ionisation of oxygen is associated with the reduction of the surface of the silver during the period corresponding to the cathodic curve. This is confirmed by the polarisation curves for the ionisation of oxygen measured at various amplitudes of triangular potential pulses applied to the silver electrode: from -0.2 V to *x* V, where *x* varies from 1 to 0 V (Fig. 13). These curves show that the degree of oxidation of the electrode increases, the current at the disc electrode falls, and the amount of hydrogen peroxide detected at the ring increases, as with the rhodium electrode. The retardation of the ionisation of oxygen when the degree of oxidation of silver increases may be due to the retardation of the reduction of hydrogen peroxide. It is also not impossible that on silver a fraction of the total current is associated with four-electron ionisation of oxygen, which takes place without intermediate formation of hydrogen peroxide [reactions (5) and (6)] and that this fraction varies with the potential.

Study of the kinetics of the ionisation of oxygen on silver in 1 *N* KOH solution showed that the *b* coefficient in

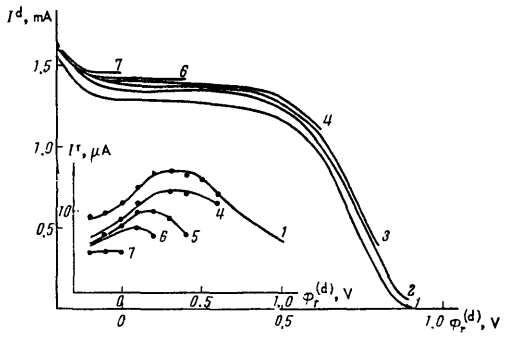



Fig. 13. Polarisation curves for the reduction of oxygen ($I^d$) and the variation of the current $I^r$ at the ring electrode with the potential of the disc electrode at $m$ = 2400 rev × ×min$^{-1}$ for different amplitudes of triangular pulses: 1) $\Delta\varphi$ between 1.0 and -0.2 V; 2) $\Delta\varphi$ between 0.9 and -0.2 V; 3) $\Delta\varphi$ between 0.8 and -0.2 V; 4) $\Delta\varphi$ between 0.6 and -0.2 V; 5) $\Delta\varphi$ between 0.4 and -0.2 V; 6) $\Delta\varphi$ between 0.2 and -0.2 V; 7) $\Delta\varphi$ between zero and -0.2 V; data of Zhutaeva et al.[75]

Eqn. (14), i.e. the slope of the polarisation curves and of the curves representing the variation of the potential with the logarithm of the partial pressure of oxygen, is 0.025–0.030 V. The value of the coefficient

$$\left(\frac{\partial\varphi}{\partial\,\mathrm{pH}}\right)_{i,\,P_{O_2}}$$

is approximately the same.

Fig. 14 presents the polarisation curve for the ionisation of oxygen and the oxidation of hydrogen peroxide in alkaline solution with added hydrogen peroxide, and shows that the cathodic and anodic branches form a single continuous curve merging into one another without an intermediate step. The continuity of the mixed polarisation curve and the displacement of the potential towards cathodic values with increase in the concentration of hydrogen peroxide show unambiguously that in the vicinity of the steady-state potential the system oxygen–hydrogen peroxide is at equilibrium. Thus the data suggest that relations similar to those observed with the mercury electrode obtain in the reduction of oxygen in an alkaline solution at potentials close to the steady-state value.

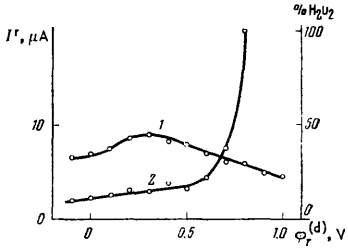



Fig. 12. Variation of the current at the ring electrode (curve 1) and of the ratio of hydrogen peroxide which failed to react at the disc electrode to $I^d_{exp}$ (curve 2) with the potential of the disc electrode at $m$ = 600 rev min$^{-1}$; data of Zhutaeva et al.[75]

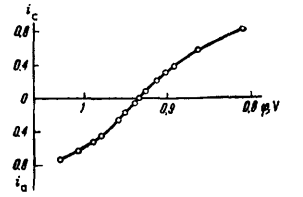



Fig. 14. Mixed anodic–cathodic polarisation curve for the reduction of oxygen and oxidation of hydrogen peroxide on silver in 1 *N* KOH solution.

The problem of different pathways for the reduction of surface silver oxides was also elucidated by a combination of the methods based on the rotating disc electrode with a ring and triangular potential pulses. It was shown that, over the entire range of rates of application of the potential, hydrogen peroxide was not detected at the ring. This suggests that oxygen adsorbed on silver during anodic polarisation is reduced directly to hydroxide ions.

The form of oxygen and the nature of its bond with the surface significantly affect the kinetics of its reduction. Silver is known to adsorb oxygen in large amounts. The presence of various forms of oxygen adsorbed on silver[77-83], with different reactivities, has a considerable effect on the kinetics of its reduction.

The effect of the form of adsorbed oxygen on its reduction on a carbon electrode was studied in detail by Frumkin and Burshtein[84]. They clearly showed that hydrogen peroxide is formed only from freshly adsorbed molecular oxygen. After the oxygen has remained for some time on the surface of the carbon, it is converted into the atomic form and is reduced to water.

It must be emphasised that many workers have concluded that at least part of the oxygen adsorbed on the surface of silver is present in the molecular form[85]. The method involving the application of trapezoidal potential pulses to the electrode can be usefully employed to characterise the strength of the bond between adsorbed oxygen and the surface of silver, which is to a large extent determined by the residence time of oxygen on the surface. In the experiments of Shumilova et al.[76] trapezoidal potential pulses were applied to a silver electrode at a rate of change of potential of 10 V $s^{-1}$, with an amplitude of 0–1.0 V, the electrode being maintained at 1.0 V for various times. At the same time $i-t$ curves were recorded at the potential corresponding to the horizontal section of the trapezium. The curves obtained show (Fig. 15) that, for periods during which the electrode is kept at a constant potential not exceeding the duration of the pulse (0.1 s), the amount of electricity passing through the electrode during the cathodic half-period of the pulse ($Q_c$) increases continuously with the period at fixed potential and the increment in $Q_c$ coincides with the value of $Q$ calculated from the $i-t$ curves. For periods exceeding 0.1 s, $Q$ remains constant while the amount of electricity passed through the electrode during this time continues to increase. The curves in Fig. 15 show that the current corresponding to the cathodic curves decreases in the potential range 1.0–0.75 V.

The observed increase of $Q_c$ when $\tau \leq 0.1$ s may be associated with the accumulation of oxygen on the surface of the electrode during the period at a constant potential. The phenomena which occur on further increase in this period (increase in the overvoltage for oxygen desorption processes and attainment of a constant value of $Q_c$) suggest that the bond between oxygen and the surface of silver becomes strengthened. The penetration of oxygen into the bulk of the metal is also possible. The latter possibility is confirmed by the observation of a current on $i-t$ curves up to $\tau = 1$ s, which indicates the occurrence of some processes on the electrode during the period when it is maintained at $\varphi = 1.0$ V.

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The electrochemical reduction of oxygen is a complex electrochemical reaction whose mechanism can be established only by a wide variety of investigations. The present review shows that undoubted advances have been made in the study of this reaction on metallic electrodes, largely as a result of the development and application of new experimental techniques.

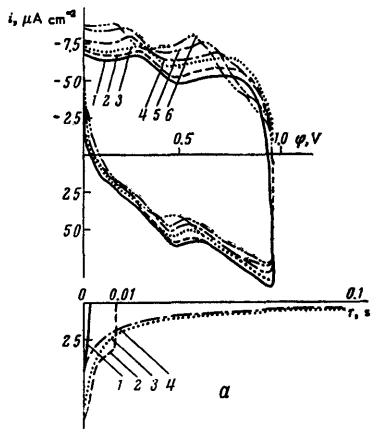



Fig. 15. $i-\varphi$ curves for silver in 1 $N$ KOH solution with pulses applied at a rate of change of potential of 10 V $s^{-1}$ and amplitude 0–1.0 V, and $i-t$ curves for the electrode maintained at $\varphi = 1.0$ V (horizontal section of the trapezium) for various times; $i-\varphi$ curves:
1) 40 μs; 2) 10 ms; 3) 100 ms; 4) 1 s; 5) 17 s; 6) 2 min;
*a*) $i-t$ curves at $\varphi = 1.0$ V:
1) 40 μs; 2) 10 ms; 3) 100 ms; 4) 300 ms; data of Shumilova et al.[76]

A large number of the experiments whose results are described in this article have been carried out in the Department of Electrochemistry in the Lomonosov Moscow State University and in the Institute of Electrochemistry of the USSR Academy of Sciences under the direction of A. N. Frumkin, who is responsible for many ideas on which the study of the electrochemical reduction of oxygen is based.

Despite these achievements, the problem of the cathodic reduction of oxygen is not exhausted. Many questions still remain unresolved. For example, the mechanism of the heterogeneous catalytic decomposition of hydrogen peroxide still remains obscure; the available data on the nature of the energy heterogeneity of the surface of solid electrodes, the nature and forms of adsorbed oxygen at various electrode potentials, etc., are inadequate.

However, bearing in mind the rapid development of the theory of electrochemical kinetics and the progress in the field of experimental techniques, there are grounds for a firm belief that many problems which are at present obscure will be successfully solved in the near future.

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# STUDY OF THE STRUCTURE OF THE ELECTRICAL DOUBLE LAYER ON PLATINUM BY THE RADIOACTIVE TRACER METHOD

N. A. Balashova and V. E. Kazarinov

When a metal is immersed in a solution of an electrolyte, a layer whose structure has a powerful influence on the course of electrochemical reactions (as first pointed out by Frumkin) appears at the phase boundary.

The primary process in the formation of this surface layer is adsorption of ions, atoms, and molecules, determined by the electrical and chemical forces which operate at the interface and by the properties of the adsorbed species. The complexity of these processes and their specificity with respect to particular systems necessitate a detailed study by methods of very high accuracy and sensitivity.

The structure of the surface layer is usually investigated by a variety of electrochemical methods. These give an insight, specifically, into the very important influence of the potential drop at the electrode–electrolyte interface upon the primary process. A large number of these studies, particularly at the liquid mercury electrode, have been reported.

However, electrochemical methods cannot give direct access to the qualitative and quantitative composition of the surface layer. For this, the methods of analytical chemistry are required. Euler was the first to study the adsorption of silver ions on silver by a chemical method[1]. Frumkin and Obrucheva first demonstrated the relationship between ion adsorption and the formation of an electrical double layer on platinum by chemical titration[2]. Kolthoff and Kameda[3] studied the adsorption of electrolytes by similar methods. The determination of amounts adsorbed by chemical methods is very difficult, and sometimes even impossible, because of the minute amounts involved and of the lack of suitable analytical techniques: therefore, chemical methods have not been widely applied to these problems.

The radioactive tracer method, in which the element under study is labelled with one of its radioactive isotopes in solution or in the solid phase, has proved very fruitful in this respect. Changes in the radioactivity of the experimental system give a fast, accurate, and very reliable indication of the transfer of species across the phase boundary. This method is the most sensitive of all the existing methods for observing the behaviour of the components of a metal–electrolyte system, and has achieved increasing importance in recent years. Its earliest applications to the study of metal ion adsorption, exchange, and discharge processes are due to Hevesy and Paneth[4-7] and to Spitsyn[8], who used naturally occurring radioactive isotopes, and more recently to Joliot-Curie[9], Haissinsky[10], and Erbacher[11-13], who also used artificial radioactive isotopes. In recent years, the rate of publication of papers on the adsorption of ions on metals, using radioactive tracers, has been increasing steeply. Among the most noteworthy are those by Hackerman[14], who studied the adsorption of $SO_4^{2-}$ ions on iron, Heusler and Cartledge[15] and Iofa and Rozhdestvenskaya[16] on the adsorption of iodine on iron, Kolotyrkin and his coworkers on the adsorption of iodine on lead and silver[17,18], Schwabe and his coworkers on the adsorption of various ions on platinum[19-23], and others[24,26].

In all this work little attempt was made to measure the potentials of the adsorbents, and therefore the results cannot be used to characterise the relationship between the adsorption and the electrochemical behaviour of the metal–electrolyte system. A notable exception is the paper by Frumkin et al.[27], in which the adsorption of ions on platinum was studied by chemical titration, the change in the concentration of hydrogen ions in solution, due to the adsorption of cations and anions at different potentials, being determined. However, these changes characterise only the difference in extent of adsorption between anions and cations.

The present review discusses the results of the investigations of the double-layer structure and of the adsorption of ions on platinum, carried out in Frumkin's laboratory, using radioactive isotopes as indicators of the behaviour of the ions of interest. This work has relied on the simplest and most general radiochemical procedures, used in conjunction with electrochemical measurements — the typical approach of the Soviet workers in this field.

Concurrent measurements of adsorption and of the electrochemical parameters of the electrode provide information on the detailed structure of the surface layer, and on the direct relationship between the adsorption and the electrochemical behaviour of the layer. The radiochemical methods of identification and estimation of the amount adsorbed offer highly sensitive, simple, rapid, and specific measurements, and are therefore the most convenient. Frequently, they are the only direct method for investigating the dependence of the electrochemical behaviour of a metal upon the structure of the boundary between the metal and an electrolyte.

We shall show that this dependence is extremely important, and often determines the overall ionic adsorption at a metal surface resulting from electrostatic and also from other types of force operating at the solution boundary. In

addition to the studies of adsorption as a function of potential, work has been done on the kinetics of the adsorption of ions, their dependence on the concentration of ions in solution, the degree of irreversibility of the adsorption (as measured by desorption under various conditions and by the exchange of adsorbed ions with the ions of the electrolyte), the influence of pretreatment of the metal on the adsorption, and the possibility of penetration of adsorbed ions into the bulk of the metal.

Different variants of the procedure have been developed and used to deal with particular problems; these consist in measuring the radioactivity of the solution, or alternatively in measuring the radioactivity of the electrode still wet with a layer of solution or rinsed under specified conditions.

Great care was taken into the experiments to observe the particular conditions needed to achieve correct results. These conditions include: standard preparation of the electrode surface, radiochemical and chemical purity of the tracers, and correct choice of the ratios of area of the adsorbing surface to volume of solution and of concentration of stable ions to concentration of radioactive ions in solution.

There are now available several new methods, in a number of variants, for measuring adsorption from the change in radioactivity of a metal specimen without removing the specimen from the solution where adsorption has taken place. Many of these are developments of the method of Joliot-Curie, put forward as long ago as 1930. Modern methods of measuring adsorption by using radioactive tracers have already been reviewed[28,29]. Most of the researches discussed in this paper have made use of a method, developed at the Institute of Electrochemistry of the Academy of Sciences of the USSR, in which adsorption is measured from the change in radioactivity of the electrode, withdrawn from the solution at predetermined intervals. A correction for the activity of the wetting layer is applied.

Studies of the surface layer at a metal–solution interface become more complicated if the metal is corrodible. The platinum electrode is particularly convenient in this respect because exchange between ions in solution and the metal is practically absent, and also because its electrochemical behaviour is known in fair detail and this facilitates comparison with the adsorption behaviour. The electrochemical behaviour of the platinum electrode has been studied by a variety of methods by Frumkin and some of his students — Shlygin, Ershler, Veselovskii — and also by a number of foreign workers — Breiter, Knorr, Wicke and Weblus, Wiebe and Winkler, and others. On the basis of the experimental results[27] obtained by his school, Frumkin has developed a theory of the platinum electrode.

The results show that the electrochemical behaviour of platinum changes in the region between the hydrogen and the oxygen electrode potential, and that this can be explained by the adsorption of hydrogen, of ions from the solution, and of oxygen. Experiments with labelled ions on a platinum electrode polarised to a known potential have made possible a quantitative study of the fine details of the ion adsorption process.

If the simplest picture of the structure of the electrical double layer on metals in the absence of specific adsorption is adopted, preferential adsorption of cations and of anions should occur in the region of negative and positive potentials respectively. The adsorption of both kinds of ion should vanish at the zero-charge potential. If the adsorption of ions is not determined exclusively by the surface charge, adsorption can occur at the zero-charge potential as well as on a charged surface. Ions showing strong specific adsorption shift the point of zero charge of the metal. These predictions of the theory have been repeatedly confirmed by experiments on mercury, but for solid metals there were practically no data of this type prior to the use of radioactive tracers.

According to their adsorption behaviour on mercury, ions can be classified into two groups: the surface-active and the surface-inactive.

We shall give an account of the results which have been reported on the adsorption of sulphate and phosphate anions, considered to be surface-inactive, and on the adsorption of chloride, bromide, and iodide anions, which are typical surface-active anions. Anion adsorption has been studied either separately from or jointly with the adsorption of the surface-inactive cations of sodium, caesium, calcium, and barium in acid and in alkaline solutions, and the surface-active cadmium cations in acid solutions.

Analysis of the results on the simultaneous adsorption of cations and anions leads to a complete picture of the structure of the electrical double layer and of the position of the point of zero charge of the metal. The idea was put forward by Frumkin and developed by his school.

Different anions are adsorbed to different extents at a given potential. Plots of anion and cation adsorption against potential for platinised platinum in acid and alkaline solutions of their salts are shown in Figs. 1–6. In some experiments the change in hydrogen ion concentration in solution corresponding to the difference between anion and cation adsorption was measured in parallel with the radiochemical measurements of the adsorption of anions and cations. In Figs. 2 and 3 this change is denoted by $\Gamma_{H^+}$, and referred to 1 cm² of true surface area. Increase in hydrogen ion concentration indicates preferential adsorption of cations ($-\Gamma_{H^+}$), whereas a decrease indicates preferential adsorption of anions ($+\Gamma_{H^+}$).

In Figs. 2 and 3, taken from Kazarinov[31], the curves for the anions, obtained from measurements of hydrogen ion concentration, are shown by broken lines (curves *2*). The intersection between these curves and the adsorption curves for $Na^+$ cations (curves *1*) provides an accurate value for the zero-charge potential of platinum. In the

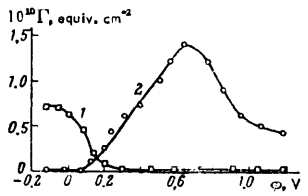



Fig. 1. Variation of the extent of adsorption of $SO_4^{2-}$ anions (curve 2) and $Cs^+$ cations (curve 1) with potential of the platinum in $10^{-2}$ *N* $Cs_2SO_4$ + $10^{-2}$ *N* $H_2SO_4$; data of Kazarinov and Balashova[30].

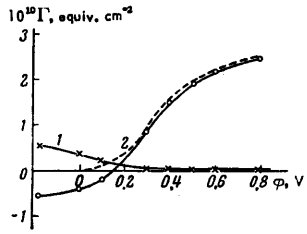



Fig.2. Variation of the quantities $\Gamma_{Na^+}$ (curve 1), $\Gamma_{Cl^-}$ (curve 2), and $\Gamma_{H^+}$ (curve 3) with potential; original solution $1 \times 10^{-3}$ *N* NaCl + $1 \times 10^{-3}$ *N* HCl.

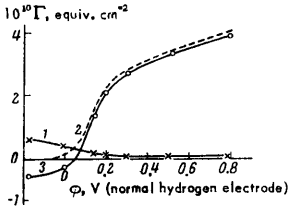



Fig.3. Variation of the quantities $\Gamma_{Na^+}$ (curve 1), $\Gamma_{Br^-}$ (curve 2), and $\Gamma_{H^+}$ (curve 3) with potential; original solution $1 \times 10^{-3}$ *N* NaBr + $1 \times 10^{-3}$ *N* $H_2SO_4$.

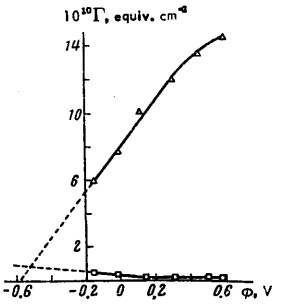



Fig.4. Variation of the quantities $\Gamma_{I^-}$(Δ) and $\Gamma_{Na^+}$(□) with potential; original solution $5 \times 10^{-3}$ *N* NaI + $5 \times 10^{-3}$ *N* $H_2SO_4$.

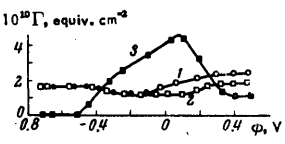



Fig.5. Variation of the extent of adsorption of $Br^-$ anions and $Na^+$ cations with platinum potential; solution $10^{-2}$ *N* NaBr + + $10^{-2}$ *N* NaOH (curve 2 for $Na^+$ and curve 3 for $Br^-$); curve 1 is for a $10^{-2}$ *N* NaOH solution; data of Kazarinov[32].

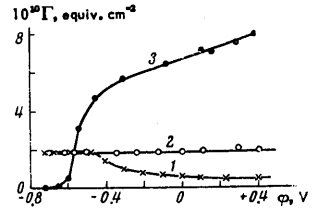



Fig.6. Variation of the extent of adsorption of $I^-$ anions and $Cs^+$ cations with potential in alkaline solution; curve 1 is for $Cs^+$ and curve 3 is for $I^-$ in $10^{-2}$ *N* CsI + $10^{-2}$ *N* CsOH; curve 2 is for $Cs^+$ in $10^{-2}$ *N* CsOH; data of Kazarinov[32].

absence of specific adsorption of ions, the charge of the ionic double layer should be zero, but it is easy to see from the Table and from the figures that such is not the case, even in a solution of sulphuric acid and caesium sulphate. The extent of adsorption at the zero-charge potential in this solution amounts to $1.50 \times 10^{-11}$ g-ion × × cm$^{-2}$, or 1/6 of the maximum extent of adsorption, corresponding to 0.01 of a monolayer. The tabulated data show that on changing from sulphate to halide anions, the extent of the superequivalent anion adsorption increases in the sequence $Cl^- < Br^- < I^-$ (since the cation remains the same). The same is true of changing from acid to alkaline solutions.

Figs. 1–6 show that the zero-charge potential in halide solutions is shifted towards more negative values as compared with its position in sulphate solutions. This shift is more marked, the higher the surface activity of the anion, i.e. it increases in the series $Cl^- < Br^- \ll I^-$. In an iodide solution and at potentials between -0.2 V and 0.06 V, in which the platinum surface carries a positive charge, $Na^+$ cations are adsorbed at the same time as iodide ions (Fig. 4). This means that iodide ions are adsorbed on the positively charged surface in greater numbers than required by the charge. The superequivalent adsorption of anions causes cation adsorption. Consequently, adsorption of iodide ions from acid solution reverses the charge of a platinum surface.

The zero-charge potentials obtained for acid solutions containing $SO_4^{2-}$, $Cl^-$, and $Br^-$ anions are in satisfactory agreement with the results given by other methods[27,33],

TABLE*.

| Solution | Zero-charge potential $\varphi_0$, V (n. hydrogen e-de) | Shift of $\varphi_0$, V | $10^{11}$ × extent of adsorption at $\varphi_0$, g-ion cm$^{-2}$ |
|---|---|---|---|
| $10^{-2}$ *N* $Cs_2SO_4$ + $10^{-2}$*N* $H_2SO_4$ | 0.17 | — | 1.5 |
| $10^{-2}$ *N* NaCl + $10^{-2}$*N* HCl | 0.10 | —0.07 | 1.6 |
| $10^{-2}$ *N* NaBr + $10^{-2}$ $H_2SO_4$ | 0.04 | —0.13 | 3.5 |
| $5 \cdot 10^{-2}$ *N* NaI + $5 \cdot 10^{-2}$*N* $H_2SO_4$ | —0.50 | —0.70 | ~10.0 |
| $10^{-2}$ *N* NaBr + $10^{-2}$*N* NaOH | —0.38 | | 15.5 |
| $10^{-2}$ *N* CsI + $10^{-2}$ *N* CsOH | —0.58 | | 20.0 |
| $10^{-2}$ *N* $CdSO_4$ + $10^{-2}$*N* $H_2SO_4$ | ~0.9 | 0.7 | 3.0 |
| $10^{-2}$ *N* $CdSO_4$ + $10^{-2}$*N* $H_2SO_4^+$ + $10^{-2}$*N* KBr | 0.5 | 0.3 | 20.0 |
| $10^{-2}$ *N* $CdSO_4$ + $10^{-2}$*N* $H_2SO_4^+$ + $10^{-2}$*N* KI | 0.01 | —0.05 | 80.0 |

* All potentials are relative to the normal hydrogen electrode.

thus confirming the value of the radiochemical method in these systems. Comparative data for the other zero--charge potentials do not exist in the literature.

As Fig. 1 shows, the extent of cation adsorption in an acid solution of caesium sulphate is practically constant in the neighbourhood of the hydrogen potential. This is because the adsorption of cations depends on the number of hydrogen atoms adsorbed, which also contribute to the creation of a potential drop in this region.

In accordance with theory, the extent of anion adsorption increases and that of cation adsorption decreases as the platinum surface acquires a positive charge in acid solution, until a potential is reached where oxygen adsorption sets in (as shown by the charging curves). Oxygen and platinum form dipoles which are oriented with their negative ends towards the solution[27]. Before oxidation begins, the anions differ in extent of adsorption, in their influence on the position of the zero-charge potential, and in the degree of irreversibility of their adsorption. These differences are more marked, the greater the difference in surface activity of the anions. The $SO_4^{2-}$ anions are the least surface-active on platinum, the surface activity increasing from sulphate to phosphate and further to the chloride, bromide, and iodide anions. These differences, associated with the nature of the anion, completely determine the behaviour of platinum towards oxygen. If the surface activity of the anion is much less than that of oxygen, oxygen is readily adsorbed on the platinum and displaces previously adsorbed anions into the solution. This effect has been observed under equilibrium conditions only with the sulphate anion. In this case, changing the potential from the hydrogen potential towards more positive values produces an adsorption curve with a maximum at the potential of incipient oxygen adsorption. At this maximum, the adsorption of sulphate anions amounts to ~18% of full coverage by sulphate. Therefore, even though ~80% of the surface remains free of $SO_4^{2-}$ anions, the oxygen dislodges into the solution most of the adsorbed anions when it becomes adsorbed and forms dipoles with the platinum. The $SO_4^{2-}$ anions which are more firmly held (not by electrostatic forces) may not be fully desorbed under these conditions, as shown by the curves of Fig. 1.

In every other solution which has been examined, the previously adsorbed anions are so firmly bound to the platinum that oxygen adsorption is hindered in proportion to the stability of the anion–metal bond, i.e. in proportion to the observed irreversibility of the adsorption. These barriers to oxygen adsorption take the form of an increase in the adsorption potential, as shown by the charging curves. The effect was first reported by Ershler[34] for $Cl^-$, and later by Obrucheva[35] for $Cl^-$ and $Br^-$. Adsorption–potential curves for the anions $H_2PO_4^-$, $Cl^-$, $Br^-$, and $I^-$ on a platinum surface not previously oxidised do not show a maximum.

The adsorption maximum observed (Fig. 5) for bromide anions in alkaline solution can be explained as follows. In the potential region from -0.2 V to the potential of the adsorption maximum the whole of the charge is expended effectively upon bromine adsorption, since the electrode capacity as calculated from the adsorption curves and the charging curves has the constant value 70 $\mu F\ cm^{-2}$. Hence, oxygen adsorption does not occur in this region. It can be seen from the charging curve that oxygen adsorption sets in at the potential of the maximum on the adsorption curve. The adsorbed oxygen displaces most of the bromine from the platinum surface. The residual trace of chemisorbed bromine is probably incorporated into the oxide film which forms on the platinum. Thus, the behaviour of the strongly surface-active bromide ions in alkaline solution is reminiscent of that of the weakly surface-active $SO_4^{2-}$ anions in acid solution.

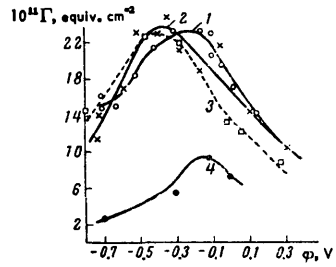



Fig. 7. Variation with potential of the extent of adsorption of cations from alkaline solution:
1) for $Ca^{2+}$ from $10^{-3}$ *N* $Ca(OH)_2$; 2) for $Ba^{2+}$ from $10^{-3}$ *N* $Ba(OH)_2$; 3) for $Ba^{2+}$ from $10^{-3}$ *N* $Ba(OH)_2$ + 1 *N* NaOH; 4) for $Ca^{2+}$ from $10^{-3}$ *N* $Ca(OH)_2$ + 1 *N* NaOH.

It is interesting to note that adsorption curves of the same general trend are observed during cation adsorption, in particular with calcium and barium on non-oxidised platinum in alkaline solutions (Fig. 7), although the maximum is entirely different in nature[36]. In the adsorption of these cations the increase of adsorption with potential up to a maximum may be due to oxygen adsorption. This is suggested, firstly, by the lack of a cation adsorption maximum on platinum which has not been carefully reduced. Secondly, it has been shown experimentally that complete desorption of calcium and barium cations requires decomposition of the oxide film (achieved by prolonged exposure to acid or, more rapidly, by cathodic polarisation of the electrode in an acid medium). Radiochemical measurements of the exchange between adsorbed $Ca^{2+}$ and $Ba^{2+}$ cations and the same cations in solution have shown that the strength of the bond between the adsorbed cations and the platinum depends on the adsorption potential. When adsorption takes place from alkaline solution at the hydrogen potential, exchange in a hydrogen atmosphere and in $Ca(OH)_2$ or $Ba(OH)_2$ solution proceeds to the extent of 26% in one minute, but after adsorption at the maximum potential or at still more positive potentials the exchange is strongly retarded. Thus, at an adsorption potential of 0.48 V exchange occurs to the extent of only ~6% in the same time. It is evident that over the whole of the potential region examined the cations are incorporated into the oxide film, but at potentials more positive than the maximum the binding of the cations to the adsorbed oxygen is weaker than at less positive potentials and some of the cations pass into the solution. This effect may be associated with the different degree of hydration of oxides formed at different potentials in alkaline solution.

The doubly charged cations $Ca^{2+}$ and $Ba^{2+}$, when adsorbed from acid solution, are more weakly bound to the platinum over the whole range of potentials than cations similarly adsorbed from alkaline solutions. Thus, $Ca^{2+}$ and $Ba^{2+}$ undergo almost complete exchange with their ions in solution (~96–100% in one minute) when adsorbed from acid solution at the hydrogen potential, at which the platinum

remains unoxidised. If the platinum is not given a preliminary reducing treatment the exchange proceeds only to the extent of 70–80%. At the potential which platinum attains in air, exchange of adsorbed cations is either undetectable or relatively small.

All these results show that cations are firmly bound to the oxide film on platinum after being adsorbed. As a result of this work, we are able to explain the mechanism of the influence of doubly charged cations on the reduction of oxygen on platinum in acid and in alkaline solutions. The phenomenon was observed in studies[37,38] of the electrochemical reduction of oxygen at a platinum electrode. It was found that small amounts ($10^{-3}$ *N* in 1 *N* NaOH) of calcium, strontium, or barium salts decrease, in that order, the current efficiency of the formation of hydrogen peroxide by oxygen reduction. Balashova and Kulezneva[36] showed that under the conditions of the electrolysis experiments these cations are adsorbed and form adsorbed compounds with oxygen and platinum which are more stable than the compounds formed in the absence of the cations. The presence of a thousandfold excess of sodium cations decreases the extent of adsorption of $Ca^{2+}$ (see curve *4* of Fig. 7), but has practically no effect on the adsorption of $Ba^{2+}$ (curve *3* of Fig. 7), which accounts for the more marked effect of the latter cation.

In acid solutions the adsorption of the doubly charged cations $Ca^{2+}$ and $Ba^{2+}$ varies with potential in much the same way as the adsorption of singly charged cations (Fig. 8); at the potentials corresponding to incipient electrochemical reduction of oxygen the extent of adsorption of the cations $Ca^{2+}$ and $Ba^{2+}$ is small, and cannot have an appreciable effect on the process.

Müller and Sobol'[38] also concluded that the oxide film is stabilised by calcium, strontium, and barium cations. Those workers studied the effect of these cations on the polarisation curves obtained at a rotating disc platinum electrode combined with a ring electrode, and were able to demonstrate by their sensitive procedure the features of the separate stages in the reduction of oxygen in the presence of doubly charged cations.

Radiochemical and electrochemical measurements of the adsorption of anions on previously oxidised platinum have shown that the greater the adsorption of oxygen and the more stable its bonding to the platinum, the slower is the adsorption of anions, even when their surface activity is quite high. Thus, for example, bromide anions are adsorbed very slowly on platinum oxidised to a potential of 1.2 V, because they are required to dislodge previously adsorbed oxygen. However, if some of the adsorbed oxygen is removed by cathodic polarisation, rapid adsorption of the anion occurs and continues until the oxygen is completely removed[39]. Desorption of the anions begins at potentials such that hydrogen already imparts a negative charge to the surface. As a result, a maximum appears on the extent of adsorption–potential curves for the adsorption of a surface-active anion on previously oxidised platinum.

The retardation of anion adsorption by previously adsorbed oxygen is easily followed by radiochemical measurements of adsorption on platinum oxidised in air for different times. Experiments of this type have shown that the adsorption of the anions $Br^-$, $H_2PO_4^-$, etc., becomes slower, the longer the oxidation time of the platinum, i.e. the greater the adsorption of oxygen and the stronger its binding to the metal surface[39,40]. The difference in time of adsorption on oxidised platinum of different anions demonstrates the higher stability of the anion–platinum bond as compared with the oxygen–platinum bond. Slow anion adsorption on platinum is observed only in the presence of oxygen adsorbed on the platinum. As Schwabe and his coworkers have shown[20], on vacuum-deposited platinum the adsorption of surface-active anions goes to completion very rapidly (in less than one minute), whereas many hours are needed when the surface has been oxidised.

Some very interesting results have been obtained by the radiochemical method on the kinetics of simultaneous adsorption of iodide anions and caesium cations from alkaline solution on platinised platinum (Fig. 9). Curves *1* and *1′* describe the adsorption kinetics of the two kinds of ion on platinum previously oxidised in air for 30 min, curves *2* and *2′* refer to platinum oxidised for 16 h. During the initial period of the adsorption process cation adsorption is significantly higher than anion adsorption. The iodide anions are adsorbed slowly because they have to dislodge the previously adsorbed oxygen, whereas the cations can attach themselves directly to the oxide film. However, the extent of anion adsorption increases with time whilst that of cation adsorption decreases. The longer the preliminary oxidation of the platinum, the more is the falling off of the extent of cation adsorption delayed. The slope of the kinetic curves for the anions varies with time, denoting a change in the rate of adsorption, which is consistent with the displacement, initially, of the less firmly bound oxygen, and afterwards of the oxygen which

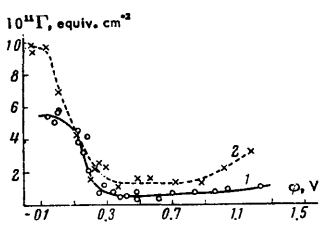



Fig. 8. Variation with potential of the extent of adsorption of the cations $Ca^{2+}$ (curve 1) and $Ba^{2+}$ (curve 2) from acid solutions [$10^{-3}$ *N* $HClO_4$ + $10^{-3}$ *N* $Ca(ClO_4)_2$ and $10^{-3}$ *N* $HClO_4$ + + $10^{-3}$ *N* $Ba(ClO_4)_2$ respectively].

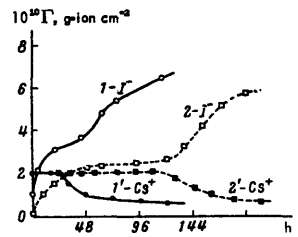



Fig. 9. Kinetics of the adsorption of $I^-$ anions and $Cs^+$ cations on previously oxidised platinum.
1) and 1′) 30 min oxidation; 2) and 2′) 16 h oxidation.

is more firmly bound by virtue of the incorporation of cations. When the Pt–O–Cs bond is disrupted, the stable Pt–I bond can be formed.

We have recently obtained† some results on the adsorption of the surface-active $Cd^{2+}$ cations on platinised platinum which demonstrate an appreciable similarity in behaviour (and in the effect on the structure of the surface layer at the platinum–solution boundary) between cation adsorption and anion adsorption in the presence of sufficiently high surface activity. A proof of the surface activity of cadmium cations was given by Frumkin and his coworkers in a series of investigations by different methods[41–45]. In our own work, we showed with the help of the radioactive isotope $^{115}Cd$ that the adsorption of doubly charged $Cd^{2+}$ cations is very sensitive to the potential and is closely bound up with the adsorption of hydrogen and oxygen on platinum.

Fig. 10 shows the variation of the adsorption of $Cd^{2+}$ with potential: a large maximum occurs near the reversible hydrogen potential. Its origin is not entirely clear, but the maximum is evidently related to the adsorption of hydrogen atoms.

The most interesting feature of the adsorption of $Cd^{2+}$ cations is the positive shift by 700 mV of the point of zero charge as compared with its position in a solution of $Na_2SO_4$.

The extent of adsorption of $Cd^{2+}$ is greatly in excess of that of $Na^+$ cations at all potentials. At the hydrogen potential the extent of adsorption of $Cd^{2+}$ cations amounts to $3 \times 10^{-10}$ g-ion per $cm^2$ of true surface area, i.e. about ten times higher than the extent of adsorption of $Na^+$ cations. This value is unusually high for ionic adsorption: it corresponds to a ratio of 1 cadmium ion to 6 platinum atoms, as compared with 1 singly charged ion to 36 platinum atoms in the case of $Na^+$ adsorption.

Charging curves obtained under the same conditions as the experiments on ion adsorption show that cadmium cations lower the extent of adsorption of hydrogen and oxygen on platinum whilst the charging curve is being explored. $Cd^{2+}$ cations compete with these gases for adsorption on the platinum, just as in the adsorption of the surface-active anions $Br^-$ and $I^-$. The high extent of adsorption of the $Cd^{2+}$ cations, the great stability of their bonds with platinum, and the large shift of the zero-charge point of platinum all point to a chemisorptive type of adsorption for these cations. The $Cd^{2+}$ ions form dipoles with the platinum atoms, with their positive ends pointing into the solution, which should give rise to a negative potential jump at the metal–solution interface. However, the $Cd^{2+}$ ions which are adsorbed in amounts more than equivalent to the charge attract $SO_4^{2-}$ anions at potentials more negative than the zero-charge potential in $CdSO_4$ solution, and as a result the potential jump is actually positive.

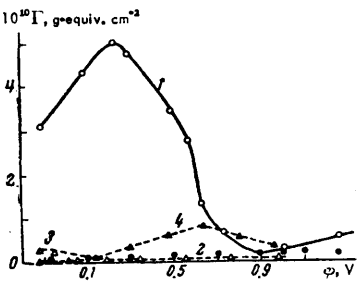



Fig. 10. Variation with potential of the extent of adsorption of cations and anions in acid solution; solutions:
1) and 2) $10^{-2}$ *N* $CdSO_4 + 10^{-2}$ *N* $H_2SO_4$; 3) and 4) $10^{-2}$ *N* $Na_2SO_4 + 10^{-2}$ *N* $H_2SO_4$.

† With the assistance of G. Mansurov.

When the electrolyte contains both surface-active $Cd^{2+}$ cations and surface-active $Br^-$ and $I^-$ anions, the resulting effects on the structure of the surface layer are very complex. Cations and anions compete for adsorption on the platinum, and the net mutual effect is a sensitive function of the surface activities, of the rate of approach to adsorption equilibrium, and of the initial state of the surface.

As an example, the Table shows the zero-charge potentials of platinum under conditions of simultaneous adsorption of surface-active $Cd^{2+}$ cations and $Br^-$ and $I^-$ anions. It is evident from these data that the anions $Br^-$ and $I^-$ have a more pronounced influence on the value of the zero-charge potential than the $Cd^{2+}$ cations under the experimental conditions described above. As a result, the zero-charge potential shifts towards more negative values than cadmium sulphate solution in both cases, but especially so in the case of $I^-$. The effect of adsorbed cadmium cations is quite appreciable, however, since the zero-charge potential is more positive in cadmium bromide or cadmium iodide solutions than in sodium bromide or sodium iodide solutions.

Thus, all the results obtained for the adsorption of cations and anions on platinised platinum from acid or alkaline solutions point to the great complexity and specificity of the phenomena occurring at the platinum–electrolyte boundary. Detailed analysis of these data and comparison with the analogous data obtained for mercury indicates that the structure of the electrical double layer on platinum has a number of specific features. It follows that the concepts of the structure of the double layer on liquid mercury are not always applicable to solid metallic electrodes.

Allowance for the effect of cation and anion adsorption from the electrolyte and for the structure of the surface layer at the platinum–electrolyte boundary is essential in studies of the kinetics of electrode processes with platinum electrodes. This has recently been discussed by Frumkin[46].

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# ORGANIC SEMICONDUCTORS BASED ON POLYETHYLENE

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## I. INTRODUCTION

The earliest observations of properties characteristic of semiconductors in organic compounds were made with some polynuclear hydrocarbons and dyestuffs. Studies of the electrophysical properties of various compounds as a function of their structure led to the conclusion that semiconductor properties arise when a sufficiently well-developed system of conjugated double bonds is present in the molecules. This problem has been the object of many investigations, and has been discussed in a number of review articles [1-3]. It is now well established that organic polymers as well as low-molecular-weight compounds can exhibit semiconductor properties. This widens the scope of possible applications, since the synthesis of polymers with technologically desirable mechanical properties offers the advantages of controlled structure and controlled properties.

Polymeric semiconductors can be prepared either by synthesis from monomers which offer the necessary system of conjugated bonds, or by inducing polyconjugation into the complete polymers by one of several methods. In the former case the possibilities of generating polymers of different structures are almost limitless, but the resulting materials are mostly insoluble and infusible powders, and their molecular weight is not very high. It is possible also to convert a polymeric dielectric gradually into a polymeric semiconductor by radiation-induced structural changes followed by heat treatment. Many studies of the pyrolysis of polymers have been published. The electrophysical properties of the products have been most fully investigated for polyvinylbenzene [4] and polyacrylonitrile [5] for which heat treatment is clearly shown to be a very effective way of raising the conductivity.

Polyethylene is a suitable material for this purpose, because it has a stable polymeric structure and the effect of radiation on it has been studied in detail. It is well known that irradiation develops a structure in polyethylene,

forming 5–7-membered rings with the loss of a significant amount of hydrogen. The basic problem is to find the cross-linking and cyclisation conditions for the linear macromolecules which will lead to the creation of a unified structure, susceptible to subsequent heat treatment, and also to identify the mechanism giving rise to semiconductor properties.

The electrophysical and paramagnetic properties of the products of the radiation-thermal modification of polyethylene (RTMP) have been studied as a function of the dose of radiation absorbed and of the heat-treatment conditions. The following properties have been studied over a wide range of values: the conductivity in a d.c. or a.c. field, its temperature coefficient, the differential thermo-e.m.f., the structure of the products (by ESR and infrared spectroscopy), and lastly the effect of additives and the photoconductivity.

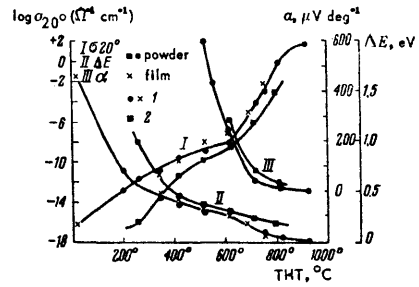



Fig. 1. Variation of electrical characteristics with dose and THT:
1) $D = 2.4 \times 10^4$ Mrad; 2) $D = 1.2 \times 10^3$ Mrad.

## II. PROCEDURE

The products of RTMP have been studied in powder form and as films. The films were deposited as already described[6] on glass or quartz substrates carrying deposited gold electrodes. The samples were irradiated in evacuated quartz bulbs (~ $10^{-5}$ mmHg) with fast electrons (5 MeV) from a U-12 accelerator. The heat treatment of the irradiated samples was by a standard procedure (brief oxidation at 260° followed by pyrolysis in a vacuum[7,8]). The d.c. electrical characteristics of specimens were studied in a vacuum (~ $10^{-5}$ mmHg).[8] Thin-film specimens were examined in surface or multilayer cells, inserted into a special holder. The electrophysical properties of the specimens in powder form were measured in a cell with platinum disc electrodes, at temperatures between 20° and 150° *in vacuo* and in air, and between 20° and -50° for the experiments on specimens with adsorbed iodine.

The d.c. measurements were made with an E6-3 teraohmmeter or with an MO-47 bridge (for low-resistance specimens). The conductivity in an alternating field was measured with an E 10-2 impedance bridge.

Iodine adsorption was measured gravimetrically on a McBain balance, with a temperature control of ±1°C.

The structural properties of the RTMP products were investigated by ESR on an RE 1301 radio-frequency spectrometer.

## III. ELECTRICAL PROPERTIES

Most of the results discussed in the present paper were obtained on RTMP films. The electrophysical properties were studied on samples of polyethylene irradiated with three distinct doses[7]: $1.2 \times 10^3$, $6.9 \times 10^3$, and $2.4 \times 10^4$ Mrad.

Conductivity measurements in the temperature range -25°–150° were in satisfactory agreement with the exponential relationship

$$\sigma = \sigma_0 \exp(-\Delta E/kT).$$

Measurements of differential thermo-e.m.f. showed that the resulting materials are *p*-type semiconductors. Between -50° and 150° the differential thermo-e.m.f. $\alpha$ is independent of the mean specimen temperature within the experimental error. Values of $\sigma_{20°}$, $\Delta E$, and $\alpha$ for specimens in powder and in film form are plotted in Fig. 1 against the temperature of heat treatment (THT) for different doses of radiation.

The figure shows that, by varying the dose and the THT, it is possible to obtain materials for which $\alpha$ varies from 1.5 $\mu$V deg$^{-1}$ to values in excess of 500 $\mu$V deg$^{-1}$, $\sigma_{20°}$ varies from $10^{-14}$ to $10^2$ $\Omega^{-1}$ cm$^{-1}$, and $\Delta E$ from 1.5 to 0 eV. The preliminary heat treatment has a profound effect on the electrophysical properties of the resulting materials. As can be seen from Fig. 1, prescribed values of $\sigma_{20°}$, $\Delta E$, and $\alpha$ are obtained at lower THT, the higher the dose of radiation absorbed by the specimens. The figure also shows that the electrical characteristics of specimens in film and in powder form are in tolerably good agreement. The electronic nature of the conductivity was demonstrated on low-resistance specimens by electrolysis.

Studies of the voltage–current characteristics of different materials have shown that Ohm's law is obeyed at fields between 1 and $2.5 \times 10^3$ V cm$^{-1}$, and that the plot of current against voltage begins to depart from linearity only at fields > $(2.5–5) \times 10^3$ V cm$^{-1}$ (see Fig. 2).

The results summarised in Fig. 1 indicate that materials of different electrophysical characteristics can be prepared by varying either the dose of radiation ($D$) or the THT. Furthermore, as we shall show below, the electrical properties of the products of RTM of polyethylene can also be altered significantly by introducing electron-acceptor impurities (oxygen, iodine). Nevertheless, it can be shown that the nature of the observed electrophysical properties is the same for all the materials, and is determined by their structural characteristics. This involves studying the electrophysical properties as a function not of the dose or the THT, which characterise the preparative conditions used, but of a parameter of the material itself, such as $\sigma_{20°}$. Fig. 3 shows the relationship between $\Delta E$, $\alpha$, and $\sigma_{20°}$ for RTM polyethylene: it is evident that the materials, whether in powder or in film form, obey a common, fairly simple functional relation between $\Delta E$ and $\sigma_{20°}$ irrespective of the dose, THT, or added impurities. This leads us to conclude that the conduction mechanism is the same for all the specimens which have been examined, and that the change in electrical characteristics is fundamentally dictated, as will be shown below, by changes in the height of the potential barriers $\Delta E$ separating regions of polyconjugation.

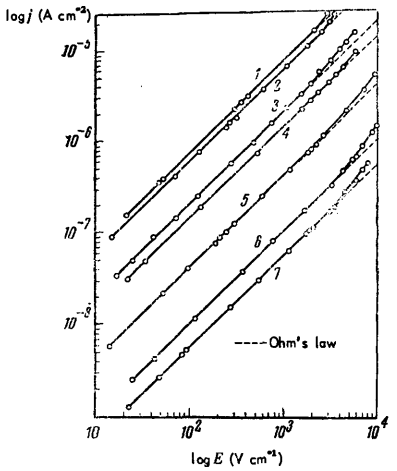



Fig. 2. Current–voltage characteristics of the specimens;
$D = 1.2 \times 10^3$ Mrad: 1) THT = 620°; 6) THT = 520°;
$D = 6.9 \times 10^3$ Mrad: 2) THT = 620°; 4) THT = 520°;
7) THT = 360°;
$D = 2.4 \times 10^4$ Mrad: 3) THT = 530°; 50 THT = 440°.

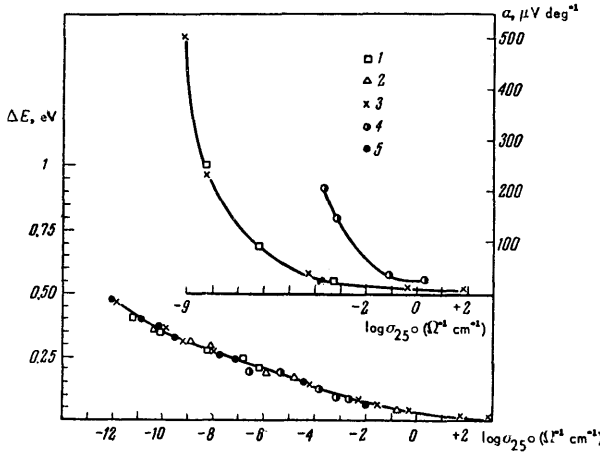



Fig. 3. Relationship between $\sigma_{20°}$, $\Delta E$, and $\alpha$.
Powders: 1) $D = 1.2 \times 10^3$ Mrad; 2) $D = 6.9 \times 10^3$ Mrad; 3) $D = 2.4 \times 10^4$ Mrad; 4) $D = 2.4 \times 10^4$ Mrad + $I_2$ at 20°.
Films: 5) $D = 2.4 \times 10^4$ Mrad.

The change in work function of the products of RTMP as a function of THT is of considerable interest. Boguslavskii's measurements[9] of contact potential difference (CPD) of RTMP films with respect to the glass electrode by the vibrating condenser method reveal a systematic lowering in work function with increasing THT. Table 1 gives the values of work function of the films, and also the activation energies for conduction, as a function of THT. The changes in work function and in activation energy for conduction of specimens prepared at different THT, relative to a specimen prepared at a THT of 720°, are also tabulated.

The agreement between the values of $\Delta E$ and $\varphi$, listed in the last two columns of Table 1, is satisfactory.

TABLE 1.

| $D = 2.4 \times 10^4$ Mrad THT, °C | Contact p.d., V | $\Delta E$, eV | $\varphi$, V | $\Delta E - \Delta E_{720°}$, eV | $\varphi - \varphi_{720°}$, V |
|---|---|---|---|---|---|
| 360 | +0.16 | 0.50 | 5.23 | 0.35 | 0.51 |
| 510 | −0.16 | 0.33 | 4.91 | 0.18 | 0.19 |
| 650 | −0.22 | 0.25 | 4.85 | 0.10 | 0.13 |
| 720 | −0.35 | 0.15 | 4.72 | 0 | 0 |

The frequency dependence (up to 30 Mc/s) of the conductivity of films prepared at different THT has also been investigated[6]: the results are shown in Fig. 4. As a rule, the conductivity increases with increase of frequency and reaches a plateau at 10–20 Mc/s, the frequency at which saturation is reached being lower for the higher THT. For a high-conductivity specimen prepared at a THT of 750°, practically no dispersion of conductivity with frequency is observed. Whereas the d.c. conductivity $\sigma_{20°}$ lies between limits 10 orders of magnitude apart, the conductivity of the same specimens in the region of the plateau ($\sigma_f$) at 10–20 Mc/s frequency spans only two orders of magnitude.

The variation of conductivity with frequency has been measured at different temperatures. Fig. 5 shows that higher measurement temperatures lower the frequency at which the conductivity plateau is reached. (These data refer to a THT of 420°.) The increase of conductivity with temperature in the region of the plateau gives an activation energy of $\Delta E_f \simeq 0.05$ eV, whereas the same specimen in a d.c. field has $\Delta E \simeq 0.5$ eV.

The effect of oxygen on the a.c. conductivity has been investigated. In contrast to the d.c. measurements, where oxygen raises the conductivity and lowers the activation

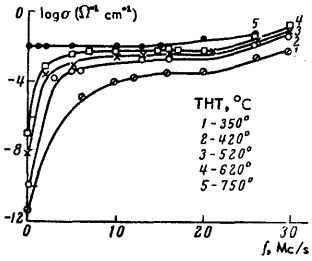



Fig. 4. Frequency dependence of the conductivity of specimens with different THT;
$D = 2.4 \times 10^4$ Mrad.

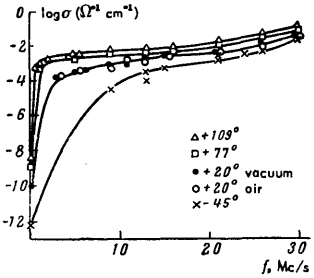



Fig. 5. Variation of conductivity with frequency at different temperatures; specimen with a THT of 440°; $D = 2.4 \times 10^4$ Mrad.

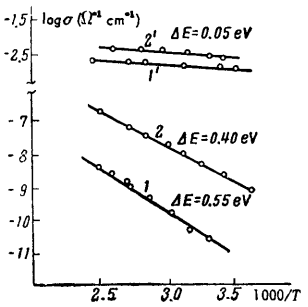



Fig. 6. Temperature dependence of conductivity:
1) and 2) d.c.; 1′) and 2′) 16 Mc/s; 1) and 1′) THT 330°; 2) and 2′) THT 460°.

energy, the conductivity in an a.c. field is quite insensitive to oxygen: Fig. 5 shows that measurements *in vacuo* and in oxygen give identical results.

Fig. 6 shows the temperature variation of the conductivity in a d.c. field and at a frequency of 16 Mc/s (i.e. in the plateau region) for two specimens. It is interesting to compare the values of $\sigma_0$ (from measurements in a d.c. field) and $\sigma_f$ (in the plateau region) for given specimens. As shown in Table 2, $\sigma_0$ and $\sigma_f$ are of the same order of magnitude for all specimens.

In the surface cell film conductivities could be studied up to the temperatures at which the specimens had been prepared, even while the heat treatment was in progress. It was found that conductivity measurements above 250° gave an activation energy for conduction well in excess of the value obtained from measurements between 20° and 150°. Thus, the activation energy calculated from the temperature dependence in the region 20–200° for polyethylene films prepared at a THT of 440° is 0.40 eV, whereas in the temperature range from 250° to 420° the value is 0.90 eV. The corresponding values for specimens with a THT of 520° are 0.30 and 0.75 eV in the low- and the high-temperature region respectively.

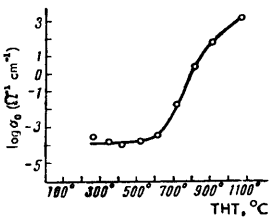



Fig. 7. Variation of $\sigma_0$ with THT.

TABLE 2*.

| THT, °C | $\sigma_0$, Ω⁻¹ cm⁻¹ | $\sigma_f$, Ω⁻¹ cm⁻¹ |
|---|---|---|
| 350 | $1 \times 10^{-3}$ | $2.5 \times 10^{-4}$ |
| 420 | $1.5 \times 10^{-3}$ | $4 \times 10^{-3}$ |
| 520 | $3 \times 10^{-3}$ | $4 \times 10^{-3}$ |
| 620 | $5 \times 10^{-3}$ | $6 \times 10^{-3}$ |
| 760 | $2 \times 10^{-2}$ | $1 \times 10^{-3}$ |

* The variation of $\sigma_0$ with THT is presented in Fig. 7.

Optical and photoelectric effects on RTMP films have been examined[10]. The long-wave absorption edge and the photoelectric sensitivity maximum are both shifted towards the infrared region as the THT is raised.

These observations on the frequency and temperature dependence of the conductivity have led to the hypothesis that the products of RTM of polyethylene have a micro-heterogeneous structure, characterised by regions of high conductivity separated by poorly conducting regions which give rise to the barrier mechanism of current flow.

## IV. ELECTRON SPIN RESONANCE

The electron spin resonance (ESR) method has been used to examine the correctness of this hypothesis. ESR studies of the products of radiation-induced and radiation--thermal modification of polyethylene rely on observations of the shape and width of the ESR line, of the saturation effect, and also of the interaction between paramagnetic centres (p.m.c.) and oxygen molecules as a function of the dose of radiation absorbed and temperature of the subsequent heat treatment. According to published results[11,12], ESR detects alkyl radicals ($-CH_2-\dot{C}H-CH_2-$) in polyethylene which has been irradiated with a dose of less than 10 Mrad, allyl radicals ($-CH_2-\dot{C}H-CH=CH-CH_2-$) for doeses of $10-10^{-2}$ Mrad, and linear polyene radicals ($-CH=CH-\dot{C}H-CH=CH-$) if the dose rises to $4 \times 10^3$ Mrad. The effect of still higher doses had not been previously investigated. We have found[13,14] that at doses in the region of $6 \times 10^3$ Mrad a new ESR line appears, with a width of 7.5 oersted, when the measurements are carried out in the presence of oxygen. The intensity of this line increases with dose.

Material prepared by irradiation of polyethylene to an absorption of $2.2 \times 10^4$ Mrad was used to study the effect of subsequent heat treatment. The variation of line-width with THT is shown in Fig. 8: it is clear that the width measured under moderate vacuum remains constant at 7.5 oersted up to a THT of 400°, and at more elevated THT the line-width initially drops to 0.5 oersted (at 720°) before rising again very steeply, reaching 50 oersted at 1100°.

Specimens prepared at temperatures below 450°, and also the original irradiated material without any heat treatment, show a characteristic saturation effect of the ESR line, which gradually vanishes as the THT is raised. It has been shown that the line width does not vary as a result of saturation. It follows that the observed line is not evenly developed, and is the envelope of a set of

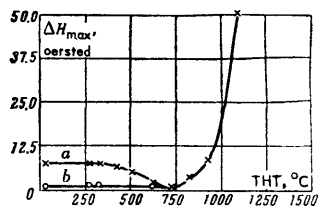



Fig. 8. Variation of ESR line width with THT:
*a*) 2 h evacuation at $10^{-5}$ mmHg and 20°;
*b*) 30 h evacuation at $10^{-6}$ mmHg and 20°.

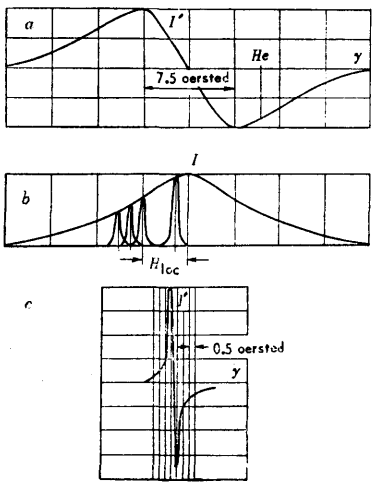



Fig. 9. ESR spectra of materials prepared at THT = 270°:
*a*) differential form, 2 h evacuation at $10^{-5}$ mmHg and 20°; *b*) integral form of spectrum *a*; *c*) differential form, 30 h evacuation at $10^{-6}$ mmHg and 20°.

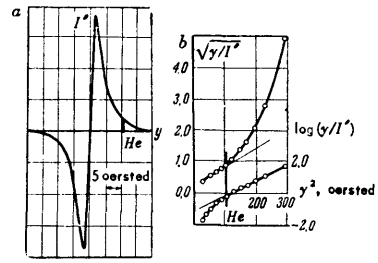



Fig. 10. *a*) ESR spectrum of products obtained at THT = 550°; *b*) linearisations of spectrum *a*.

TABLE 3.

| Material | Measurement conditions $\Delta H_{max}$, $10^{-5}$ mmHg | −196° $10^{-5}$ mmHg | | 20° $10^{-5}$ mmHg | | 20° $O_2$; 150 mmHg | |
|---|---|---|---|---|---|---|---|
| | | shape of line | $He_1$, oersted | shape of line | $He_2$, oersted | shape of line | $He_3$, oersted |
| RMT $2.2\times10^4$ Mrad | 7.5 | mixed | 3 | mixed | 6 | mixed | 12 |
| RTMP THT = 270° | 7.5 | mixed | 6 | mixed | 9 | mixed | 12 |
| THT = 420° | 6.2 | mixed | 9 | mixed | 13 | Lorentz | |
| THT = 550° | 5.0 | mixed | 10 | Lorentz | | Lorentz | |
| THT = 720° | 0.5 | Lorentz | | Lorentz | | Lorentz | |

separate spin packets, as shown in Figs. 9*a* and 9*b*. However, the individual spin packets are not the unresolved components of a hyperfine structure, and do not arise from the anisotropy of the *g*-factor, since the spectrum changes to a single line of Lorentz form and $\Delta H_{max}$ = 0.5 oersted when the initial products of radiation-modified polyethylene and also the products of subsequent heat treatment at 270° and 350° are subjected to prolonged vacuum treatment (up to many tens of hours) at $10^{-6}$ mmHg (see Figs. 8*b* and 9*c*). Thus, in the RTM products of polyethylene prepared at temperatures below 720° the commonly observed dependence of line-width upon THT is misleading and is due to the presence of a paramagnetic gas — oxygen — whose complete removal requires several days' vacuum treatment [15,16]. This effect is completely reversible and occurs without affecting the total concentration of paramagnetic centres. The Lorentz shape and the 0.5 oersted width of the line suggest considerable delocalisation of the paramagnetic centres. The reversible oxygen effect is easily explained by assuming the presence of separate delocalisation regions for paramagnetic centres. Molecular oxygen creates localised magnetic fields which are randomly distributed with respect to these regions. This must lead to a Gaussian distribution of very narrow lines, i.e. to a Gaussian shape for their envelope, if exchange interaction between the isolated delocalisation regions is absent. It has been shown [17,18] that in the presence of exchange the line adopts the Lorentz form in the centre, and the abscissa (*He*) of the point of transition from the Lorentz to the Gaussian form gives directly the frequency of the exchange interaction (see Fig. 10). Using the products of radiation-induced and radiation-thermal modification of polyethylene, we have analysed the shape of the line obtained both in the presence of oxygen at 150 mmHg pressure and after incomplete removal of the oxygen. In Fig. 10 the linear variation of $\log(y/I')$ with $y^2$ denotes a Gaussian shape, that between $\sqrt{y/I'}$ and $y^2$ denotes a Lorentz shape [18]. The results of the analysis are given in Table 3.

It is obvious from Table 3 that a line of mixed form is characteristic of the products obtained at temperatures below 550°: Lorentz in the middle and Gaussian at the tails. This means that in the presence of oxygen the system shows a characteristic exchange interaction between delocalisation regions. Deliberate addition of oxygen raises the frequency of the interaction. Inspection of Table 3 also shows that the exchange interaction increases as the measurement temperature is raised. It increases also on going from the deeply irradiated products to the products of subsequent heat treatment and on increasing the THT temperature, which determines the gradual loss of saturation of the ESR line with intensification of the RTM treatment. These results indicate a growth of the delocalisation regions. In the products of the modification of polyethylene discussed here these regions are thought to correspond to structural units with favourable polyconjugation, which grow at higher THT at the expense of the intervening, less structurally developed, layers. Since in the absence of oxygen all the products of RTM of polyethylene prepared below 750°, including the original specimens which have only been irradiated to an absorption of $2.2\times10^4$ Mrad, are characterised by a line of equal width (0.5 oersted) and shape (Lorentz), we may conclude that the structure of the polyconjugation regions themselves is not appreciably affected by the modification conditions. The narrow line, the independence of the line-width of measurement temperature, and the presence of line saturation in the low-temperature products all point to weak spin–orbital interaction in the system, i.e. to a low symmetry of the regions of favourable polyconjugation.

Infrared spectroscopic studies have yielded more concrete information on the nature of these regions, and have reliably demonstrated the presence of polyconjugated structures of a cyclic type in the products of RTMP. [19] The ESR and infrared data, when taken together, justify the conclusion that the polyconjugated formations detected by the ESR method correspond to these cyclic structures. As was said above, the line of width 7.5 oersted in the presence of oxygen begins to be registered by the ESR method at doses of the order of $6 \times 10^3$ Mrad. It follows that the cyclic polyconjugated structures characteristic of the products of RTMP are formed at the first stage in the modification of polyethylene, i.e. during irradiation, if the dose is high enough.

As regards the products prepared at THT > 750°, we saw in Fig. 8 that their line-width increases sharply with THT. Furthermore, the line-width in these products increases also with measurement temperature. It follows that the width of the line in these materials is determined by the spin–lattice interaction. It has been found that, in contrast to the products prepared at lower temperatures, increased duration of heat treatment transforms the line from the symmetrical Lorentz shape to an asymmetric shape, and considerably increases its width [20]. All these results point to a change in the structure of the polyconjugation regions at temperatures above 750°, in the sense of increased symmetry. Special experiments have shown that the symmetry of the polyconjugation regions increases not only with increase of the temperature of heat treatment, but also with increase of the time of heat treatment.

Thus, the structure of the RTMP products as established by the ESR method provides a complete explanation of the effects of temperature and frequency upon conductivity, listed above. Indeed, some results obtained from ESR spectra show that the polyconjugation regions are separated by narrow, structurally less perfect interlayers. These interlayers can be identified with the potential barriers opposing the drift of current carriers, whose height determines the activation energy of conduction in a d.c. field. The conductivity of the polyconjugation regions themselves is measured at high frequencies, in the region of the plateau. As shown by ESR measurements, the polyconjugation regions grow with increase of THT at the expense of the interlayers, and this leads to a decrease in the activation energy for conduction, an increase in conductivity, and a decrease in thermo-e.m.f. At the same time, the ESR data show that the structure of the polyconjugation regions themselves is practically unaffected by THT up to 750°, but begins to change appreciably with THT at higher temperatures. This is in keeping with the fact, mentioned above, that the a.c. conductivity is barely affected by changes of THT in the region between 350° and 700°.

The variation with THT of the pre-exponential term, which (as we shall show) characterises the conductivity of these regions, also suggests that changes of this type are occurring in the polyconjugation regions.

Fig. 7 shows that below 600–700° the pre-exponential term is an insensitive function of the THT, but it begins to increase sharply with THT at higher temperatures.

We have already pointed out that addition of oxygen to RTMP specimens brings about, on the one hand, a decrease in the activation energy for conduction, and, on the other hand, an intensification of the exchange interaction between polyconjugation regions. In both cases, the observed interaction occurs between the oxygen and the interlayers, and assists the transfer of electrons between regions. In accordance with this interpretation, the high-frequency conductivity in the region of the plateau should be unaffected by the presence of oxygen: this is confirmed by the experimental results (Fig. 5).

## V. INFLUENCE OF IMPURITIES ON THE ELECTRICAL PROPERTIES

The effect of adsorbed oxygen on the behaviour of RTMP products suggested that a study of the interaction of these materials with iodine would be of interest, since it could be expected to produce more clear-cut effects.

It was indeed found [21,22] that the adsorption of iodine from the gas phase has a profound effect on the electrical properties of RTMP products, raising the conductivity by several orders of magnitude and at the same time lowering the activation energy, the conductivity remaining $p$-type for iodination temperatures up to 200°. Isotherms plotted between 100° and 200° showed that the adsorption decreases with increase of the measurement temperature, has all the characteristics of physical adsorption, and increases with increase of the temperature of heat treatment of the specimens. The degree of saturation adsorption, which obtains at $p_{I_2}$ of 19 and 22 mmHg for THT of 420° and 720° respectively, is quite considerable, reaching values of ~ 0.2 and ~ 0.4 g of $I_2$ per g RTMP at an adsorption temperature of 100°. However, changes in $\sigma$ and $\Delta E$ can be detected at the very much lower extents of iodine adsorption corresponding to 20–25° (i.e. at $p \simeq 1$ mmHg). This has enabled the effect of iodine to be investigated quantitatively by comparing the iodine adsorption kinetics with the kinetics of the change in electrical characteristics. The experiments were made in the presence of air rather than in a vacuum in order to decrease the rate of adsorption of iodine.

The kinetic curves obtained for a specimen subjected to a THT of 420° are reproduced in Fig. 11. It can be seen that $\sigma$ increases by 6 orders of magnitude. The curve has a number of notable features: a threshold preceding the increase of $\sigma$, the narrow range over which $\sigma$ increases to a maximum value, and the constancy of this maximum despite the steadily increasing extent of iodine adsorption. Fig. 12 shows the variation of $\sigma$ with the extent of iodine adsorption for specimens subjected to a THT between 420°

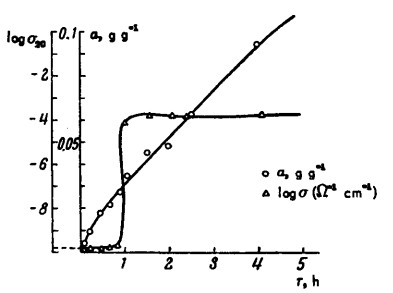



Fig. 11. Comparison of iodine adsorption kinetics and kinetics of the change of electrical conductivity for a specimen with THT = 420°.

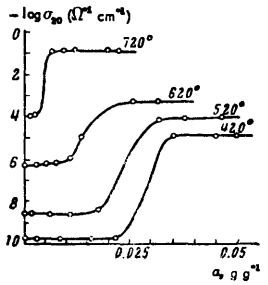



Fig. 12. Variation of $\sigma_{20}$ with amount of iodine adsorbed.

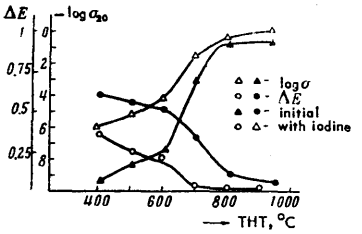



Fig. 13. Effect of THT on $\sigma_{20}$ and $\Delta E$ in the presence and in the absence of iodine.

and 720°: it is evident that the amount of adsorbed iodine needed to produce a sharp change in the values of $\sigma$ decreases with increase of THT, whilst the magnitude of the effect also decreases. The activation energy for conduction also changes sharply at a well defined degree of iodine adsorption: as might have been expected, the activation energy drops. Fig. 13 gives values of $\sigma_{20}$ and $\Delta E$ for different THT in the absence and in the presence of iodine.

These results are in complete agreement with the ideas on the structure of RTMP products derived from ESR studies, which were discussed in the previous Section. Thus, the fact that the amount of iodine necessary to shift $\sigma$ is smaller, the higher the THT, shows that iodine adsorption on the intermediate layers plays the effective role. It assists the motion of current carriers, and thus raises $\sigma$ and lowers $\Delta E$. Iodine adsorption in this case affects the potential barriers, but not the structure of the polyconjugation regions themselves, as shown by the constancy of the conductivity type. It has also been pointed out that the ESR spectra remain unchanged over the whole range of adsorption for a THT of 420°. When the polyconjugation regions become very extensive, as in the case of a THT of 720°, the ESR spectra begin to show evidence of the formation of charge-transfer complexes. This interpretation of the observed effects is also confirmed by the frequency dependence of the conductivity in the presence of adsorbed iodine. As was to be expected from the fact that potential barriers are removed, no dispersion of $\sigma$ is observed in this case.

## VI. CONDUCTION MECHANISM

We have shown above that the conductivity observed in the products of RTM of polyethylene is electronic and is determined by the concentration and mobility of free current carriers:

$$\sigma = e(n\mu_n + p\mu_p),$$

where $e$ is the electronic charge, $n$ and $p$ are the concentrations of electrons and positive holes, and $\mu_n$ and $\mu_p$ are their respective mobilities.

In the majority of cases we shall ignore the contribution of electrons to the conductivity, since the materials of interest are $p$-type semiconductors, and we shall use the expression

$$\sigma = ep\mu^*, \quad (1)$$

where $\mu^*$ is the hole mobility.

It has been shown that the conductivity in the temperature range from -25° to 150° is an exponential function of the reciprocal of temperature:

$$\sigma = \sigma_0 \exp(-\Delta E/kT). \quad (2)$$

The mechanism of electrical conductivity is determined, essentially, by whether the activation energy generates charge carriers or whether it activates mobility of the carriers in the material. Measurement of thermo-e.m.f. is a convenient method for distinguishing between the generation and the carrier transport mechanisms in organic semiconductors. For semiconductors with carriers of a single type the thermo-e.m.f. is given by the expression

$$\alpha = \frac{k}{e}\left[A + \ln \frac{2(2\pi m^* kT)^{3/2}}{h^3 P}\right],$$

where $k$ is Boltzmann's constant, $m^*$ is the effective mass of the carriers, $h$ is Planck's constant, and $A$ is a constant whose value varies from 0.5 to 4 according to the scattering mechanism. This expression can be converted to the form

$$\alpha = B + C\ln T - D\ln p,$$

where $B$, $C$, and $D$ are temperature-independent to a first approximation.

As was recently pointed out[23,24], the temperature variation of the concentration of current carriers for organic semiconductors can be derived from measurements of the thermo-e.m.f. as a function of temperature. Thus, if $p$ = const, $\alpha$ is a very insensitive function of temperature ($\alpha \propto \ln T$), and any increase of thermo-e.m.f. may be masked by the normal experimental error over small temperature intervals. If $p$ is an exponential function of $1/T$, we obtain a steeper variation of $\alpha$ with $T$, easily detected experimentally, namely $\alpha \propto 1/T$. Since $\alpha$ is independent of temperature in every sample of RTMP, we conclude that over the temperature range of the experiments

$$p = \text{const and } \mu^* = \mu \exp(-\Delta E/kT).$$

The physical significance of this expression stems from the detailed study of the structure of RTMP, based mainly on ESR spectra, which has shown that materials prepared at THT > 420° are characterised by regions with a single type of well-developed structure in which polyconjugation is prevalent, separated by narrow regions with a less well-developed structure which can be associated with the potential barriers opposing the drift of carriers.

The conductivity of the regions of polyconjugation in RTMP can be estimated from measurements at various frequencies. The observed dispersion of conductivity with frequency can be ascribed to microheterogeneity in the

specimens. The Maxwell–Wagner double-layer condenser is a classical prototype of the processes occurring in this system. Its constants $C_c$, $R_c$, $C_b$, and $R_b$ are determined by the characteristics of the regions containing conjugated bonds (dielectric constant $\epsilon_c$ and resistivity $\rho_c$) and by those of the barriers ($\epsilon_b$ and $\rho_b$). If $x$ is the ratio of barrier thickness to grain thickness and $x \ll 1$, $\epsilon_c = \epsilon_b$, and $\rho_c \ll \rho_b$ — conditions which the above arguments show to be applicable to RTMP specimens — it is possible to derive[25,26] the following limiting values for the characteristics $\rho_{sp}$ and $\epsilon_{sp}$ of the specimen:

$$\rho_{sp}^0 = \rho_c + x\rho_b, \quad \varepsilon_{sp}^0 = \varepsilon_c \frac{\rho_c^2 + x\rho_b^2}{(\rho_c + x\rho_b)^2}, \tag{3a}$$

$$\rho_{sp}^\infty = \rho_c, \qquad \varepsilon_{sp}^\infty = \varepsilon_c, \tag{3b}$$

where the superscripts 0 and ∞ refer to zero frequency and to the high frequencies at which $\rho_{sp}$ and $\epsilon_{sp}$ become independent of frequency. Thus, in the high-frequency region we measure the characteristics of the regions of polyconjugation (Figs. 4 and 5). It is evident from Fig. 4 that the lower the THT of the specimen, the higher is the frequency at which the conductivity plateau is reached. This is due to the increase in size of the polyconjugation regions, and to the decrease in barrier height, which occur as the THT is raised. For high THT, when $\Delta E \to 0$, the barriers become vanishingly small and no dispersion of conductivity with frequency can be detected. We may conclude that, when the THT is raised, the conductivity $\sigma_c = \sigma_f$ of the regions with polyconjugated bonds does not differ very much from the observed d.c. conductivity $\sigma$, and that whilst $\sigma_{20°}$ covers a range of some 10 orders of magnitude for different specimens, $\sigma_f$ for the same specimens varies only by ~ 2 orders (Fig. 4). Studies of the temperature dependence of the plateau conductivity $\sigma_f$ show an insignificant variation as compared with that of $\sigma$ (Fig. 5). Therefore, in keeping with what has already been said, the activation energy for conduction in a d.c. field can be ascribed to the potential barriers. The small activation energy for conduction $\Delta E_f$ in the polyconjugation regions is associated either with the generation of current carriers or with the motion of the carriers within these regions. No data on which to base a choice between these two processes are at present available.

It follows from our discussion that

$$\sigma_f = \sigma_c = ep\mu_c, \tag{4}$$

where $\mu_c$ is the carrier mobility in the polyconjugation regions.

The barrier mechanism of conduction is applicable to the model for the structure of the material which we have been considering[27]. To obtain an expression for the macroscopic conductivity, we ignore the resistance of the polyconjugation regions and we express the current as a function of the applied voltage across the barriers[27]:

$$j = \frac{Mp}{4}[\exp(-e\psi/kT)]\,[\exp(e\Delta V_b/kT) - 1], \tag{5}$$

where $j$ is the current density, $p$ is the average concentration of intrinsic carriers (holes) in the polyconjugation regions, $\psi$ is the height of the potential barrier, $\Delta V_b$ is the drop in potential across one barrier, and $M$ is a parameter which does not depend on $\psi$ but is a function of the specific nature of the barrier. For a barrier of 5–20 Å thickness, such as is likely to be found in our system, $M = ev_T$, where $v_T$ is the mean thermal velocity of holes. Ohm's law is obeyed up to ~ $10^3$ V cm$^{-1}$ in the products of RTMP (Fig. 2). This suggests that the potential drop at each barrier, $\Delta V_b$, is much less than $kT/e$. We can therefore re write Eqn. (5) in the form

$$j = \frac{v_T p e^2 \Delta V_b}{4kT} \exp(-e\psi/kT). \tag{6}$$

Since we are dealing with $N$ polyconjugation regions connected in series, we can evaluate $\Delta V_b$ as

$$\Delta V_b = \frac{V}{N} = \frac{V}{nl} = \frac{\varepsilon}{n}, \tag{7}$$

where $V$ is the voltage applied to the specimen, $\epsilon$ is the field strength, $l$ is the length of the specimen, and $n$ is the number of polyconjugation regions per unit length. For $\epsilon > (2.5–5) \times 10^3$ V cm$^{-1}$ the current–voltage relationship begins to depart from Ohm's law. From this figure we can make an approximate estimate of the size of the polyconjugation regions. Since the precision of the measurements is ~ 5%, deviations from Ohm's law will be detectable at $e\Delta V_b = kT/10$. (This corresponds to $2.5 \times 10^{-3}$ eV at room temperature.) Hence, from formula (6), $n \simeq (1–2) \times 10^6$ cm$^{-1}$. Ignoring the linear dimensions of the barriers in comparison to those of the polyconjugation regions, we estimate the size of the latter as $L \simeq$ (50–100) Å.

The macroscopic conductivity is given by the expression

$$\sigma = j/\varepsilon,$$

which when combined with Eqns. (6) and (7) gives

$$\sigma = \frac{v_T p e^4}{4kTn} \exp(-e\psi/kT) = ep\mu \exp(-e\psi/kT), \tag{8}$$

where

$$\mu = \frac{v_T e}{4nkT}.$$

The term $\exp(-e\psi/kT)$ is characteristic of the barriers. Eqn. (8) can be written in two forms:

$$\sigma = ep\mu^* \quad \mu^* = \exp(-e\psi/kT), \tag{9a}$$

$$\sigma = ep^*\mu \quad p^* = p\exp(-e\psi/kT). \tag{9b}$$

The macroscopic value of the Hall coefficient, $R_H$, has been found to give the value of $p$ in systems of this type. This is because the polyconjugation regions have a much lower resistance than the barriers[27], i.e. $R_H = \frac{3}{8}\frac{\pi}{ep}$, and the Hall mobility is given by

$$\mu_H = R_H\sigma = \frac{3}{8}\pi\mu^*.$$

Therefore, the Hall mobility gives a direct measure of $\mu^*$ and includes the barrier effects.

The thermo-e.m.f. in systems of this type is also determined by the more extensive system, i.e. by the polyconjugation regions, if the temperature gradient across the barriers is insignificant[4]. This measurement therefore gives the carrier concentration $p$ in the polyconjugation regions. It follows that the mobility derived from measurements of conductivity and thermo-e.m.f. is also equal to $\mu^*$, and that formula (9a) is applicable. Since the hole concentration as measured from the conductivity at high frequencies and from the thermo-e.m.f. varies only slightly, we may suggest that carriers are generated by the impurity mechanism.

On comparing the equations which describe the experimentally observed relations (2) and (9a) with those deduced from the barrier mechanism, we obtain

$$\Delta E = e\psi, \quad \mu = \frac{v_T e}{4nkT}, \quad \sigma_0 = \frac{v_T e^2 p}{4nkT}. \tag{10}$$

The expressions for $\sigma$ and $\mu^*$ enable $\mu^*$ and $p$ to be calculated for RTMP specimens of different THT. In semiconductors with a non-degenerate system of carriers

$$\frac{m^*v^2}{2} = \frac{3}{2}kT. \quad (11)$$

The effective mass $m^*$ is not known, but we can assume that in organic semiconductors the effective mass is greater than the free electron mass $m$, since many experimental and calculated results suggest that the bands are narrow. Table 4 lists the values of $\mu^*$ and $p$ calculated by formulae (8) and (11) from the experimental values of $\sigma_{20°}$ and $\Delta E$, assuming $m^*$ to be $m$ and $10m$ and making use of the size of the polyconjugation regions calculated above.

Let us consider now the expression for $\mu$ in greater detail. From (10) and (11), we have

$$\mu = \frac{3}{4}\frac{e}{m^*}\frac{L}{v_T}. \quad (12)$$

On comparing this with the expression for the mobility in the polyconjugation regions,

$$\mu_c = \frac{e}{m^*}\frac{d}{v_T} = \frac{e}{m^*}\tau, \quad (13)$$

where $d$ is the carrier mean free path, we conclude that $\sigma$ is directly determined by the conductivity of the polyconjugation regions through (12), (13), and (8):

$$\sigma = \mu_c p \frac{3}{4}\frac{L}{d}\exp(-\Delta E/kT) = \frac{3}{4}\frac{L}{d}\sigma_c \exp(-\Delta E/kT). \quad (14)$$

Thus we find that the d.c. conductivity in systems of this type is clearly determined by the conductivity of the polyconjugation regions ($\sigma_c$) and by the interlayers of structurally less perfect material ($\Delta E$).

We showed in the experimental section that the relationship

$$\sigma_0 \simeq \sigma_f = \sigma_c \quad (15)$$

holds for specimens of RTM polyethylene. Hence, $\frac{3}{4}\frac{L}{d} \simeq 1$, the mean free path $d$ is approximately equal to the dimensions ($L$) of the polyconjugation regions, and Eqn. (14) takes the following form for RTM polyethylene specimens:

$$\sigma \simeq \sigma_c \exp(-\Delta E/kT).$$

In general, $\sigma_0$ can be greater or smaller than $\sigma_c$ according to the value of the ratio $L/d$, and this ratio can be evaluated from measurements in a d.c. and an a.c. field.

TABLE 4.

| THT, °C | $D = 2.4 \times 10^4$ Mrad, $L = 100$ Å | | | |
|---|---|---|---|---|
| | $m^* = m$ | | $m^* = 10m$ | |
| | $\mu^*$, cm$^2$ V$^{-1}$ s$^{-1}$ | $p$, cm$^{-3}$ | $\mu^*$, cm$^2$ V$^{-1}$ s$^{-1}$ | $p$, cm$^{-3}$ |
| 420 | $5 \times 10^{-7}$ | $1.3 \times 10^{18}$ | $1.5 \times 10^{-5}$ | $4.2 \times 10^{18}$ |
| 520 | $6.3 \times 10^{-4}$ | $2 \times 10^{19}$ | $1.8 \times 10^{-3}$ | $6.6 \times 10^{19}$ |
| 620 | $2 \times 10^{-2}$ | $2.3 \times 10^{19}$ | $6 \times 10^{-4}$ | $7.6 \times 10^{19}$ |
| 725 | $2 \times 10^{-1}$ | $2 \times 10^{15}$ | $7 \times 10^{-3}$ | $6 \times 10^{16}$ |
| 825 | 20 | $2 \times 10^{17}$ | 6 | $6 \times 10^{17}$ |
| 930 | 115 | $3.5 \times 10^{18}$ | 35 | $1.2 \times 10^{19}$ |
| | $D = 2.4 \times 10^4$ Mrad, $L = 50$ Å | | | |
| 420 | $2.5 \times 10^{-5}$ | $2.6 \times 10^{18}$ | $7.5 \times 10^{-4}$ | $8.4 \times 10^{18}$ |
| 520 | $3.1 \times 10^{-3}$ | $4 \times 10^{19}$ | $9 \times 10^{-2}$ | $1.3 \times 10^{14}$ |
| 620 | $1.0 \times 10^{-2}$ | $4.6 \times 10^{19}$ | $3 \times 10^{-1}$ | $1.5 \times 10^{14}$ |
| 725 | $1 \times 10^{-1}$ | $4 \times 10^{15}$ | $3.5 \times 10^{-2}$ | $1.2 \times 10^{16}$ |
| 825 | 10 | $4 \times 10^{17}$ | 3 | $1.2 \times 10^{16}$ |
| 930 | 57 | $7 \times 10^{18}$ | 17 | $2.4 \times 10^{19}$ |

The regions of bond polyconjugation are characterised by high mobility (~ 17–115 cm$^2$ V$^{-1}$ s$^{-1}$) and conductivity (~ $10^{-4}$–$10^{-2}$ $\Omega^{-1}$ cm$^{-1}$), but the effective mobility $\mu^*$ and the conductivity $\sigma_{20°}$ of RTMP specimens are very much lower, due to the presence of potential barriers.

This discussion is only approximate, because it is confined to carriers of a single kind. However, we have observed[7] an increase in positive thermo-e.m.f. in the presence of oxygen which can be explained by postulating an electronic contribution to the conductivity in addition to the hole conductivity.

## VII. NATURE OF THE PARAMAGNETISM

A limited understanding of the nature of the paramagnetism of the RTM products of polyethylene was derived from studies of the reversible oxygen effect and from comparisons of the paramagnetic and electrical properties of given specimens. As stated above, the reversible oxygen effect in products prepared at temperatures below 500° consists in the generation of localised fields and in the intensification of exchange interactions between delocalisation regions of paramagnetic centres. The latter effect indicates that overlap of electron orbitals is taking place between an oxygen molecule and the paramagnetic centres, but that the overlap is not affecting the paramagnetic centre concentration. With products obtained at temperatures in excess of 500° the delocalisation regions grow at the expense of the intervening layers to such an extent that the steric conditions leading to a more intimate overlap of the orbitals are satisfied. In these products the concentration of paramagnetic centres varies on admission of oxygen. A comparison of the reversible oxygen effect has been made on RTM products of polyethylene which had been subjected to vacuum pyrolysis with and without a preliminary oxidation: such a comparison is essential to an understanding of the role of the oxygen present in the structure of the pyrolysis products.

If the samples for irradiation are pre-oxidised, the concentration of unpaired spins in the products prepared at temperatures between 550° and 750° increases reversibly upon admission of oxygen. Measurements on a number of materials which had been heat-treated for various times at ~ 700° showed that the adsorption is physical in nature since it has a heat of 2 kcal mole$^{-1}$. It was shown that the adsorption of 1 molecule of oxygen on pre-oxidised products heated at moderate temperatures causes the loss of 2 unpaired spins. This ratio justifies the conclusion that the paramagnetism of RTM of polyethylene is due to the presence of isolated paramagnetic centres, and not to a weak interaction between strongly conjugated systems[28]. A further conclusion from the observed relationship is that the physical adsorption of oxygen on pre-oxidised products involves reversible pairing of two unpaired electrons from the specimen with two unpaired electrons from an oxygen molecule without disruption of the O=O bonds.

If the pre-oxidation stage is omitted in the preparation of these materials, the paramagnetic centre concentration in the products treated at moderately high temperatures does not increase, but rather decreases reversibly upon admission of oxygen. A similar effect is observed for many organic compounds with well developed polyconjugation systems. The effect is universally ascribed to the formation of charge-transfer surface complexes of the donor–acceptor type[13]. A comparison of the number of

adsorbed oxygen molecules with the number of the resulting paramagnetic centres has been made for RTM products prepared at 700°. The adsorption is again physical in nature, since it increases on lowering the temperature, the heat of adsorption being 2.5 kcal mole$^{-1}$. It has been shown that each oxygen molecule adsorbed causes the appearance of 1 paramagnetic centre. From this comparison of the effect of oxygen on the concentration of paramagnetic centres in RTM products of polyethylene with and without a preliminary oxidation treatment, we may conclude that oxygen-containing groups hinder the formation of charge-transfer complexes. This is probably because they compete with molecular oxygen, "drawing" the electron cloud around themselves. It has been found that the adsorption of 1 oxygen molecule induces 1 paramagnetic centre even in products prepared above 750°, whether or not the products are pre-oxidised before vacuum pyrolysis. This effect is probably associated with practically complete removal of the oxygen-containing groups from the structure of the products during high-temperature pyrolysis.

Fig. 14 shows, as a function of THT, the concentration of paramagnetic centres in vacuum-treated RTMP samples and the concentration of current carriers calculated for assumed carrier effective masses ($m^*$) of $m$ and $10m$ (lower and upper boundaries of the cross-hatched band respectively).

It is clear that the concentration of paramagnetic centres in materials prepared below 800° is higher than the carrier concentration by many orders of magnitude, and that the two concentrations vary with THT in different ways.

The conclusion to be drawn from this comparison is that the paramagnetic centres in materials of this type (including specimens subjected to irradiation only) cannot be identified directly with charge carriers. The centres are apparently caused by structural defects. As stated above, the analysis of the ESR spectra indicates that the unpaired electrons bound to structural defects are delocalised within the individual polyconjugation regions. It is obvious from Fig. 14 that for temperatures above 600° the concentration of defects decreases whilst the concentration of charge carriers increases steeply with THT. Furthermore, in the materials prepared at THT > 800° the concentration of paramagnetic centres begins to increase once again with increase of THT at much the same rate as the concentration of current carriers. Unlike the low-temperature and the intermediate-temperature products, freshly prepared high-temperature products show an increase in paramagnetic centre concentration with increase in measurement temperature. This result has led to the conclusion that current

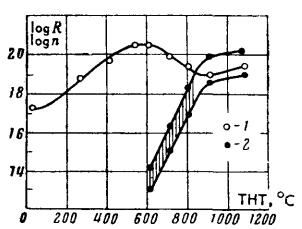



Fig. 14. Effect of THT on the concentration of paramagnetic centres (curve 1) and on the concentration of charge carriers (curves 2).

TABLE 5.

| THT | $\mu^*$, cm$^2$ V$^{-1}$ s$^{-1}$<br>$p$, cm$^{-3}$ or g$^{-1}$ | Electrical measurements | | ESR | |
|---|---|---|---|---|---|
| | | $m^* = 10m$ | $m^* = m$ | $m^* = 10m$ | $m^* = m$ |
| 930 | $\mu^*$ | 17 | 115 | 13 | 130 |
| | $p$ | $2.4\times10^{19}$ | $3.5\times10^{18}$ | $7\times10^{18}$ | |
| 1100 | $\mu^*$ | 17 | 115 | 13 | 130 |
| | $p$ | $3.6\times10^{19}$ | $5.2\times10^{18}$ | $1.5\times10^{19}$ | |

carriers are responsible for the ESR signal in this particular case. When surface oxides are formed on these products, the concentration of paramagnetic centres becomes independent of measurement temperature. The relaxation time $\tau_R$ of the carriers[30] has been obtained from the parameters of the ESR spectra — line width (Fig. 8) and the $g$-factor (2.0027) — for materials prepared at 930° by means of the formula

$$T_1 = \left(\frac{3\times10^{-8}}{\Delta H_{max}}\right) = \frac{1}{30}\,\frac{\tau}{(g-g_{free})^2},$$

given by Elliott[29]. As in the case of the electrical measurements, the numerical values of mobility were obtained from formula (13) by assuming effective masses of $1m$ and $10m$.

In this way, the mobility and carrier concentration have been calculated by independent methods: it is evident from the values obtained, which are set out in Table 5, that the agreement between the two sets of results is satisfactory. The measured conductivity of a specimen prepared at THT = = 930° is 56 $\Omega^{-1}$ cm$^{-1}$. Assuming that the density of the products is 1.5 g cm$^{-3}$, we conclude that $m^* \simeq 4m$, since the mobility is 50 cm$^2$ V$^{-1}$ s$^{-1}$ at a carrier concentration of $7 \times 10^{18}$ g$^{-1}$ (as determined by the ESR method).

These results prove that the application of the ESR method to studies of polymeric materials having semiconducting properties can assist in the identification of some of the features of the conduction mechanism in these materials as well as giving information on their structural characteristics.

In conclusion, we can say that the radiation-thermal modification of linear polymers, which we have studied in the particular case of polyethylene, offers the possibility of preparing organic semiconductors showing a wide range of properties.

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# EFFECT OF CHEMISORBED GASES ON THE WORK FUNCTION OF METALS

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Most of the work on the mechanism of the adsorption and chemisorption of gases on metals has been concerned with the kinetics of these processes and with the relevant heats of adsorption. Yet, attempts were made as long ago as in the 1930's to establish a connection between the rate of interaction of gases with metals and the change in work function of the metals.

Rideal and his coworkers [1] studied the relationship between the activation energy and the work function. Langmuir [2], de Boer [3], Lukirskii [4], and others, measured the change in contact potential difference (c.p.d.) resulting from the adsorption of alkali metal atoms on tungsten, and from the adsorption of oxygen and hydrogen on alkali metals. However, the literature of that period contains various contradictory results as well as some very valuable papers: this state of affairs, which was due to the inadequacy of existing measurement techniques, was responsible for the loss of interest in this problem. In recent years, modern theories of gas–metal interactions and the development of high-vacuum and electronic measurement techniques gave new impetus to studies of the mechanism of the adsorption of gases on metals and of their influence on the work function. Recent investigations include the effect of the adsorption of hydrogen, oxygen, carbon monoxide, the noble gases, etc., on the work function of metals, and some attempts at establishing the relation between the changes in work function and in heat of adsorption under conditions of increasing surface coverage [5,6].

The results of work function measurements as a function of gas adsorption were used by several workers to calculate heats of adsorption. Eley [7] suggested the use of a semi-empirical formula, based on Pauling's equation for the energy of a covalent bond:

$$-\Delta H_0 = H_c + 23.06\,(x_m - x_a)^2, \qquad (1)$$

where $H_C$ is the initial energy of the covalent bond, and $(x_m - x_a)$ is the electronegativity difference between the adsorbent and the adsorbate.

Calculations of the heat of adsorption of hydrogen chemisorbed on tungsten, using this equation, agree satisfactorily with experimental data. However, the adsorption of oxygen, nitrogen, and also some organic molecules gave appreciable discrepancies between calculated and experimental values. Eley's calculation presupposes a linear change of contact p.d. with surface coverage, which is not always borne out by the experimental results.

The contact p.d. method has been used also to examine the mechanism of catalytic and electrochemical processes.

Work function values are of major significance [8,9] in problems involving the Volta potential, which, according to the ideas developed by Frumkin, determines the relation between the points of zero charge of metals and their work functions.

The contact potential difference in the chemisorption of gases on metals depends on the nature of both the adsorbent and the adsorbate [5,6,10]. In most cases, chemisorption of gases produces a covalent bond of partially ionic character. Under these conditions, the appearance of a surface potential is associated with the transfer of an electron from the adsorbent to the adsorbate or *vice versa*. These processes lead to an increase or a decrease in the work function respectively. According to the ideas of a number of workers [5,6,10], the sign of the surface potential of the metal, $\Delta\varphi$, is determined by the difference between the work function ($\varphi$) and the electronegativity of the adsorbate ($\psi$):

$$\Delta\varphi = \varphi - \psi. \qquad (2)$$

Hence

$$\psi = {}^1/_2(I + E), \qquad (3)$$

where $I$ is the ionisation potential and $E$ is the electron affinity.

This model predicts that chemisorption of gases having a high electron affinity, such as oxygen and the halogens, should raise the work function. Yet even some of the earlier work[11-14] showed that oxygen chemisorption on certain metals raises $\varphi$ while according to others chemisorption lowers it.

The influence of chemisorption conditions and of the nature of adsorbates of different electron affinity (fluorine, oxygen, chlorine, iodine) on the work function has been investigated as part of a detailed study of the mechanism of the chemisorption of gases on metals and of their effect on electrochemical processes such as metal passivation and corrosion.

In most of the published studies of chemisorption processes by the contact potential difference method no allowance is made for the change in surface potential of the reference electrode induced by the adsorbate.

The measurements of contact p.d. in our work were made by the vibrating condenser method and by the thermionic method (from the change in diode characteristics). For the condenser method we used an apparatus in which the reference electrode was a molybdenum sheet fused to a thin layer of glass, which protected the reference electrode from gas adsorption[15]. When the measurements were made by the thermionic method, we used an apparatus which enabled the cathode to be protected from adsorption of the experimental gases[16]. The values of contact p.d. obtained for oxygen chemisorption on iron by the condenser method[17] are in good agreement with our own results by the thermionic method under similar conditions[16,18].

The preparation of a clean metal surface is a very complicated problem. The usual procedures are either cleaning of the metal surface by reduction with carbon monoxide, followed by lengthy degassing in an ultra-high vacuum, or evaporation of the metal in an ultra-high vacuum. In the second method there is a possibility of absorption by the evaporating metal of the gases evolved from the massive metal. Furthermore, the structure of thin films is different from that of bulk metal, and this can affect the work function[19-23]. For these reasons we used the first method in our researches.

The metals were reduced at 450° and degassed at 700–900° (iron[17,18] and nickel[24]), or at 1200° (platinum[25]). Special experiments were made to check that when this procedure was used, a change in vacuum from $10^{-7}$ to $10^{-9}$ mmHg had no significant effect on the change in contact p.d. caused by oxygen chemisorption[26].

Vacuum work with halogens presents considerable difficulty. To ensure that the gases were pure, we used spherical diaphragms instead of taps[27,28].

The chemisorption of oxygen on tungsten is a classical example showing the correctness of the above ideas on the change in work function in terms of the difference in electron affinity between adsorbate and adsorbent. Both published results[29-32] and measurements in our own laboratory[16] have shown that the work function of tungsten is decreased by oxygen chemisorption over a wide range of pressures and temperatures. In most of the investigations, made by different methods, the contact p.d. $\Delta\varphi$ is found to be 1.7–1.9 V.

In order to understand the variation of the surface potential with the conditions of interaction of electronegative gases with iron, we measured the contact p.d. between a clean metal surface and a surface covered with chemisorbed gases.

To study the kinetics of oxygen chemisorption, an iron surface was exposed to small increments of oxygen pressure, and the rate of absorption of each portion was observed. The variation of the rate of oxygen absorption with surface coverage is shown in Fig. 1 (curve *1*), where the rate of the process is expressed as $\log(1/\tau)$ and $\tau$ is the time required for absorption of one-half of the aliquot of oxygen. The chemisorption of oxygen on iron occurs in two stages. The fast stage is characterised by relative insensitivity of the rate to the degree of surface coverage. This stage is completed, both for the bulk metal and for the powder, when the extent of absorption is $2 \times 10^{15}$ $O_2$ molecules per cm² of true surface area. If absorption is allowed to proceed further, the rate of chemisorption falls off sharply[33,34]. No desorption occurs upon heating iron covered with chemisorbed oxygen. However, after being heated and subsequently cooled, iron acquires the ability to absorb additional oxygen [see Fig. 1, curve *2* (100°), curve *3* (200°), curve *4* (300°)]. This activating treatment of the iron can be repeated a number of times. Thus, the increase in oxygen absorption at higher temperatures stems from disruption of the protective properties of the film formed at 20° As the temperature is increased, the limiting thickness of the film also rises, and additional chemisorption of oxygen must take place[17].

The results of our work on the interaction between iron and oxygen by the contact p.d. method are shown in Figs. 2, 3, and 4. The data of Figs. 2 and 3 were obtained by the

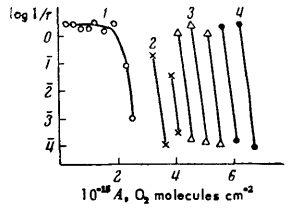



Fig. 1. Effect of temperature on the kinetics of oxygen chemisorption on iron.

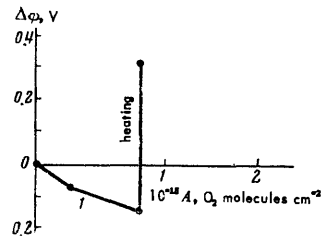



Fig. 2. Effect of oxygen, chemisorbed on iron at -120° and 100°, on the contact p.d.

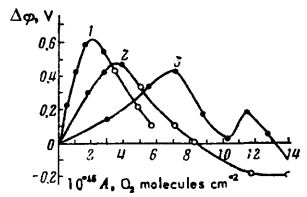



Fig. 3. Variation of contact p.d. of iron with amount of oxygen chemisorbed: 1) at 100°; 2) at 200°; 3) at 300°.

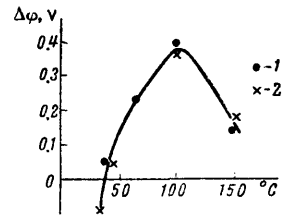



Fig. 5. Effect of temperature on the contact p.d. of nickel covered with $1.3 \times 10^{15}$ $O_2$ molecules $cm^{-2}$. Points 1 and 2 refer to different experiments.

thermionic method. Adsorption of oxygen on iron at -120° raises the work function (Fig. 2), in agreement with the ideas discussed above. However, when the temperature is increased to 100° for the same amount of chemisorbed oxygen ($0.8 \times 10^{15}$ $O_2$ molecules per $cm^2$), the work function decreases to a level 0.3 V lower than for clean iron. If the amount of chemisorbed oxygen is increased to $2 \times 10^{15}$ $O_2$ molecules per $cm^2$, the work function drops by 0.6 V. When the extent of oxygen chemisorption is very high, the work function increases (Fig. 3).

A similar variation of contact potential with amount of absorbed $O_2$ is found at 150° and 270°. However, the work function minimum shifts towards higher coverages by chemisorbed oxygen as the temperature of chemisorption is increased. As Fig. 3 shows, the work function becomes 0.2 V higher than that for reduced iron when the amount of $O_2$ exceeds $8 \times 10^{15}$ molecules per $cm^2$.

Experimental results[17] obtained by the condenser method with iron covered to the extent of $2 \times 10^{15}$ $O_2$ molecules per $cm^2$ are in quantitative agreement with the results given above. At 100° the decrease in work function goes through a maximum of 0.6 V (Fig. 4).

Since the most reliable value[35] for the work function of iron is 4.7 V, which agrees with our own measurements, the lowest work function of iron in the presence of $O_2$ absorption is 4.1 V, and the highest is 4.9 V.

Our results for the adsorption of oxygen on nickel and for the influence of chemisorbed $O_2$ on the work function show much the same features as the results for iron (Fig. 5). We again find two types of adsorption: a fast and a slow adsorption. At 20° the fast stage accounts for $1.3 \times 10^{15}$ $O_2$ molecules per $cm^2$ of true surface area. As Fig. 5 shows, at 35° the fast chemisorption stage causes an increase in work function of 0.1 V. When the temperature of oxygen absorption is raised to 45° and 100°, the work function decreases by 0.02 and 0.35 V respectively as compared with that of reduced nickel. At still higher temperatures (150°), an increase in work function is observed[24] with respect to the above value.

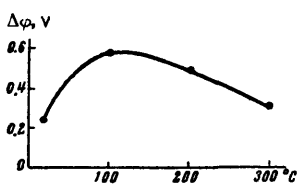



Fig. 4. Effect of temperature on the contact p.d. of iron covered with $2 \times 10^{15}$ $O_2$ molecules $cm^{-2}$.

However, there have been several reports[14,36-40] of an increase in work function following oxygen chemisorption at 20° on thin films of nickel and iron prepared by evaporation in a vacuum. This disagreement is probably due, as was suggested above, to inadequate purity of the films and to their structural peculiarities.

It should be noted that the two forms of chemisorbed oxygen affect the electrochemical properties of iron in different ways. The fast stage of oxygen chemisorption has been shown, by a vacuum-electrochemical method, to increase the rate of anodic oxidation of iron, whereas the slow stage lowers the rate of the anodic process. The absorption of $4 \times 10^{15}$ $O_2$ molecules per $cm^2$ produces complete passivation of this process[33,34,41]. Near the steady-state potential small amounts of $O_2$ ($2 \times 10^{15}$ molecules $cm^2$) chemisorbed on the surface from the gas phase cause an increase in capacitance associated with increased electrochemical adsorption[42].

Comparison of data on the influence of chemisorbed oxygen on the work function[16-18] with data on the electrochemical behaviour of iron[33,34,41] shows that the activation of the iron electrode results from absorption of oxygen under conditions leading to a decrease in work function, whereas passivation occurs when the oxygen chemisorption is accompanied by an increase in work function.

The contact p.d. method has also been used to study the mechanism of gas-phase corrosion of iron in a moist atmosphere[17].

As stated above, oxygen chemisorption at 20° lowers the work function by 0.2 V. After exposure to $H_2O$ vapour, the work function drops by a further 0.3 V. However, there is no change of $\Delta\varphi$ after complete desorption of the water vapour, whilst the iron acquires the ability to adsorb additional amounts of oxygen. This activation of the iron towards interaction with oxygen can be repeated a number of times. As Fig. 6 shows, oxygen adsorption in amounts of $2.5 \times 10^{15}$ $O_2$ molecules per $cm^2$ causes a drop of about 3 orders of magnitude in the rate of chemisorption of oxygen (curve *1*). After exposure of iron covered with an oxide film of limiting thickness to water vapour, the rate of absorption of $O_2$ increases again to its initial value. However, after further absorption of a small amount of oxygen the reaction rate decreases sharply, but it can be increased by repeated exposure to water vapour (curves *2*, *3*, *4*, and *5* of Fig. 6). The values of contact p.d. obtained for iron in the presence of oxygen and water vapour and

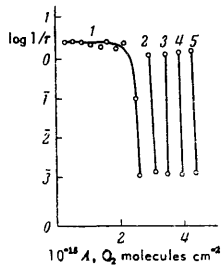



Fig. 6. Effect of water vapour on the kinetics of oxygen chemisorption by iron.

after degassing are summarised in Fig. 7. From adsorption measurements in conjunction with data on the influence of water vapour on the work function, we may conclude that the adsorption of $H_2O$ vapour facilitates migration of metal atoms. Under these conditions, an electrical double layer with its positive pole directed outwards is formed on the metal surface, as evidenced by the decrease in work function.

We shall now consider the effect of halogens on the work function of iron.

Chemisorption of the most electronegative gas, fluorine[28], produces a most striking decrease in work function. Fig. 8*a* shows the change in surface potential of iron after exposure to fluorine. The chemisorption of fluorine was studied at a pressure of $6 \times 10^{-2}$ mmHg. The results indicate that the largest decrease in work function caused by the chemisorption of fluorine on iron occurs at room temperature and amounts to 0.6–0.7 V. This value is unaffected by removal of the fluorine from the gas phase. When the iron with chemisorbed fluorine is heated in a vacuum to 100°, a slight increase in work function is observed between 20° and 100°. Further increase in temperature to 300° has practically no effect on the work function. Under these conditions, $\varphi$ is lower than the value for clean iron by 0.4 V.

The change in surface potential of iron on chemisorption of chlorine was investigated[27] in the pressure range $4 \times 10^{-4}$– $6 \times 10^{-1}$ mmHg. The results are reproduced in Figs. 8*b* and 8*c*. At all the pressures examined, chlorine chemisorption at 20° raises $\Delta\varphi$ from 0.1 to 0.27 V. As

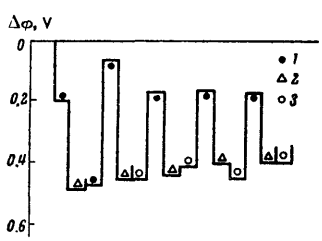



Fig. 7. Effect of oxygen, water vapour, and degassing on the contact p.d. of iron:
1) oxygen; 2) water; 3) vacuum.

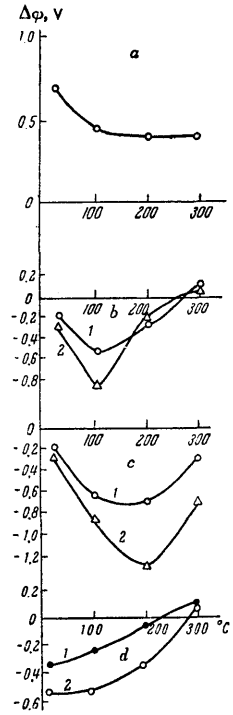



Fig. 8. Effect of halogens on the contact p.d: *a*) iron with chemisorbed fluorine heated *in vacuo* ($p_{F_2} = 6 \times 10^{-2}$ mmHg); *b*) iron with chemisorbed chlorine heated *in vacuo* [1) $p_{Cl_2} = 5 \times 10^{-2}$ mmHg; 2) $p_{Cl_2} = 6 \times 10^{-1}$ mmHg]; *c*) iron heated in the presence of chlorine in the gas phase [1) $p_{Cl_2} = 5 \times 10^{-2}$ mmHg; 2) $p_{Cl_2} = 6 \times 10^{-1}$ mmHg]; *d*) iron with chemisorbed iodine heated *in vacuo* [1) $p_{I_2} = 1 \times 10^{-2}$ mmHg; 2) $p_{I_2} = 7 \times 10^{-2}$ mmHg].

Fig. 8*b* shows, very significant changes in surface properties take place when the iron with chemisorbed chlorine is heated in a vacuum. At 100° we observe an increase in $\Delta\varphi$ from 0.1 to 0.85 V over the range of pressures stated above. With further increase of temperature the work function decreases, and reaches a value 0.1 V lower than that for a clean iron surface after heat treatment at 300°. If chlorine is present in the gas phase, a similar temperature variation is observed (see Fig. 8*c*). The only difference between these results and those of Fig. 8*b* is that the maximum contact p.d. occurs at 200° and amounts to 1.3 V.

The experiments on the effect of chemisorbed iodine on the work function[27] were done at pressures of 0.01 and 0.07 mmHg. The results are shown in Fig. 8*d*. In contrast to the behaviour of chlorine, the greatest increase in work function is found when iodine is chemisorbed on iron at 20°, and amounts to 0.3–0.5 V for the stated pressures. The chemisorption of iodine at a pressure of $7 \times 10^{-2}$ mmHg amounts to $2.7 \times 10^{15}$ $I_2$ molecules per $cm^2$ of true surface area. After heating to 300°, the work function becomes smaller by 0.1–0.15 V than the work function of a clean iron surface. In contrast to the results

obtained with chlorine, the contact p.d. decreases continuously when iron with chemisorbed iodine is heated in a vacuum.

As we have already remarked, the adsorption of gases with a high electron affinity (such as oxygen and the halogens) on a metal should be accompanied by an increase in work function, according to generally accepted principles. The results on oxygen chemisorption reported here indicate that the work function can either increase or decrease, depending on the adsorption conditions (temperature and amount of chemisorbed gas). Comparison of the results for the effect of oxygen and of the halogens at 20°, shows that the higher the electronegativity of the adsorbate the lower is the work function. The relationship between $\Delta\varphi$ and $x$ (the Pauling electronegativity) is shown by curve *1* of Fig. 9. Curve *2* of the same figure shows the variation of contact p. d. with the ionic radius of the adsorbates used in this work. These results show that the amount of positive charge on the surface increases with decreasing ionic radius of the adsorbate.

According to the view previously developed by us [16-18,24,28] and now adopted by others [43-45], the decrease in electronic work function following adsorption of an electronegative gas is due to penetration of the adsorbate below the uppermost layer of metal atoms, or to migration of the latter to the surface of the adsorption layer. In the first case the size of the adsorbed ion plays the major role in determining its penetration between the surface atoms of the metal. The experiments which we have described show that adsorption at 20° of fluorine (the gas with the smallest ionic radius) produces the greatest decrease in work function. The results also indicate that the temperature at which the greatest positive shift in potential is observed is lower, the smaller the ion of the adsorbate considered. The observed changes in contact p.d. with temperature can be explained by the following argument. The positive shift of the potential of iron and nickel is caused by penetration of the adsorbate to a certain depth. Due to the difference in ionic radius, our adsorbates achieve this depth of penetration at different temperatures (at 20° for fluorine, at 100° for oxygen, upwards of 300° for chlorine and iodine). The potential of the surface become less positive as the oxygen penetrates deeper into the metal. The penetration of chemisorbed oxygen into the bulk of the metal is confirmed also by our results for platinum [25], reported below.

When penetration of the electronegative adsorbates into iron or other metals cannot take place, as in the case of chlorine or iodine at 20°, the surface becomes negatively charged. In the chemisorption of chlorine on iron, increase of temperature from 20° to 100° causes a further increase in work function, probably due to a change in the nature of the chlorine–iron bond. At temperatures above 100° the halogen can evaporate from the surface, with loss of negative charge.

Anderson [43] studied the kinetics and the mechanism of chlorine adsorption on deposited nickel films at pressures between $5 \times 10^{-6}$ and $5 \times 10^{-3}$ mmHg and at temperatures of 20° and -122°. Under these conditions, chlorine adsorption is very fast up to monolayer coverage. At low coverages ($\theta < 0.1$) the contact potential acquires a positive value of 0.2 V. The observed decrease in work function is attributed by the author to penetration of the chemisorbed chlorine below the surface layer of metal. At high coverages the contact potential becomes negative, with a maximum value of -1.6 V. When the nickel film covered with chemisorbed chlorine is heated to 300°, the work function decreases, in complete agreement with the results of our own work [27] reported above.

Oxygen has a different effect on the work function of platinum [25]. At room temperature and at low pressure the adsorption of oxygen on platinum is negligible and has practically no effect on the contact potential difference. Between 200° and 800° platinum can absorb significant amounts of oxygen, corresponding to 600 monolayers at 800°.

When platinum absorbs oxygen in amount of $15 \times 10^{15}$–$40 \times 10^{15}$ molecules $cm^{-2}$ at 200° there is a small increase (0.2 V) of work function, which disappears if the electrode is kept for 12 h in a vacuum. The work function of the platinum is now practically the same as that of the clean metal. This can be explained by postulating that oxygen pentrates into the bulk of the platinum. The same amount of oxygen ($40 \times 10^{15}$ molecules $cm^{-2}$) has no effect at all on the work function when chemisorption occurs at 400°. This is evidently because the oxygen reaches the interior of the platinum so rapidly that $\Delta\varphi$ is not measurable.

However, as the amount of oxygen absorbed at 400° increases, the layers of platinum adjacent to the surface become saturated and the penetration of oxygen into the interior of the platinum is retarded. A larger amount of oxygen ($100 \times 10^{15}$–$200 \times 10^{15}$ $O_2$ molecules $cm^{-2}$) causes the work function to increase by 1.5 V. However, the contact potential difference decreases with time, and after 12 h the work function becomes equal to that of clean platinum, due, as before, to the penetration of the oxygen into the deeper layers of platinum (Fig. 10). Oxygen absorbed by platinum at 800° behaves quite differently. The results

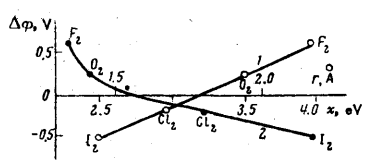



Fig. 9. Variation of the work function of iron with electronegativity $x$ (curve 1) and ionic radius $r$ (curve 2) of the adsorbate.

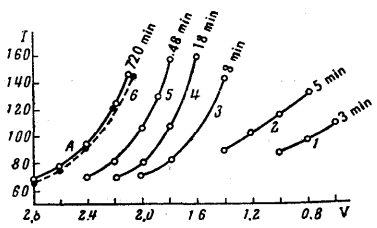



Fig. 10. Current–voltage characteristics. *A*) platinum; 1)–6) platinum covered with $125 \times 10^{15}$ $O_2$ molecules $cm^{-2}$, measured 3–720 min after completion of chemisorption.

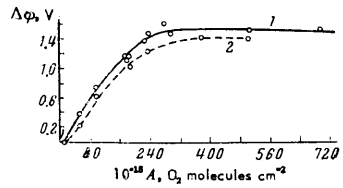



Fig. 11. Variation of contact p.d. with amount of oxygen absorbed by platinum at 800°: 1) immediately after adsorption; 2) after 12 h.

of one series of experiments are shown in Fig. 11. Increasing the amount of chemisorbed oxygen raises the work function, which remains practically constant with time and reaches 1.5 V when the extent of absorption is $233 \times 10^{15}$ $O_2$ molecules $cm^{-2}$. Further oxygen chemisorption has practically no effect on the work function. The results suggest that a relatively small proportion of the chemisorbed oxygen is firmly held at the metal surface, whereas the bulk of the oxygen penetrates into the bulk of the platinum.

These conclusions are satisfactorily confirmed by measurements of the charging curve of a platinum electrode treated with oxygen at 200–800°. Cathodic polarisation can remove only a small proportion of the oxygen, equivalent to approximately one monolayer, from the platinum surface. If the cathodic polarisation is applied again after some time, it is possible to remove an additional quantity of oxygen, originally dissolved in the metal, which has now diffused to the surface of the platinum[46].

The diffusion of large volumes of oxygen into silver at elevated temperatures was demonstrated by the work of Temkin and Kul'kova[47].

It follows from the results discussed here that with a number of metals the chemisorption of gases having a high electron affinity can be accompanied by migration of the adsorbate below the surface layer of metal atoms, which causes a positive charge to appear on the metal surface. The ionic radius of the adsorbate plays an essential part in this process. The resulting decrease in work function is responsible for the activation of the electrochemical dissolution processes of metals such as iron. Chemisorption leading to an increased work function causes passivation of iron. When oxygen can penetrate into the metal to an appreciable depth, the influence of absorbed oxygen on the surface properties of the metal is relatively small.


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# ADSORPTION OF ORGANIC COMPOUNDS [AT THE MERCURY ELECTRODE-SOLUTION INTERFACE]

B. B. Damaskin

Among various direct and indirect methods for the investigation of the adsorption of organic substances on the surface of electrodes, the most widely used are those based on measurements of the interfacial tension ($\sigma$) and differential capacitance ($C$) as a function of electrode potential ($\varphi$). Most of these data have been obtained for the mercury-aqueous solution interface in the presence of small amounts of organic additives. In this connection, the theory of the adsorption or organic compounds described below is mainly based on experimental data obtained for the mercury electrode by the measurement of $\sigma-\varphi$ and $C-\varphi$ curves.

Starting with the work of Gouy [1,2] and Frumkin [3,4], the method based on the measurement of electrocapillary curves has been widely used up to the present time for the study of the adsorption on the mercury electrode of a wide variety of organic substances [5-20]. Fig. 1, taken from the paper by Gouy [1], shows that the adsorption of an organic compound (in this case pentanol) appreciably lowers the interfacial tension of mercury, the lowering being a maximum near the zero-charge point (z.c.p.) in a solution of an inorganic electrolyte, decreasing with increase in the negative or positive surface charge. In most cases, when the charge is sufficiently positive or negative, the lowering of the interfacial tension under the influence of an organic substance is not observed and the electrocapillary curve obtained in the presence of the additive coincides with the $\sigma-\varphi$ curve measured in the supporting electrolyte solution (Fig. 1). According to the Gibbs adsorption equation,

$$d\sigma = -RT\Gamma\, d\ln c, \qquad (1)$$

where $\Gamma$ and $c$ are the extent of adsorption and the concentration of the organic substance. This means that at high surface charges organic molecules are desorbed from the electrode surface. Qualitatively this effect is associated with replacement of a layer of organic molecules, having a low dielectric constant, by a layer of water molecules whose dielectric constant is much higher.

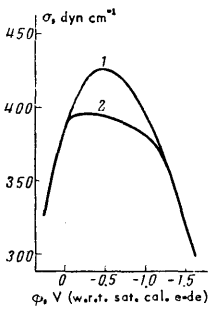



Fig. 1. Electrocapillary curves in different solutions:
1) 1 $N$ $Na_2SO_4$; 2) 1 $N$ $Na_2SO_4$ + + 0.1 M $C_5H_{11}OH$ (Gouy's data [1]).

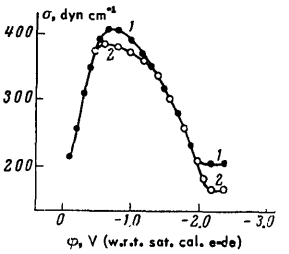



Fig. 2. Electrocapillary curves in different solutions:
1) 0.2 M NaI; 2) 0.2 M NaI + 0.1 M n-$C_5H_{11}OH$ (data of Smirnov and Demchuk [21]).

Fig. 2 shows $\sigma-\varphi$ curves measured by Smirnov and Demchuk [21] in 0.2 M aqueous solution of sodium iodide in the presence of 0.1 M n-pentanol over a wide range of potentials, up to the potential corresponding to the discharge of $Na^+$ ions with formation of sodium amalgam. In the authors' view, the divergence of the electrocapillary curves at highly negative potentials is due to the same cause as in the vicinity of the zero-charge point of mercury, i.e. it is associated with the adsorption of pentanol near the zero-charge point of the sodium amalgam.

A quantitative theory of the effect of the electric field on the adsorption of neutral molecules was developed by Frumkin [22]; according to Frumkin, when allowance is made for the attractive forces between the adsorbed molecules, the lowering of the interfacial tension ($\Delta\sigma$) and the degree of surface coverage ($\theta = \Gamma/\Gamma_\infty$) by the organic substance are related as follows:

$$\Delta\sigma = -A[\ln(1-\theta) + a\theta^2], \qquad (2)$$

where $A$ and $a$ are constants: $A = RT\Gamma_\infty$, while $a$ is a measure of the interaction between the molecules of the adsorbed species (attraction constant).

The equation for the adsorption isotherm can be readily obtained from Eqn. (2) and the Gibbs equation (1):

$$Bc = \frac{\theta}{1-\theta}\exp(-2a\theta), \qquad (3)$$

where $B$ is the adsorption equilibrium constant which determines the variation of the extent of adsorption with electrode potential. Eqn. (3) has been called the Frumkin isotherm.

In order to find the explicit relation between $B$ and $\varphi$, Frumkin suggested that the boundary between the electrode and solution may be represented by two condensers connected in parallel: the space between the plates of one of them contains only molecules of the organic substance and that between the plates of the other only the molecules of the solvent (water). The charge of the electrode ($\epsilon$) can then be represented by an equation of the following form:

$$\varepsilon = \varepsilon_0(1-\theta) + C'\theta(\varphi - \varphi_N), \qquad (4)$$

where $\epsilon_0 = \int_0^{\varphi} C_0 d\varphi$, $C_0$ and $C'$ are the double layer capacitances at $\theta = 0$ and $\theta = 1$ respectively, $\varphi$ is the potential reckoned from the zero-charge point at $\theta = 0$, and $\varphi_N$ is the shift of the zero-charge point on going from $\theta = 0$ to $\theta = 1$.

On combining Eqn. (4) with the principal equation of electrocapillarity,

$$d\sigma = -\varepsilon d\varphi - RT\Gamma d\ln c, \quad (5)$$

the following relation between $B$ and the potential is obtained:

$$B = B_0 \exp\left[-\frac{E + C'\varphi\left(\varphi_N - \frac{\varphi}{2}\right)}{A}\right], \quad (6)$$

where $E = \int_0^{\varphi} \epsilon_0 d\varphi$, i.e. the lowering of $\sigma$ under the influence of the adsorption of inorganic ions only.

Eqns. (6) and (3) permit the calculation of the dependence of the degree of coverage $\theta$ on the potential $\varphi$ and then the determination from Eqn. (2) of the lowering of the interfacial tension under the influence of the adsorption of organic molecules on the surface of the electrode. Such calculations have been made by Frumkin[22] for the adsorption of t-pentanol from 1 $N$ NaCl solution and showed satisfactory agreement with experimental $\sigma-\varphi$ curves.

However, even in these experiments a more detailed comparison of the calculated and experimental $\sigma-\varphi$ curves showed that the break in the experimental electrocapillary curves at $\epsilon > 0$ is more pronounced than would follow from theory. This result was explained[22] by a decrease in the area occupied by one adsorbed alcohol molecule as $\theta$ increases, which is equivalent to a parabolic relation between the potential and the attraction constant $a$.

In Butler's theory[23] an attempt was made to interpret electrocapillary curves on the basis of the molecular properties of the adsorbed substances, in particular by taking into account the polarisability of organic molecules. However, in Butler's theory the dipole moments of the adsorbed molecules are determined from experimental data on interfacial tension. Furthermore, this theory gives an incorrect variation of the extent of adsorption of the organic substance with its concentration in the solution, since it is based on the hypothesis that Henry's law holds.

Further development of the theory of the adsorption of organic compounds was possible on the basis of experimental measurements of the differential capacitance of the mercury electrode in the presence of organic additives, since differential capacitance is a much more sensitive function of the double-layer structure than interfacial tension[24]. On the basis of the electrocapillary data and Lippman's equation, it was to be expected that the differential capacitance curves obtained in the presence of organic additives would include a region of low capacitance (of the order of 4–5 $\mu$F cm$^{-2}$) bounded on either side by desorption peaks. Proskurnin and Frumkin[24] were able to demonstrate for the first time that $C-\varphi$ curves measured in the presence of n-octanol have indeed this shape (Fig. 3). Capacitance curves of similar shape were also obtained subsequently by a number of other investigators. Thus, starting with the work of Proskurnin and Frumkin[24], the method based on the measurement of differential capacitance has been widely used to study the adsorption of various organic substances on mercury[25–44].

However, quantitative application of these data has been limited in practice only to the range of potentials corresponding to maximum adsorption, where the $C-\varphi$ curves show a decrease in capacitance in the presence of organic

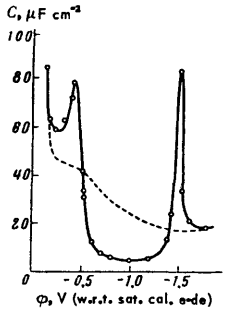



Fig. 3. Differential capacitance curves in 1 $N$ $Na_2SO_4$ solution and in 1 $N$ $Na_2SO_4$ solution saturated with n-$C_8H_{17}OH$ (data of Proskurnin and Frumkin[24]).

substances (Fig. 3) and where the following relation obtains between the capacitance and the degree of surface coverage:

$$C = C_0(1-\theta) + C'\theta. \quad (7)$$

This equation has been used[34,38,42] for the calculation of the adsorption isotherms on mercury of various organic compounds. Recently the variation of the capacitance at the potential of maximum adsorption with the degree of coverage was used by Dobren'kov to develop a theory for the simultaneous adsorption of two organic substances on the electrode surface[45,46].

In order to interpret the overall differential capacitance curve in the presence of an organic substance, it is necessary to choose an independent electrical variable and a particular equation for the adsorption isotherm. The controversy which has arisen concerning these problems[47–49] makes it necessary to examine them in greater detail.

## 1. CHOICE OF ELECTRICAL VARIABLE

Either the electrode potential[22] or the electrode charge[47] can be chosen as the electrical variable in the investigation of adsorption of organic substances on electrodes. It will be assumed initially that the experimental variation of the extent of adsorption of an organic substance $\Gamma$ with its bulk concentration and the potential may be written thus:

$$Bc = f(\Gamma), \quad (8)$$

where $B$ is a function of $\varphi$ only and $f(\Gamma)$ a function of $\Gamma$ only. It is evident that under these conditions it is useful to choose the potential as the independent electrical variable, since the shape of the isotherm [Eqn. (8)] in dimensionless coordinates is then independent of $\varphi$. It follows from Eqn. (8) that

$$\frac{d\ln B}{d\varphi} = -\left(\frac{\partial \ln c}{\partial \varphi}\right)_{\Gamma} = \frac{1}{RT}\left(\frac{\partial \varepsilon}{\partial \Gamma}\right)_{\varphi}, \quad (9)$$

where the second equality is a consequence of the basic equation of electrocapillarity [Eqn. (5)]. On integrating Eqn. (9), we find

$$\varepsilon = RT\left(\frac{d\ln B}{d\varphi}\right)\Gamma + \varepsilon_0 = A\left(\frac{d\ln B}{d\varphi}\right)\theta + \varepsilon_0, \quad (10)$$

where, as before, $A = RT\Gamma_\infty$.

Let the charge at $\theta = 1$ and the given potential be $\epsilon'$, so that

$$\varepsilon' = A\left(\frac{d\ln B}{d\varphi}\right) + \varepsilon_0. \quad (11)$$

It follows from Eqns. (10) and (11) that

$$\varepsilon = \varepsilon_0(1-\theta) + \varepsilon'\theta. \quad (12)$$

On differentiating Eqn. (12) with respect to the potential at $\theta$ = const, we obtain Eqn. (7). Thus representation of the sorption isotherm by Eqn. (8) and hence the choice of the electrode potential as the independent electrical variable are consistent with the model of the electrical double layer previously proposed by Frumkin [22].

If it is assumed as a first approximation that the capacitance $C_0$ is independent of $\varphi$, then evidently $\epsilon_0 = C_0\varphi$ and for $\epsilon = 0$ Eqn. (4) yields

$$\varphi_{\varepsilon=0} = \frac{\varphi_N 0}{\frac{C_0}{C'}(1-\theta)+\theta}, \quad (13)$$

where $\varphi_{\epsilon=0}$ is the difference between the zero-charge point at a given $\theta$ and the zero-charge point at $\theta = 0$, i.e. the jump in potential due to adsorption. Eqn. (13) shows that the variation of $\varphi_{\epsilon=0}$ with $\theta$ (or $\Gamma$) is not linear when the potential is chosen as the electrical variable, and deviates from linearity to a greater extent the higher the value of $C_0/C'$.

It will be assumed first that the experimental data can be described by an equation of the type

$$Gc = f(\Gamma), \quad (14)$$

where $G$ is a function of $\epsilon$ only and $f(\Gamma)$ a function of $\Gamma$ only. In this case it is reasonable to choose the electrode charge as the independent electrical variable, since the shape of the isotherm defined by Eqn. (14), in dimensionless coordinates, is then independent of $\epsilon$. It follows from Eqn. (14) that

$$\frac{d\ln G}{d\varepsilon} = -\left(\frac{\partial \ln c}{\partial \varepsilon}\right)_\Gamma = -\frac{1}{RT}\left(\frac{\partial\varphi}{\partial\Gamma}\right)_\varepsilon, \quad (15)$$

where the second equality is due to the basic equation of electrocapillarity corresponding to $\epsilon$ = const. [50] On integrating Eqn. (15), we obtain

$$\varphi = -RT\left(\frac{d\ln G}{d\varepsilon}\right)\Gamma + \varphi_0 = -A\left(\frac{d\ln G}{d\varepsilon}\right)\theta + \varphi_0, \quad (16)$$

where $\varphi_0$ is the value of $\varphi$, when $\theta = 0$, corresponding to the given value of $\epsilon$.

If the potential at a given $\epsilon$ and $\theta = 1$ is denoted by $\varphi'$, then

$$\varphi' = -A\left(\frac{d\ln G}{d\varepsilon}\right) + \varphi_0. \quad (17)$$

Eqns. (16) and (17) show that

$$\varphi = \varphi_0(1-\theta) + \varphi'\theta. \quad (18)$$

On differentiating Eqn. (18) with respect to $\epsilon$ for $\theta$ = const, we obtain

$$\frac{1}{C} = \frac{1-\theta}{C_0} + \frac{\theta}{C'}. \quad (19)$$

Thus when the adsorption isotherm is represented by Eqn. (14), and therefore when the electrode charge is chosen as the electrical variable, we have a model corresponding to two condensers with capacitances $C_0/(1-\theta)$ and $C'/\theta$ connected in series. The physical interpretation of this model appears to be difficult.

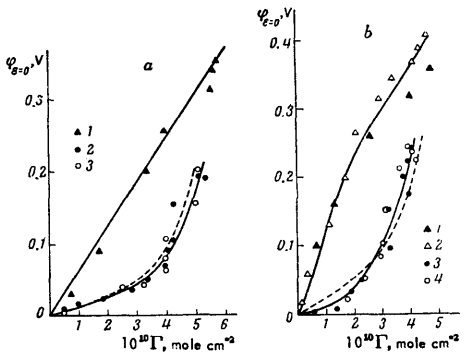



Fig. 4. Variation of the adsorption-induced potential jump with the extent of adsorption of the organic substance: *a*) adsorption of n-$C_4H_9COOH$; 1) at the solution/air interface, supporting electrolyte 0.01 *N* $H_2SO_4$; 2) and 3) at the mercury/solution interface [2] supporting electrolyte 0.01 *N* $H_2SO_4$; 3) supporting electrolyte 1 *N* $Na_2SO_4$ + 0.01 *N* $H_2SO_4$]; dashed line — calculated by Eqn. (13) for $\varphi_N$ = 0.02 V, $\Gamma_\infty = 5\times10^{-10}$ mole cm$^{-2}$, and $C_0/C' = 5$; *b*) adsorption of n-$C_5H_{11}NH_2$: 1) and 2) at the solution/air interface [1] supporting electrolyte 0.05 *N* KOH; 2) supporting electrolyte 1 *N* $Na_2SO_4$ + 0.05 *N* KOH]; 3) and 4) at the mercury/solution interface [3] supporting electrolyte 0.05 *N* KOH; 4) supporting electrolyte 1 *N* $Na_2SO_4$ + 0.05 *N* KOH]; dashed line — calculated by Eqn. (13) for $\varphi_N$ = 0.4 V, $\Gamma_\infty = 5\times10^{-10}$ mole cm$^{-2}$, and $C_0/C' = 5$.

On the other hand, if the capacitances $C_0$ and $C'$ are independent of $\epsilon$, then evidently $\varphi_0 = \epsilon/C_0$ and $\varphi' = \epsilon/C' + \varphi$. In this case Eqn. (18) can be rewritten thus:

$$\varepsilon = \frac{\varphi - \theta\varphi_N}{\frac{1-\theta}{C_0} + \frac{\theta}{C'}}. \quad (20)$$

Putting $\epsilon = 0$ in Eqn. (20), we obtain a linear variation of the adsorption-induced potential jump with $\theta$ (or $\Gamma$):

$$\varphi_{\varepsilon=0} = \theta\varphi_N. \quad (21)$$

Thus the variation of the adsorption-induced potential jump with $\Gamma$ makes it possible to decide whether condition (8) or condition (14) holds, and hence which choice of the electrical variable ($\varphi$ or $\epsilon$) is more reasonable in the investigation of the adsorption of an organic substance at the interface.

Fig. 4 shows the variation of $\varphi_{\epsilon=0}$ with $\Gamma$ for the adsorption of n-butyric acid and n-pentylamine at the mercury/solution and solution/air interfaces [51]. It is evident that the relation between $\varphi_{\epsilon=0}$ and $\Gamma$ at the mercury/solution interface is satisfactorily consistent with Eqn. (13), regardless of the concentration of the supporting electrolyte, and sharply deviates from the linear variation predicted by Eqn. (21). At the same time at the solution/air interface the relation is approximately consistent with Eqn. (21)†. Similar results were obtained by the present author also for the adsorption of n-propanol and n-butanol at both interfaces.

† Certain deviations of the $\varphi_{\epsilon=0}$–$\Gamma$ plot from linearity for the solution/air interface may be associated with a change in the orientation of the adsorbed molecules as $\Gamma$ increases.

It follows from these results that both the physical interpretation of the model of the double layer and the experimental variation of the adsorption-induced potential jump with the extent of adsorption suggest that the electrode potential and not the electrode charge be chosen as the electrical variable in the investigation of the adsorption of organic compounds at the mercury/solution interface.

## 2. CHOICE OF ADSORPTION ISOTHERM

Since experimental adsorption isotherms for organic compounds can have both the form of a logarithmic curve and the characteristic S-shape (Fig. 5), in choosing the equation for the adsorption isotherm it is reasonable to consider only those equations which can represent various shapes of the experimental isotherms, depending on the quantity $a$ (the attraction constant). This condition is satisfied by the following equations for adsorption isotherms:

(1) Frumkin's isotherm — Eqn. (3).

(2) de Boer's isotherm [52]:

$$Bc = \frac{\theta}{1-\theta}\exp\left(\frac{\theta}{1-\theta}\right)\exp(-2a\theta), \qquad (22)$$

(3) Parsons' isotherm [47]:

$$Bc = \frac{\theta}{1-\theta}\exp\left[\frac{2-\theta}{(1-\theta)^2}\right]\exp(-2a\theta), \qquad (23)$$

(4) The general equation of Frumkin's isotherm:

$$Bc = \frac{\theta}{(1-\theta)^n}\exp(-2a\theta), \qquad (24)$$

obtained by the present author [53] and taking into account both the forces of interaction between the adsorbed molecules and the organic substance (via the quantity $a$), and the displacement by the adsorbed species of $n$ molecules of the solvent (water).

Apart from the theoretical justification of a particular type of equation for the adsorption isotherm [47,48], it appears that experimental criteria must be the deciding factor. Such criteria were proposed by Parsons [47] and Tedoradze [54], but, as shown by the present author [55], they do not allow a choice among the four equations for adsorption isotherms given above. Let us therefore consider another criterion which does permit such a choice.

It is readily seen that the above equations are all of the form

$$Bc = F(\theta)\exp(-2a\theta), \qquad (25)$$

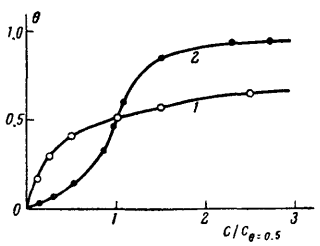



Fig. 5. Adsorption isotherms on mercury: 1) triethylammonium cations; 2) t-pentanol (data of Lorenz and coworkers [42,43]).

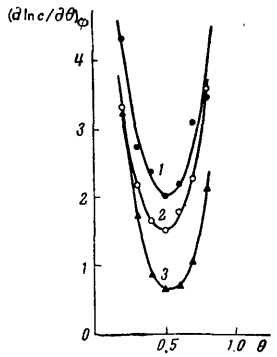



Fig. 6. Variation of $(\partial \ln c/\partial\theta)_\varphi$ with $\theta$ obtained from experimental adsorption isotherms:
1) aniline; 2) n-$C_5H_{11}NH_2$; 3) t-$C_5H_{11}OH$.

where $F(\theta)$ is a function of $\theta$ independent of $a$. On taking logarithms in Eqn. (25) and then differentiating it with respect to $\theta$ with $\varphi$ = const, we obtain

$$\left(\frac{\partial \ln c}{\partial\theta}\right)_\varphi = \frac{d\ln F(\theta)}{d\theta} - 2a. \qquad (26)$$

Analysis shows that at a certain value $\theta = \theta^*$, determined by the condition

$$\frac{d^2 \ln F(\theta)}{d\theta^2} = 0, \qquad (27)$$

the relation between $(\partial \ln c/\partial\theta)_\varphi$ and $\theta$ passes through a minimum whose position is determined only by the function $F(\theta)$ and is independent of the attraction constant $a$.

As shown elsewhere [55], the values of $\theta^*$ for Eqns. (3), (22), (23), and (24) are respectively 0.500, 0.333, 0.215, and $1/(1+\sqrt{n})$. Thus the position of the minimum on the experimental curve for the variation of $(\partial \ln c/\partial\theta)_\varphi$ with $\theta$ may serve as a convenient criterion for choosing one of the four isotherms. When this method is used, only de Boer's equation [Eqn. (22)] and Eqn. (24) with $n = 4$ are virtually indistinguishable.

Experimental $(\partial \ln c/\partial\theta)_\varphi - \theta$ curves can be obtained as follows. Initially, using the value of the capacitance at the minimum on the $C-\varphi$ curves, the $\theta - c$ adsorption isotherm is plotted in terms of Eqn. (7), which, as we have seen, is valid for any isotherm of the type represented by Eqn. (8) or (25). Since $d\ln c/d\theta = dc/cd\theta$, the values of $(\partial \ln c/\partial\theta)_\varphi$ can be found from the slope of this isotherm for various $\theta$, and the $(\partial \ln c/\partial\theta) - \theta$ curve can be plotted.

The characteristic curves obtained for the adsorption of aniline, n-pentylamine, and t-pentanol on the mercury electrode are presented in Fig. 6, which shows that the minimum on these curves corresponds to $\theta^* \simeq 0.5$ and therefore the adsorption of these compounds follows Frumkin's isotherm [Eqn. (3)]. Similar $(\partial \ln c/\partial\theta)_\varphi - \theta$ curves were obtained also for n-propanol, n-pentanol, isopentanol, isopentylamine, phenol, and tetrabutylammonium cations. For all these compounds the experimental values of $\theta^*$ are in the range between 0.45 and 0.55. [55]

Thus the adsorption on mercury of most organic compounds which lower the double-layer capacitance follows the equation of Frumkin's isotherm [Eqn. (3)]. Recently

Dobren'kov and Golovin[56] showed that this equation is also valid for the adsorption of dibutylnaphthalenesulphonic acid and isopentanol on the cadmium electrode‡. Therefore the equation of Frumkin's isotherm [Eqn. (3)] should be used as a basis for the theory of differential capacitance curves in the presence of organic substances.

## 3. QUANTITATIVE THEORY OF DIFFERENTIAL CAPACITANCE CURVES IN THE PRESENCE OF ORGANIC ADDITIVES

The fact that experimental data suggest the choice of the electrode potential as the electrical variable and of Frumkin's equation (3) as the equation of the adsorption isotherm means that the theoretical relations obtained by Lorenz and coworkers[42,43] and Parsons[47] and also the Devanathan[60] and Bockris–Devanathan–Müller[61] theories must be rejected, particularly as the last two theories have a number of significant disadvantages, which are discussed in detail in Ref. 62.

If the potential is chosen as the independent electrical variable, then under the condition that the adsorption of the organic substance on the electrode surface is not complicated by the formation of multilayers and micellar films, the electrode charge is a function of electrode potential and degree of coverage only:

$$\varepsilon = \varepsilon(\varphi, \theta). \tag{28}$$

Thus the overall expression for the differential capacitance can be put in the following form:

$$C = \frac{d\varepsilon}{d\varphi} = \left(\frac{\partial \varepsilon}{\partial \varphi}\right)_\theta + \left(\frac{\partial \varepsilon}{\partial \theta}\right)_\varphi \frac{d\theta}{d\varphi}. \tag{29}$$

The quantities $(\partial\epsilon/\partial\varphi)_\theta$ and $(\partial\epsilon/\partial\theta)_\varphi$ in this equation can be found immediately from Eqn. (4):

$$\left(\frac{\partial \varepsilon}{\partial \varphi}\right)_\theta = C_0(1-\theta) + C'\theta, \tag{30}$$

$$\left(\frac{\partial \varepsilon}{\partial \theta}\right)_\varphi = -[\varepsilon_0 + C'(\varphi_N - \varphi)]. \tag{31}$$

The derivative $d\theta/d\varphi$ is found from Eqn. (3). On taking logarithms in this equation and then differentiating it with respect to $\varphi$, we obtain after algebraic rearrangement,

$$\frac{d\theta}{d\varphi} = \frac{d\ln B}{d\varphi} \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \tag{32}$$

It follows from Eqn. (6) that

$$\frac{d\ln B}{d\varphi} = -\frac{\varepsilon_0 + C'(\varphi_N - \varphi)}{A} \tag{33}$$

and therefore

$$\frac{d\theta}{d\varphi} = -\frac{\varepsilon_0 + C'(\varphi_N - \varphi)}{A} \frac{\theta(1-0)}{1-2a\theta(1-\theta)}. \tag{34}$$

On substituting the values of the derivatives from Eqns. (30), (31), and (34) in Eqn. (29), we obtain the final expression for the differential capacitance in the presence of an organic substance:

$$C = C_0(1-\theta) + C'\theta + \frac{[\varepsilon_0 + C'(\varphi_N - \varphi)]^2}{A} \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \tag{35}$$

This equation was obtained for the first time by Hansen and coworkers[28].

As already pointed out above, Eqns. (3) and (6) make it possible to calculate the variation of $\theta$ with $\varphi$ at a given concentration of the organic substance. Once this variation has been found, and the constants $C'$, $A$, $a$, and $\varphi_N$ are known, the total differential capacitance curve in the presence of an organic substance may be calculated by Eqn. (35). Such calculations, made by Hansen and coworkers[28] and by the present author[63], show that, despite the qualitative agreement between the calculated and experimental $C-\varphi$ curves, there is a very significant quantitative discrepancy between them. Analysis shows that the discrepancy is evidence of a change with potential of the attraction constant in the equation of Frumkin's isotherm [Eqn. (3)]. Furthermore, in contrast to Frumkin's hypothesis[22], the variation of $a$ with $\varphi$ for most organic compounds is linear and not parabolic.

Thus it is of interest to develop a theory assuming an arbitrary variation of $a$ with $\varphi$ [$a = a(\varphi)$].

In this case on taking logarithms in Eqn. (3) and differentiating with respect to the potential, we obtain, after rearrangement, the following expression instead of Eqn. (32):

$$\frac{d\theta}{d\varphi} = \left(\frac{d\ln B}{d\varphi} + 2\theta\frac{da}{d\varphi}\right) \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \tag{36}$$

At the same time differentiation with respect to $\varphi$ when $\theta$ = const gives

$$\left(\frac{\partial \ln c}{\partial \varphi}\right)_\theta = -\left(\frac{d\ln B}{d\varphi} + 2\theta\frac{da}{d\varphi}\right). \tag{37}$$

Taking into account the second equality in Eqn. (9), we obtain

$$\frac{1}{A}\left(\frac{\partial \varepsilon}{\partial \theta}\right)_\varphi = \frac{d\ln B}{d\varphi} + 2\theta\frac{da}{d\varphi}. \tag{38}$$

On integrating this equation and remembering that the integration constant is $\epsilon_0$, we obtain

$$\varepsilon = \varepsilon_0 + A\frac{d\ln B}{d\varphi}\theta + A\theta^2\frac{da}{d\varphi}. \tag{39}$$

Since $\epsilon = \epsilon' = C'(\varphi - \varphi_N)$ when $\theta = 1$, it follows from Eqn. (39) that

$$\frac{d\ln B}{d\varphi} = -\frac{\varepsilon_0 + C'(\varphi_N - \varphi)}{A} - \frac{da}{d\varphi}. \tag{40}$$

After integrating this equation from 0 to $\varphi$ and taking antilogarithms, we have

$$B = B_0 \exp\left[-\frac{E + C'\varphi\left(\varphi_N - \frac{\varphi}{2}\right)}{A}\right] \exp(a_0 - a), \tag{41}$$

where $a_0$ is the value of $a$ when $\varphi = 0$.

Eqn. (41) represents the variation of the adsorption equilibrium constant with potential for any relation between $a$ and $\varphi$. It is readily seen that it becomes identical with Eqn. (6) when $a$ = const.

On substituting Eqn. (40) in Eqn. (39), we obtain the equation for the electrode charge in the general case, when $a = a(\varphi)$:

$$\varepsilon = \varepsilon_0(1-\theta) + C'\theta(\varphi - \varphi_N) - A\frac{da}{d\varphi}\theta(1-\theta). \tag{42}$$

‡ The satisfactory agreement of Eqn. (3) with experimental data implies that in the more general equation (24) $n = 1$ and therefore one adsorption site on the surface of the electrode is occupied by a group of several water molecules[53]. When allowance is made for the considerable attractive interaction between the $H_2O$ molecules adsorbed on mercury[57-59], this result may be explained by the fact that the work associated with the transfer of this group of molecules, taken as a whole, from the surface into the bulk of the solution is smaller than the overall work of transfer of each of these molecules separately.

As was to be expected, Eqn. (42) becomes identical with Eqn. (4) when $a$ = const.

Finally, we shall find an expression for the differential capacitance in the presence of an organic substance under the condition that $a = a(\varphi)$. From Eqn. (42), we have

$$\left(\frac{d\varepsilon}{\partial\varphi}\right)_\theta = C_0(1-\theta) + C'\theta - A\frac{d^2a}{d\varphi^2}\theta(1-\theta), \quad (43)$$

$$\left(\frac{\partial\varepsilon}{\partial\theta}\right)_\varphi = -\varepsilon_0 + C'(\varphi-\varphi_N) - A\frac{da}{d\varphi}(1-2\theta). \quad (44)$$

On substituting Eqn. (40) in Eqn. (36), we find

$$\frac{d\theta}{d\varphi} = -\left[\varepsilon_0 - C'(\varphi-\varphi_N) + A\frac{da}{d\varphi}(1-2\theta)\right]\frac{1}{A}\frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \quad (45)$$

If we now substitute the values of the derivatives from Eqns. (43), (44), and (45) in Eqn. (29), we obtain the final expression for the differential capacitance:

$$C = C_0(1-\theta) + C'\theta - A\frac{d^2a}{d\varphi^2}\theta(1-\theta) + \frac{1}{A}\left[\varepsilon_0 + C'(\varphi_N-\varphi) + A\frac{da}{d\varphi}(1-2\theta)\right]^2\frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}. \quad (46)$$

Evidently Eqn. (46) becomes identical with Eqn. (35) when $a$ = const.

Earlier the present author obtained expressions for the adsorption equilibrium constant $B$, the electrode charge $\epsilon$, and the differential capacitance $C$ under the condition that the attraction constant is a linear function of electrode potential:

$$a = a_0 + \beta\varphi. \quad (47)$$

In the expressions for $B$, $\epsilon$, and $C$ the variation of $a$ with $\varphi$ was allowed for by introducing a new constant:

$$\varphi_N^0 = \varphi_N + \frac{\beta A}{C'}. \quad (48)$$

Eqns. (41), (42), and (46) obtained in this work are free from the limitations imposed by condition (47), and are valid for any relation between the attraction constant and the electrode potential. Since the experimental variation of the attraction constant with potential satisfied condition (47) in most cases, the formulae obtained in Ref. 64 led to satisfactory agreement between calculated and experimental $C-\varphi$ curves[63,65-68]. Fig. 7 illustrates this result using as an example the adsorption of n-valeric acid on mercury[68]. Similar satisfactory agreement between calculation and experiment was observed by the author for the adsorption on mercury of n-propanol, n-butanol, n-pentanol, isopentanol, t-pentanol, n-butylamine, n-pentylamine, isopentylamine, and diethyl ketone.

The calculated and experimental $C-\varphi$ curves for the adsorption of aniline[69] and pyridine[70] on mercury coincide only in the range of negative surface charges (Fig. 8). On going from $\epsilon < 0$ to $\epsilon > 0$, there is a change in the orientation accompanied by partial desorption of aniline or pyridine molecules due to their $\pi$-electron interaction with the positive charges on the surface of mercury. It is this process and not total desorption of the molecules of the organic substance from the electrode surface which corresponds to the anodic maxima on the $C-\varphi$ curves in the presence of aniline or pyridine. Clearly, under these conditions when $\epsilon > 0$ theoretical $C-\varphi$ curves, which do not take account of the above anomalies in the adsorption of an organic substance, cannot coincide with the experimental differential capacitance curves.

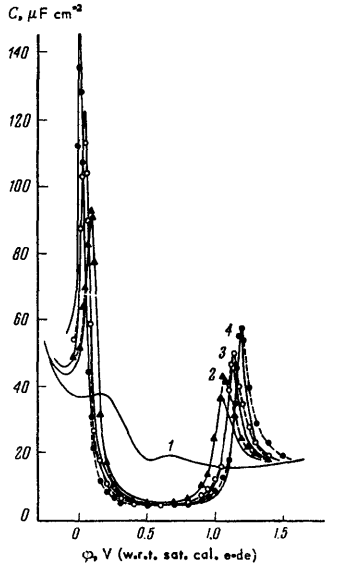



Fig. 7. Differential capacitance curves for 0.05 $N$ $Na_2SO_4$ solution with different concentrations of added n-$C_4H_9COOH$ (M): 1) 0; 2) 0.05; 3) 0.08; 4) 0.12; continuous lines — experimental data for 400 c/s; symbols and dashed lines — calculated values.

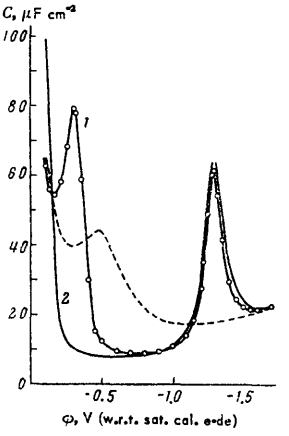



Fig. 8. Differential capacitance curves for 0.1 $N$ KCl solution alone (dashed curve) and in the presence of 0.1 M aniline: 1) experimental data; 2) calculated curve.

Finally, in the adsorption of phenol on mercury[71] the planar disposition of molecules, associated with strong $\pi$-electron interaction, is characteristic of the entire range of its adsorption potentials. In this case the constants which enter into the equations for the quantity $B$ [Eqn. (41)] and the differential capacitance [Eqn. (46)] characterise the planar configuration of the phenol molecules in the adsorbed state, so that the calculated and experimental $C-\varphi$ curves agree with one another over the entire range of potentials (Fig. 9). However, the effect of the $\pi$-electron interaction

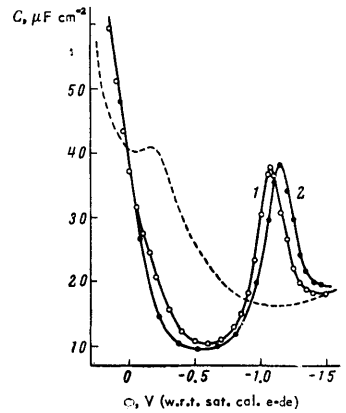



Fig. 9. Differential capacitance curves for 1 $N$ $Na_2SO_4$ solution alone (dashed curve) and in the presence of 0.05 M phenol: 1) experimental data; 2) calculated curve.

leads nevertheless to less satisfactory agreement between calculation and experiment for phenol than for the adsorption of aliphatic compounds (Fig. 7).

Apart from the quantitative interpretation of the differential capacitance curves in the presence of an organic substance, Eqns. (3), (41), and (46) make it possible to investigate certain general features of equilibrium (i.e. extrapolated to zero frequency) and non-equilibrium $C-\varphi$ curves, in particular the dependence of the potentials corresponding to the peaks on the $C-\varphi$ curves and the height of these peaks on the concentration of the organic substance. Study of these relations is very important, since it leads to methods for the determination of the principal constants in Eqns. (41) and (46) and the relations between $a$ and $\varphi$ from experimental differential capacitance curves. Recently the present author and Tedoradze [72-76] considered the problems involved in the determination of such general relations, which are of independent scientific interest.

I should like to take this opportunity to express my profound gratitude to A. N. Frumkin for continued interest in this work and discussion of the results obtained.

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# THEORY OF HOMOGENEOUS AND HETEROGENEOUS ELECTRONIC PROCESSES IN LIQUIDS

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## I. INTRODUCTION

The theory of electronic processes in liquids occupies a very specific place in the general theory of chemical kinetics. A comparison of various electronic processes occurring in the liquid phase and in solids reveals a great similarity of physical mechanisms. Yet, no such analogy is normally found between gas-phase and liquid-phase reactions. For example, we may consider the electron exchange reaction between ions of the same sign. If we compare the rate of charge transfer between ions in gases with the rate of analogous oxidation–reduction reactions in water, we find that charge transfer in gases not only occurs significantly faster than in solutions, but also, and this is less trivial, that the phenomenon of resonance charge transfer is in general absent in solutions. It is well known that charge transfer between similar ions differing only in valence state proceeds much faster in the gas phase than reactions between unlike ions[1]. At the same time, the reaction $Fe^{2+} + Fe^{*3+} \rightarrow Fe^{3+} + Fe^{*2+}$ is much slower, in solutions, than a reaction like $Fe^{2+} + FeOH^{2+} \rightarrow \rightarrow Fe^{3+} + FeOH^{+}$. On the other hand, it has been possible[2-7] to apply the theory of $F$-centres and polarons, which was developed for crystals[4], in the study of the absorption spectra and of the conductivity of solutions of metals in liquid ammonia.

The lack of similarity between gas-phase reactions and electronic processes in liquids makes it very difficult to apply the transition state theory effectively to the latter processes. Indeed, this is easily verified by noting that the potential energy surfaces for electronic reactions in a condensed phase must be multidimensional, since we assume that the electron interacts strongly with a very large number of solvent molecules. This does not mean, of course, that the rate of the process will not show activational features: the situation involves, on the one hand, the Franck–Condon principle (i.e. the quasi-classical motion of heavy atoms), and, on the other hand, fluctuation theory (the Boltzmann formula). We are only considering the actual calculation of activation energies by means of the transition state theory. Furthermore, in the case of non-adiabatic reactions with multidimensional electronic energy levels (i.e. potential energy surfaces) there is no method of calculating the pre-exponential factor (the so-called transmission coefficient) similar to the Landau–Zener method for one-dimensional levels, used to calculate the rates of gas reactions. In this sense, the transition state theory hardly justifies its name of theory of absolute reaction rates.

Lastly, we have one further reason for renouncing the formal use of the transition state theory: it is the absence of any criterion whatsoever for its applicability, which has the effect of creating the illusion that the method is of universal applicability. Yet, we know from the most general considerations that such criteria must exist. We shall show below, using a concrete example (see Sections II, 2 and II, 3), that the absolute reaction rate theory is applicable only at high enough temperatures. Formally, this shortcoming stems from the absence of a sufficiently rigorous method of deriving the formulae of the transition state theory. We are not only concerned with the need for a quantitative criterion of the exactness of a theoretical discussion: such a criterion, in conjunction with experimental data, would also throw light on the mechanism of various reactions.

The physical analogy between various electronic processes in liquids and in solids suggests the possibility of applying to electronic processes in liquids the mathematical formalism which has been developed to deal with kinetic phenomena in solids (polar crystals, impurity semiconductors, alloys, etc.). A very wide range of contemporary problems in chemistry, electrochemistry, and biochemistry could be solved by the application of some of the techniques of the quantum theory of irreversible processes. There are a number of problems, however, in which the difference between a liquid and an ordered crystal can prove to be a fundamental one (see, for example, Section II, 5). This is especially true of the calculation of mobilities. In an ideal crystal, the electrical conductivity is infinitely high in the absence of thermal vibrations, whereas in liquids (as in any disordered system) the electronic electrical conductivity remains finite even if the thermal motion of the atoms is ignored. We shall show in Section II, 5 that in this case it is possible to apply (in a slightly modified form) the quantum statistics used to describe disordered solids (alloys, or impurity semiconductors).

In compiling the present article, we have relied mainly on our earlier theoretical results, which we have compared with the results of other workers. This restriction is due to the fact that the method presented here differs very considerably from the theoretical approach of other workers, so that an attempt at unification would not be expedient. However, the list of references includes a selection of reviews[5-8] and original papers by both experimental and theoretical workers.

## II. THEORY OF HOMOGENEOUS REACTIONS

### 1. Model of a Liquid

Since the present review will be concerned mostly with polar liquids, this Section is devoted exclusively to liquids of this type. Non-polar liquids will be discussed to some extent in Section II, 5 in connection with the study of electronic spectra.

A polar liquid can be completely described by specifying the coordinates of all the dipoles in the medium. To simplify the discussion, we shall adopt the following scheme: let the position of the dipole be characterised by the coordinate of the centre of gravity $R_i(t)$ and by the angle $\theta_i(t)$ which defines the orientation of the dipole. The subscript $i$ denotes the number of the dipole, and $t$ indicates that both $R_i$ and $\theta_i$ are time-dependent. In accordance with modern ideas on the liquid state, the variation of $R_i$ and $\theta_i$ with time can be visualised as follows: the dipole resides in a certain temporary equilibrium position $R_i^0$, $\theta_i^0$, about which it executes small oscillations. The average time interval between sudden changes of $R_i^0$ and $\theta_i^0$, $\tau_g$, can be calculated from diffusion data. Thus, for water $\tau_g \simeq 10^{-9}$ s, whereas the libration frequency of the dipole (describing changes of the angle $\theta_i$ in the neighbourhood of $\theta_i^0$) is of the order of $10^{11}$ s$^{-1}$. One of the most important postulates of the theory states that the most fundamental dynamic role is played by the librational oscillations of the dipole, and not by its diffusional jumps. This assumption can be explained as follows. A fairly accurate description would be obtained if the desired physical quantity (say, the probability of electron transfer) could be calculated for fixed values of $R_i^0$ and $\theta_i^0$, and the result averaged over all $R_i^0$ and $\theta_i^0$. Unfortunately, this procedure is far from being generally possible. For example, in the presence of strong interaction between the electron and the solution the distribution function of $R_i^0$ and $\theta_i^0$, i.e. the probability of finding the dipole in the position $R_i^0$, $\theta_i^0$, is itself, obviously, a function of the distribution of the electronic charge density or of the quantum state of the electron. In practice, this means that if we are interested only in the probability of an electronic transition from some initial state to a final state, we should first calculate the probability for the conditions $R_i^0 = (R_i^0)_{\text{init}}$ at the beginning of the transition and $R_i^0 = (R_i^0)_{\text{fin}}$ at the end of the transition, and we should then sum the probabilities over all possible $(R_i^0)_{\text{fin}}$ and average over $(R_i^0)_{\text{init}}$. We shall assume that the transition from an arbitrary state $R_i^0$ to a state of thermodynamic equilibrium occurs faster than the time $\tau_e$ between electronic transitions. In this case it is no longer necessary to average over $R_i^0$. Thus, for $\tau_e \gg \tau_g$ we can ignore the effect of discontinuous changes in the coordinates $R_i^0$ and $\theta_i^0$, and consider only the librational oscillations of the dipole as the total or intramolecular vibrations of the liquid. Lastly, we shall make one further observation, of which we shall make use in what follows. If the static dielectric constant $\epsilon_s$ is calculated for a system of oscillating dipoles, it is found to be independent of temperature. Thus, yet another criterion for the applicability of our model is that $\epsilon_s$ should be an insensitive function of temperature. In particular, for water $\epsilon_s = a/T$, so that the relative change

of $\epsilon_s$, $\left(\left|\frac{\Delta\epsilon_s}{\epsilon_s}\right| = \left|\frac{\Delta T}{T}\right|\right)$, is not large at ordinary temperatures. As for our fundamental criterion $\tau_e \gg \tau_g$, we shall merely state at this point that it is always satisfied in practice by the systems of interest, and that a more detailed discussion (from a somewhat different viewpoint) will be given in Section II, 3.

Strictly speaking, the oscillations of dipoles in a liquid are not of the harmonic type. However, the problem of electronic processes is susceptible to fully quantitative treatment and can be solved quantum-mechanically only in the harmonic approximation. In this approximation the model of the liquid takes the form of an assembly of harmonic oscillators (phonons) whose Hamiltonian expressed in normal coordinates is

$$H_s = \frac{1}{2}\sum_k \hbar\omega_k \left(q_k^2 - \frac{\partial^2}{\partial q_k^2}\right). \qquad (2.1)$$

In this formula the normal frequencies $\omega_k$ should be treated as empirical. In general, the electron can interact both with optical and with acoustic phonons, but in polar systems only longitudinal phonons of the optical type[4] of low dispersion (i.e. $\omega_k \simeq \omega_0$) play a really important role. Physically, either intramolecular vibrations of the dipoles or librational oscillations can correspond to these types. For example, for water we have the vibrations of the O–H bond or of the H–H hydrogen bond, and also the librational oscillations of the molecule as a whole. As will be evident from what follows, it is most rational to choose the latter (librational) type of oscillation for water, with $\omega_0 \simeq \simeq 10^{11}$ s$^{-1}$. If complex or hydrated ions are relevant to the problem, it becomes necessary to consider several optical vibration types. The presence of a small dispersion in the optical type does not affect the final results in any way, but for purely computational reasons[9] it is convenient to introduce a finite dispersion at an intermediate stage and make this tend to zero in the final result.

The theory becomes particularly revealing if the model used to describe the liquid is a continuum with macroscopic specific polarisation $\vec{P}$. Strictly speaking, such a model can describe a real system satisfactorily only some distance away from the electron (or ion), but the formulae obtained from this model offer some valuable though approximate numerical results. The Hamiltonian for this system was first obtained by Pekar[4] and Fröhlich[10], and we shall not derive it here (see also Ref. 6). We shall only point out that it is of the same form as Eqn. (2.1), but we must set $\omega_k = \omega_0$, and the normal coordinates $q$ are found to be related to the Fourier amplitudes of $\vec{P}$ by the expression

$$\vec{P}(\vec{r}) = \left(\frac{c\hbar\omega_0}{4\pi V}\right)^{1/2} \sum_k \vec{Q}_k e^{i\vec{k}\vec{r}}; \quad q_k = \frac{1}{2}\begin{cases} i(Q_k - Q_k^*), & k > 0; \\ Q_k + Q_k^*, & k \leqslant 0, \end{cases} \qquad (2.2)$$

where $V(\to\infty)$ is the volume of the fundamental region of periodicity of $\vec{P}$, and

$$c = \frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_s}. \qquad (2.3)$$

$\epsilon_0$ denotes the optical dielectric constant (equal, for example, to 1.78 for water). The parameter $c$ plays a fundamental role in the polarisation model. Its function can be illustrated as follows. When expressing the potential energy of a liquid, one should consider only that part which concerns the motion of heavy particles, since the electronic part of the polarisation follows their motion without inertia and contributes a constant term to the energy. On the other hand, the interaction between a slow electron in homogeneous reactions and the electronic part of the polarisation can also be assumed constant if one considers that the electrons of the liquid molecule are moving immeasurably faster than the outer electron which is taking part in the reaction. Therefore, this term also can be omitted if the electron does not leave the liquid. The case of heterogeneous reactions, when the electron passes from the liquid into the electrode, will be considered separately (see Section III, 1). The notion of calculating the potential energy of the inertial part of the non-equilibrium polarisation, $\vec{P}_{\text{inert}}$, amounts to a calculation of the work needed to form $\vec{P}_{\text{inert}}$ by slowly applying a fictitious electrical induction $\vec{D}$ and then removing it instantaneously:

$$U_{P_{\text{inert}}} = -\frac{1}{4\pi}\int_0^D DdE - \frac{1}{4\pi}\int_D^0 DdE = -\frac{1}{4\pi\varepsilon_s}\int_0^D DdD - \frac{1}{4\pi\varepsilon_0}\int_D^0 DdD = \frac{c}{8\pi}D^2. \qquad (2.4)$$

The value of $D$ must, of course, be chosen so that the polarisation in the final state is equal to $P_{\text{inert}}$. Since the first stage (application of the induction) was carried out slowly, we can use the equilibrium formula

$$\vec{P}_{\text{inert}} = \vec{P} - \vec{P}_{\text{electr}} = \frac{\varepsilon_s - 1}{4\pi\varepsilon_s}\vec{D} - \frac{\varepsilon_0 - 1}{4\pi\varepsilon_0}\vec{D} = \frac{c}{4\pi}\vec{D}. \qquad (2.5)$$

On inserting formula (2.5) into (2.4), we find

$$U_{P_{\text{inert}}} = \frac{2\pi}{c}P^2_{\text{inert}}. \qquad (2.6)$$

This expression was first obtained by Pekar[4], and also by Marcus[11], who used an independent and somewhat more complicated method. This deduction, based on non-equilibrium thermodynamics, has one major shortcoming: the quantum-mechanical Hamiltonian is found to depend on temperature through $\epsilon_s(T)$. In practice, this means that, instead of a single statistical averaging of the final results, we have performed a partial averaging at the Hamiltonian stage. This procedure can be justified by using the concepts expressed at the beginning of this Section. Indeed, the condition that $D$ should be applied slowly implies that a preliminary averaging with respect to $R_i^0$ and $\theta_i^0$ is permissible. Hence it is evident that formula (2.6) is also correct only if the condition $\tau_e \gg \tau_g$ is satisfied. In other words, in all formal thermodynamic calculations $\epsilon_s$ is to be treated as a parameter which does not depend on temperature.

## 2. Adiabatic Perturbation Theory

As was pointed out above, the characteristic feature of a polar medium is that the interaction between an electron and the medium (i.e. the phonons) is not a weak one. Therefore, the familiar methods of the theory of small perturbations are not suitable in this case for calculating the probability of electron transfer, if the solution is wanted in the form of a power series of the electron–phonon interaction constant. Physically, this means that several phonons are emitted during the electron transfer process rather than a single phonon. One of the methods of calculation used in problems of this type relies on the so-called adiabatic perturbation theory. We shall now describe the physical concepts underlying this theory.

It is convenient to set up the Hamiltonian for the total system in the form

$$H(x, q) = H_e(x) + H_s(q) + V(x, q) + H'(x, q) = H(x, q) + H'(x, q). \qquad (2.7)$$

Here $H_e(x)$ is the total energy of an electron interacting with a given external field (for example, with ions, with

light, etc.); $H_S(q)$ is the total energy of the liquid (in the phonon model assumed here); $V(x,q)$ is the electron–phonon interaction energy. To make the treatment more general, we have introduced the term $H'(x,q)$, which is small in comparison with $H(x,q)$, as required by perturbation theory. In a sense, this term can describe the effect of, for example, neighbouring ions on an electron situated close to some specific ion. Since the calculation of $H'(x,q)$ does not present particular difficulty, we shall consider for the time being the Hamiltonian $H(x,q)$. The basic concept which we intend to use is that the rate of motion of the electron is very much higher than that of the heavy atoms of the liquid, i.e. of the phonons. Hence, as "seen from" the fast electron, the atoms of the liquid can be treated as immobile, and the problem becomes that of an electron in a given field:

$$\{H_e(x)+V(x,q)\}\psi_\alpha(x,q)=\varepsilon_\alpha(q)\psi_\alpha(x,q), \tag{2.8}$$

where $\alpha$ is the number of the electronic level, and the energy $\epsilon_\alpha(q)$ and the electron function $\psi$ depend on $q$ as a parameter. If $H_S(q)$ were to vanish, i.e. if the atoms of the liquid were immobile, $\psi_\alpha(x,q)$ would be an exact solution of the problem. However, allowance for the slow motion of the atoms introduces the possibility of electron transfer from one state $\alpha$ to another state $\alpha'$. Therefore, the exact solution of the problem takes the form of a superposition of all states $\psi_\alpha(x,q)$, with some "weighting" factors $\chi_\alpha(q)$ which are, of course, a function of $q$. Mathematically speaking, we have expanded an exact $\psi$-function into a series as a full set of orthogonalised functions $\psi_\alpha(x,q)$:

$$\psi(x,q)=\sum_\alpha \chi_\alpha(q)\psi_\alpha(x,q). \tag{2.9}$$

On substituting this expression into the wave equation for $H(x,q)$, after multiplying the left-hand side by $\psi^*_\beta(x,q)$ and integrating with respect to $x$, we obtain the following equation for $\chi_\alpha(q)$:

$$\{H_s(q)+\varepsilon_\beta(q)-E\}\chi_\beta(q)=\sum_\alpha L_{\beta\alpha}(q)\chi_\alpha(q), \tag{2.10}$$

where

$$L_{\beta\alpha}(q)=\frac{1}{2}\sum_k \hbar\omega_k\left\{\int\psi^*_\beta\frac{\partial\psi_\alpha}{\partial q_k}dx\cdot\frac{\partial}{\partial q_k}+\int\psi^*_\beta\frac{\partial^2\psi_\alpha}{\partial q_k^2}dx\right\}. \tag{2.11}$$

Since $\frac{\hbar}{i}\frac{\partial}{\partial q_k}$ is an operator for the rate of motion of heavy particles, the first term in (2.11) can be interpreted, in a sense, as a mean velocity, and the second term as a mean square velocity. Therefore, the operator $L$ must be treated as small in the adiabatic approximation (this operator is sometimes called the non-adiabaticity operator). If we use the quasi-classical approximation for the electron, we can show that $L\simeq\sqrt{m/M}$, where $m$ is the mass of the electron and $M$ the mass of the heavy particles. In the zeroth approximation, assuming $L=0$, we obtain

$$\left\{-\frac{1}{2}\sum_k\hbar\omega_k\frac{\partial^2}{\partial q_k^2}+\frac{1}{2}\sum_k\hbar\omega_k q_k^2+\varepsilon_\beta(q)\right\}\chi_{\beta n}(q)=E_n\chi_{\beta n}(q), \tag{2.12}$$

where the subscript $n$ identifies the various quantum levels of the slow subsystem. If the electron is initially in the state $\alpha$, $\chi_{\beta n}(q)\simeq\delta_{\beta\alpha}$, i.e. the electronic state $\alpha$ with $L=H'=0$ will not suffer any changes. The quantity

$$U_\beta(q)=\frac{1}{2}\sum_k\hbar\omega_k q_k^2+\varepsilon_\beta(q) \tag{2.13}$$

plays the role of potential energy for the heavy subsystem, and admits of the following simple interpretation: the first term represents the direct interaction of the heavy particles; the second term represents the interaction of the heavy particles with the blurred electron cloud (i.e. the heavy particles "perceive" the fast-moving electron only in a smeared out form). Therefore, the latter must evidently depend on the electronic state $\beta$. $U_\beta(q)$ is called the electronic energy level, or the potential energy surface.

If $L$ or $H'$ is finite, transitions can occur between the different states $\Psi_{\alpha,n}=\psi_\alpha\chi_{\alpha n}$ and $\Psi_{\alpha' n'}$ with probability $w_{\alpha n\to\alpha' n'}$. Therefore, if we are interested only in the change of electronic state, $w_{\alpha n\to\alpha' n'}$ must be summed over $n'$ and statistically averaged over $n$ (we assume that the heavy subsystem is initially in statistical equilibrium):

$$w_{\alpha\to\alpha'}=\sum_{n'}\langle w_{\alpha n\to\alpha' n'}\rangle_n. \tag{2.14}$$

To calculate $w$ it is necessary to know $\chi_{\alpha n}$, i.e. to be able to solve Eqn. (2.12). An approximate solution can be obtained by expanding $\epsilon_\alpha(q)$ in a power series of $q$ around the equilibrium value $q_0^\alpha$ and retaining only the first two terms:

$$\varepsilon_\alpha(q)\simeq\varepsilon_\alpha(q_0^\alpha)+\sum_k u^\alpha(q_k-q_{k0}^\alpha). \tag{2.15}$$

The electronic energy level then has the form

$$U_\alpha(q)=\varepsilon_\alpha(q_0^\alpha)-\sum_k u_k^\alpha\left(q_{k0}^\alpha+\frac{u_k^\alpha}{2\hbar\omega_k}\right)+\frac{1}{2}\sum_k\hbar\omega_k\left(q_k+\frac{u_k^\alpha}{\hbar\omega_k}\right)^2.$$

Since by definition $q_0^\alpha$ corresponds to a minimum value of $U_\alpha(q)$, it follows that $q_{k0}^\alpha=-\frac{u_k^\alpha}{\hbar\omega_k}$ and

$$U_\alpha(q)=\varepsilon_\alpha(q_0^\alpha)+\frac{1}{2}\sum_k\hbar\omega_k q_{k0}^2+\frac{1}{2}\sum_k\hbar\omega_k(q_k-q_{k0}^\alpha)^2=J_\alpha+$$
$$+\frac{1}{2}\sum_k\hbar\omega_k(q_k-q_{k0}^\alpha)^2. \tag{2.16}$$

This expression allows a simple physical interpretation: before the electron is introduced, the liquid executes small oscillations close to the unpolarised state $q=0$ (see curve $a$ of Fig. 1); after introduction of an electron into the state $\alpha$, the liquid becomes polarised to the value $q_0^\alpha$, and the total potential energy of the system is made up of the polarisation energy of the liquid $-\frac{1}{2}\sum_k\hbar\omega_k q_{k0}^2$, the energy of the electron in the polarised liquid $\epsilon_\alpha(q_0^\alpha)$, and the energy of the oscillatory motion of the liquid close to its equilibrium state $\frac{1}{2}\sum_k\hbar\omega_k(q_k-q_{k0}^\alpha)^2$. It is evident from this picture that the approximation (2.15) adopted here corresponds to the case where it is permissible to ignore the changes in vibrational frequency of the dipoles caused by the interaction between the electron and the liquid.

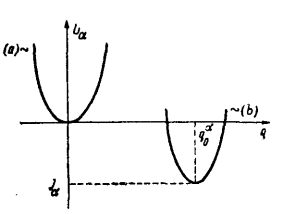



Fig. 1.

In order to apply the perturbation theory to the continuous spectrum, we shall assume that $\omega_k = p_k\Omega_0$, where $p_k$ are integers and $\Omega_0 \to 0$. Without reproducing the lengthy calculations[12-14], we shall quote the expression for the probability of electronic transition per unit time:

$$w_{\alpha\to\alpha'} = \frac{2\pi}{\hbar}|V_{\alpha'\alpha}|^2 e^{\frac{J_\alpha - J_{\alpha'}}{2kT} - \sum_k z_k \coth\frac{\hbar\omega_k}{2kT}} \sum_{m=-\infty}^{+\infty} \frac{\sin m\Omega_0 t}{\pi\hbar m\Omega_0} e^{-\frac{m\hbar\Omega_0}{2kT}} \sum_{l_k}' \prod_k I_{l_k}(z_k). \tag{2.17}$$

We have introduced the following terminology: $V_{\alpha'\alpha}$ is a matrix element of the perturbation, i.e. either $L_{\alpha'\alpha}$ or $H'_{\alpha'\alpha}$, according to which of the two is the most significant; $z_k = \frac{1}{2}(q^{\alpha}_{k0} - q^{\alpha'}_{k0})^2 \operatorname{cosech}\frac{\hbar\omega_k}{2kT}$; $I_l(z)$ is a Bessel function of imaginary argument of order $l$; lastly, the prime in the summation denotes the choice of values of $l_k$ among all possible integral values such that $\sum_k \hbar\omega_k l_k = J_{\alpha'} - J_\alpha + m\hbar\Omega_0$. The only assumption made in the derivation of this formula was $t < \frac{1}{\Omega_0} \to \infty$. The physical significance of this condition is that the times considered are small enough to make (according to the uncertainty principle) $\Delta E \sim \frac{\hbar}{t} \gg \hbar\Omega_0$, i.e. such that there is no noticeable dispersion of the energy spectrum. From the exact formula (2.17) we can obtain an asymptotic expression for the case of very small dispersion of the frequency spectrum ($p_k \simeq p_0 = \frac{\omega_k}{\Omega_0} \to \infty$). Since we are assuming that the type of dispersion plays no part, we shall choose $p_{k_1} = p_0$ and $p_{k_2} = p_0 + 1$ ($k_1 \neq k_2$). Under these conditions, division of all $k$ by $k_1$ and $k_2$ is arbitrary. Using the asymptotic properties of $I_m(z)$, it is possible to show that

$$w'_{\alpha\to\alpha'} \simeq \frac{2\pi|V_{\alpha'\alpha}|^2}{\hbar^2\omega_0} e^{\frac{J_\alpha - J_{\alpha'}}{2kT} - \frac{E_s}{\hbar\omega_e}\coth\frac{\hbar\omega_e}{2kT}} I_{m_0}\left(\frac{E_s}{\hbar\omega_0}\operatorname{cosech}\frac{\hbar\omega_0}{2kT}\right); \quad \hbar\omega_e \ll \sqrt{kTE_s}. \tag{2.18}$$

The parameter $E_S = \frac{1}{2}\sum_k \hbar\omega_0(q^{\alpha}_{k0} - q^{\alpha'}_{k0})^2$ has the significance of a "reorganisation" energy (or "transpolarisation" energy) for the liquid as a result of the electronic transition and $m_0 = \frac{J_\alpha - J_{\alpha'}}{\hbar\omega_0}$.

This formula assumes a particularly simple form at high temperatures, when $\hbar\omega_0 < kT$:

$$w_{\alpha\to\alpha'} = \left(\frac{\pi}{\hbar^2 kTE_s}\right)^{1/2}|V_{\alpha'\alpha}|^2 e^{-\frac{E_a}{kT}}; \quad kT > \hbar\omega_0, \tag{2.19}$$

where the activation energy $E_a$ is given by

$$E_a = \frac{(J_{\alpha'} - J_\alpha + E_s)^2}{4E_s}. \tag{2.20}$$

Thus, we have in fact arrived at a formula of the same type as that of the transition state theory, but only in the particular case of $kT > \hbar\omega_0$.

The advantage of the $\omega_k = \omega_0$ model, i.e. the model in which the motion of the dipoles can be characterised by a single frequency, is that a single effective coordinate $q$ can be introduced in place of the many coordinates $q_k$. (One of us[15] has given a strict mathematical proof of this.) In this case we are in fact dealing with one-dimensional potential curves $U_\alpha(q)$, and we can therefore use the Landau–Zener theory of adiabatic electronic transitions if the motion of heavy particles (dipoles) is described classically. Omitting the straightforward mathematical derivations, we shall describe the physical results obtained in the case of interest. The broken lines in Fig. 2 denote two electronic energy levels, corresponding to two electronic states $\alpha$ and $\alpha'$, between which the transition occurs. At the intersection ($q^*$) of the two levels the electronic state is doubly degenerate, i.e. the same energy $\epsilon_\alpha(q^*) = \epsilon_{\alpha'}(q^*)$ corresponds to two distinct states $\alpha$ and $\alpha'$ [this follows from Eqn. (2.13)]. However, when allowance is made for the perturbation $V_{\alpha'\alpha}$, this degeneracy is removed and resonance splitting of the levels arises at the point $q^*$. (See the solid line in Fig. 2.) If the perturbation $|V_{\alpha'\alpha}|^2$ is smaller than some critical value $|V_{cr}|^2 = \hbar\omega_0\left(\frac{kTE_s}{\pi^3}\right)^{1/2}$, we can suppose that the system, initially at the level $U_\alpha$, jumps non-adiabatically to the level $U_{\alpha'}$, but only after several passages through the intersection point. If, however, $|V_{\alpha'\alpha}| \gg |V_{cr}|$, the separation of the levels at the point $q^*$ will be large, and transitions from the level $U_\alpha$ to the level $U_{\alpha'}$ will occur in such a way that the system remains always at the lowest level: these transitions are called adiabatic transitions. Calculations of the probability of transition per unit time by the quasi-classical Landau–Zener method lead to the high-temperature approximation formula (2.19) for non-adiabatic transitions; in the case of adiabatic transitions we obtain the formula

$$w_{\alpha\to\alpha'} = \frac{\omega_0}{2\pi} e^{-\frac{E_a}{kT}}, \tag{2.21}$$

where the activation energy $E_a$ is approximately the same as in Eqn. (2.20), i.e. it equals the distance from the point of "intersection" of the levels to the minimum of the initial level (Fig. 2).

In the discussion which follows we shall make use of the above theory to investigate various concrete problems.

## 3. Theory of Oxidation–Reduction Reactions

This section deals with oxidation–reduction reactions occurring in a liquid by an electronic mechanism, i.e. a mechanism whose fundamental step does not involve either breaking or forming chemical bonds. Such a reaction can be represented schematically in the form

$$A^{z_1} + B^{z_2} \to A^{z_1+1} + B^{z_2-1}. \tag{2.22}$$

We shall classify all reactions into fast and slow. To clarify the meaning of this classification, we shall consider two ions taking part in a reaction of the type of (2.22).

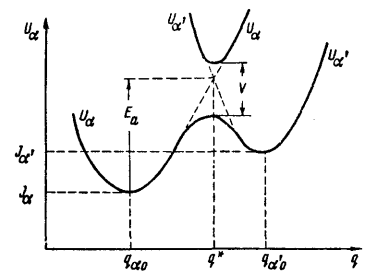



Fig. 2.

First of all, we introduce the concept of a reaction volume, this being the region within which the ions $A^{z_1}$ and $B^{z_2}$ must be to enable electron transfer to proceed from $A^{z_1}$ to $B^{z_2}$. If the residence time of the ions in the reaction volume ($\tau_g$) is much greater than the time between electronic transitions ($\tau_e$), the reaction should be called fast or proceeding by a diffusion mechanism. Since electronic equilibrium between the ions can be established at each "collision" (i.e. each time the ions fall into the reaction volume), diffusion must be the rate-determining step. We are assuming that the reaction volume is so small that the residence time of the ions in this volume is of the same order as the time between diffusional jumps ($\tau_g$).

In this review we shall be concerned only with slow reactions, i.e. with the case $\tau_e \gg \tau_g$. These reactions are characterised by the fact that electron transfer occurs only after several "collisions" between the ions. On the other hand, this is just the case where we can apply the formulae of perturbation theory, which are correct at times $t \ll \frac{1}{w_{\alpha\alpha'}} = \tau_e$. Indeed, since the ions remain in the reaction volume for a time $\tau_g \ll \tau_e$, it can be assumed that the probability of an electronic transition is directly proportional to time, which is equivalent to ignoring reverse transitions during the interval $\tau_g$. It can be shown[16] that the specific rate constant of the bimolecular reaction (2.22) is of the form

$$K_{AB} = \int w_e(R)\, w_{AB}(R)\, dv, \qquad (2.23)$$

where $w_{AB}(R)$ is the probability of finding the ions $A^{z_1}$ and $B^{z_2}$ at a distance $R$ apart, $w_e(R)$ is the probability of an electronic transition from $A^{z_1}$ to $B^{z_2}$. In view of the assumption that $\tau_g \ll \tau_e$, we can use the equilibrium distribution function of the ions (which at small distances has the form $e^{-\frac{z_1 z_2 e^2}{\varepsilon_s kTR}}$) in place of $w_{AB}$. It is surprising to find that the condition for a slow reaction obtained here corresponds to the assumption $\tau_g \ll \tau_e$, which was made in Section II.1, if the diffusion coefficients of the ions $A^{z_1}$ and $B^{z_2}$ are of the same order of magnitude as the self-diffusion coefficients of the liquid molecules.

All slow reactions can be divided into two classes: adiabatic and non-adiabatic. For the former, the quantity $w_e$ should be expressed by formula (2.21), when the resulting rate constant takes the form

$$K_{AB} = \frac{kT}{h} e^{-\frac{\Delta F^{\neq}}{kT}} v_r, \qquad (2.24)$$

where $v_r$ is the volume of the reaction region, and $\Delta F^{\neq}$ is the free energy of activation, which is related to the activation energy by the expression

$$\Delta F^{\neq} = \Delta E^{\neq} - T\Delta S^{\neq}, \qquad (2.25)$$

$$\Delta E^{\neq} = E_a + \frac{z_1 z_2 e^2}{\varepsilon_s R_r}, \qquad (2.26)$$

$$\Delta S^{\neq} = k \ln \frac{\hbar\omega_0}{kT}. \qquad (2.27)$$

Here $E_a$ is given by formula (2.20), and $R_r$ is the mean distance between the ions in the reaction region.

For non-adiabatic reactions, expression (2.19) must be used in place of $w_e$, and $V_{\alpha'\alpha}$ should be interpreted as an exchange integral[13]. The result is the following formula for $K_{AB}$:

$$K_{AB} = \varkappa \frac{kT}{h} e^{-\frac{\Delta F^{\neq}}{kT}} V_r, \qquad (2.28)$$

where the transmission coefficient $\varkappa$ is of the form

$$\varkappa = |V_{\alpha'\alpha}|^2 \left(\frac{4\pi^3}{\hbar^2\omega_0^2 kTE_s}\right)^{1/2} = \frac{|V_{\alpha'\alpha}|^2}{|V_{cr}|^2}. \qquad (2.29)$$

Experimental data for the specific rate constants of different reactions, computed by means of formula (2.28), are given in the Table together with calculated values of the corresponding transmission coefficients $\varkappa$. The Table shows that most of the reactions are non-adiabatic, with $\varkappa \sim 10^{-3}$. Only four of the reactions are exceptional, and proceed by an adiabatic mechanism.

We have recently attempted[15] a numerical evaluation of $K_{AB}$ for the $Fe^{2+}/Fe^{3+}$ system. For $R_r$ we used the value[17] 6.8 Å, and $\omega_0$ was assumed to be $10^{11}$ $s^{-1}$, whilst $E_s$ was calculated from the Born model. On the assumption that the reaction is adiabatic, we obtained $K_{AB}$ = = 50 litre $mole^{-1}$ $s^{-1}$, $\Delta F^{\neq}$ = 15.1 kcal $mole^{-1}$, and $\Delta E^{\neq}$ = = 11.5 kcal $mole^{-1}$. By comparing these with the experimental results, we find that the values obtained are in reasonable agreement with experiment, despite the coarseness of the approximation.

To conclude this Section, we shall give the quantitative formulation of the criterion for a slow reaction. From (2.23) and (2.28), the rate constant can be related to $\tau_e = 1/w_e$:

$$K_{AB} = \frac{1}{\tau_e} v_r e^{-\frac{z_1 z_2 e^2}{\varepsilon_s R_r kT}} \qquad (2.30)$$

The condition $\tau_g \ll \tau_e$ leads to the inequality

$$K_{AB} \ll \tau_g^{-1} v_r e^{-\frac{z_1 z_2 e^2}{\varepsilon_s R_r kT}}. \qquad (2.31)$$

Knowing the radius of the reacting ions, the radius $v_r$ of the reaction volume can be readily evaluated. In particular, if we adopt a value of 7 Å for $R_r$, and insert $10^{-9}$ s for $\tau_g$ in Eqn. (2.31), we obtain $K_{AB} \ll 2 \times 10^6$ litre $\times$ $\times$ $mole^{-1}$ $s^{-1}$.

## 4. Absorption of Light by Anions

The theory developed above can be applied to the study of the absorption of light by halide ions. According to the Franck–Condon principle, the light energy absorbed

TABLE.

| System | Ratio constant, litre $mole^{-1}$ $s^{-1}$ | Activation energy $E^{\neq}$, kcal $mole^{-1}$ | Temperature, °C | Transmission coefficient, $\varkappa$ |
|---|---|---|---|---|
| $Fe^{3+}/Fe^{2+}$ | 0.87 | 9.9 | 0 | $1.3\cdot10^{-3}$ |
| $Fe^{2+}/Fe^{3+}$ | 8.1 | 9.9 | 25 | $4.7\cdot10^{-3}$ |
| $FeOH^{2+}/Fe^{2+}$ | 1010 | 7.4 | 0 | $2.3\cdot10^{-2}$ |
| $FeF^{2+}/Fe^{2+}$ | 9.7 | 9.1 | 0 | $5.6\cdot10^{-3}$ |
| $FeF^{2+}/Fe^{3+}$ | 2.5 | 9.5 | 0 | $2.9\cdot10^{-3}$ |
| $FeCl^{2+}/Fe^{3+}$ | 9.7 | 8.8 | 0 | $3.1\cdot10^{-3}$ |
| $F(SCN)^{2+}/Fe^{3+}$ | 41.5 | 7.9 | 25 | $1.0\cdot10^{-2}$ |
| $Fe(SCN)_3^+/Fe^{3+}$ | 7.6 | 8.6 | 25 | $0.6\cdot10^{-3}$ |
| $EuCl^{2+}/Eu^{3+}$ | $6.5\cdot10^{11}e^{-\frac{E^{\neq}}{kT}}$ | 20.8 | 25 | ~1 |
| $Eu^{3+}/Eu^{3+}$ | $3.6\cdot10^{-4}$ | 20.8 | 25 | ~1 |
| $NpO_2^+/NpO_2^{2+}$ | 29 | 8.3 | 0 | $4.2\cdot10^{-3}$ |
| $MnO_4^-/MnO_4^{2-}$ | 710 | 10.5 | 0 | ~1 |
| $VOH^{2+}/VO^{2+}$ | $10^8 e^{-\frac{E^{\neq}}{kT}}$ | 10.7 | | $7\cdot10^{-3}$ |
| $Ce^{3+}/Ce^{4+}$ | $1.9\cdot10^{11}e^{-\frac{E^{\neq}}{kT}}$ | 16.8 | | ~1 |

$\hbar\omega_a$ is equal to the distance between energy levels at fixed polarisation. To calculate the average value of $\hbar\omega_a$, it is necessary to average out $U_\beta(q) - U_\alpha(q)$ by means of the quantum distribution function for a one-dimensional oscillator[18]:

$$dw(q) = \left(\frac{1}{\pi}\tanh\frac{\hbar\omega_0}{2kT}\right)^{1/2} e^{-q^2\tanh\frac{\hbar\omega_0}{2kT}}\,dq. \qquad (2.32)$$

The result is

$$\hbar\bar{\omega}_\beta = J_\beta - J_\alpha + E_s = \varepsilon_\beta(q_0^\alpha) - \varepsilon_\alpha(q_0^\alpha). \qquad (2.33)$$

Physically this means that, to find $\hbar\bar{\omega}_a$, we must know the ground level and the first excited level of the electron at fixed initial equilibrium polarisation, defined by the coordinate $q_0^\alpha$. The difference between these energies gives the mean energy of the light absorbed by a halide ion. The mean energy of the emitted light is found by an analogous procedure:

$$\hbar\bar{\omega}_e = J_\beta - J_\alpha - E_s = \varepsilon_\beta(q_0^\beta) - \varepsilon_\alpha(q_0^\beta). \qquad (2.34)$$

In addition to $\hbar\bar{\omega}_a$, it is interesting to calculate also the width of the absorption band, i.e. the standard deviation of the light energy absorbed:

$$D^2 = (\hbar\omega_a)^2 - (\hbar\bar{\omega}_a)^2 = \hbar\omega_0\coth\frac{\hbar\omega_0}{2kT}E_s, \qquad (2.35)$$

or in the high-temperature approximation

$$D^2 = (2kTE_s)^{1/2}. \qquad (2.36)$$

The width of the absorption band varies with temperature as $T^{1/2}$. On changing the temperature from 10° to 50°, the width of the band increases, according to Eqn. (2.36), by 7%, which agrees tolerably well with the experimental value[19] of 5%.

## 5. Theory of Electron Mobility

The problem of slow electrons in various liquids has attracted considerable attention in recent literature. In particular, the problem has been discussed extensively in radiation chemistry[27] and biological investigations[28]. Some electrochemical papers which consider the possible kinetic role of solvated electrons are beginning to appear. Not surprisingly, systems in which the liquid is water present the greatest interest. We shall therefore consider the case of a polar medium in the first part of the present subsection, and we shall report a number of results for non-polar media in the second part.

The basic problem facing us when considering polar liquids is the calculation of mobility. In order to throw some light on the physical mechanism of electrical conduction in liquids, we shall begin by stating the theory of electron mobility in polar crystals.

There is a large number of semiconductors whose properties cannot be described by the conventional band theory They show a characteristic, activational dependence of mobility upon temperature:

$$u \sim e^{-\frac{E_a}{kT}}.$$

This phenomenon cannot be explained within the framework of the normal band theory, since the thermal motion of the crystal lattice increases the probability of scattering of carriers, and should therefore lower the mobility. A mobility which increases with temperature is observed in substances with very small mobility values. For example, for $Fe_2O_3$ and NiO, $u \simeq 4\times10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, and the mean free path $\lambda$ of current carriers is found to be much smaller than the lattice constant. Contrary to the band theory, according to which the electrical conductivity depends on the changes in the velocity of the free electron as a result of scattering by lattice vibrations, Ioffe suggested[20] that the transport process in semiconductors of this type should be treated as the transition of an electron from a given cell of the crystal to a neighbouring one. Since we know that the theory developed in Section II, 2 is applicable in this case, it is obvious that the desired temperature dependence can be obtained from formula (2.19) at high enough temperatures. The difficulty, however, is that "band" solutions are found because of the translational symmetry of the crystal, which persists even in the semiconductors under discussion. A great deal of work[9,21-26] has been devoted to the problem of the change in the mechanism of electrical conduction, i.e. to the manner in which electrons in bands (or delocalised) can be correctly assigned to localised states. Unfortunately, lack of space prevents us from giving rigorous derivation of the results of the theory: we shall only point out that the criteria for the applicability of the band and of the transfer mechanism of conduction have been obtained from the above work. Calculation shows that at low enough temperatures the mobility decreases with increase of temperature, but begins to rise again exponentially with further increase of temperature: we know that this corresponds to a change from the band mechanism to the barrier (or "jump") mechanism. The model we have described is correct only for the case of strong binding, when the electron interacts strongly just with the atom in whose neighbourhood it happens to be at a given moment. In other words, the exchange integral for two nearest-neighbour atoms is fairly small. This is why the overall theory has been called the theory of small polarons. (We are using the term polaron in its usual meaning of an electron surrounded by a "coat" due to the polarisation of the dipoles.) However, in the case of weak interaction between the electrons and all the atoms of the crystal (but strong interaction with the polarisation) we must apply the theory of large polarons, developed by Pekar[4].

In polar liquids the situation is much more complex; the following cases are possible.

1. The mobility arises by the large polaron mechanism, i.e. the electron has a weak interaction with one solvent molecule. Since the radius of the large polaron is much greater than the average distance between neighbouring liquid molecules, we can apply the continuum model of the liquid, so that Pekar's original theory can be used without any modification.

2. The mobility is determined by a band polaron of small radius. This situation can arise when the correlation length between liquid molecules (i.e. the distance of short-range order) is greater than the mean free path of the polaron.

3. Lastly, one more variant is possible, in which the jump mechanism applies to polarons of small radius. In this case the difference between liquids and crystals disappears. To simplify the discussion, we shall quote the expression for the mobility:

$$u = \frac{ea^2|V|^2}{\hbar kT}\left(\frac{\pi}{kTE_s}\right)^{1/2} e^{-\frac{E_s}{4kT}}, \qquad (2.37)$$

where $a$ is the average distance between liquid molecules,

$V$ is the exchange integral, and as before $E_S$ denotes the energy of "transpolarisation". If the electron jump takes place adiabatically, we can write

$$u = \frac{ea^2}{kT}\frac{\omega_0}{2\pi}e^{-\frac{E_s}{4kT}}. \quad (2.38)$$

Formulae (2.37) and (2.38) are readily integrated using the Einstein relation $u = eD/kT$ if we introduce the diffusion coefficient of the electron:

$$D_{\text{adiab}} = \frac{a_0}{\tau_e}; \quad D_{\text{non-adiab}} = \varkappa\frac{a^2}{\tau_e}. \quad (2.39)$$

It is interesting to note that oxidation–reduction reactions in liquids can give rise to an electronic contribution to the electrical conductivity (in parallel with the ionic component). This was first pointed out by Frumkin. Since we have considered only slow reactions ($\tau_e \ll \tau_g$) in Section II,3, it is obvious that the contribution of the electronic component to the total electrical conductivity will be small. Simple calculation shows that the electrical conductivity is given by

$$\sigma_e = \frac{e^2c^2R_i^2K_{AB}}{6\,kT}. \quad (2.40)$$

To conclude this Section, we shall discuss the behaviour of electrons in non-polar liquids. The calculation of mobility in this system presents considerable difficulty, and we shall therefore confine ourselves to a study of the energy spectrum of the electron. As will be shown below, a knowledge of the spectrum offers also a qualitative understanding of the mechanism of electrical conduction in non-polar liquids.

To simplify the calculation, we shall examine the one-dimensional model of a liquid[29], i.e. a chain of identical atoms distributed in a practically random fashion. Since the concentration of electrons is assumed to be very small, the calculation can be made by the one-electron approximation. The Hamiltonian for this problem is of the form

$$H(x) = -\frac{\hbar^2}{2m}\Delta_x + \sum_i u(x - R_i), \quad (2.41)$$

where the first term is the kinetic energy of the electron, and $u(x - R_i)$ is the interaction energy between the electron and the $i$th atom of the liquid. The values of $R_i$ can be treated as random, but determined by a known distribution function $\Phi(R_1, \ldots, R_N)$. In practice, of course, the form of $\Phi$ is not known, since there is no theory of the liquid state at present. We shall therefore, in what follows, confine ourselves to a consideration of some plausible models of the liquid state which offer a basis for discussion. Thus, our problem is to determine the spectrum of the Hamiltonian (2.41), averaged with respect to $\Phi$, with arbitrary values of the parameter $R$. The most convenient mathematical approach to this problem is the method of Green functions, well known in quantum field theory and in statistics. The mean density of levels is related to a Green function by the expression[30]

$$\left\langle \frac{dn}{dE} \right\rangle = \frac{1}{\pi} Jm Sp\langle G\rangle. \quad (2.42)$$

Here $Jm$ denotes the imaginary part of the spur of $\langle G\rangle$, where the angular brackets are used to indicate averaging with respect to random values of $R_i$. The Hamiltonian (2.41) is conveniently written in the form $H = \langle H\rangle + V$, where $V = H - \langle H\rangle$ is the departure of $H$ from the value $\langle H\rangle$. Under certain conditions $V$ can be assumed to be small, so that the problem can be solved by perturbation theory. The zeroth approximation for $V$ gives the usual spectrum of a one-dimensional crystal in the strong binding approximation:

$$E_0(p) = \varepsilon_0 + 2\langle J\rangle\cos p, \quad (2.43)$$

where $\epsilon_0$ is the energy of the electron in an isolated atom of the liquid, $\langle J\rangle$ is the mean value of the exchange integral, and $p$ is the quasi-momentum of the electron. The function $E_0(p)$ is shown in Fig. 3 as a broken line. Allowance for the perturbation $V$ produces two effects in the first approximation. First, it alters the form of the spectrum within the previous band (see Fig. 3, full line):

$$E(p) \simeq \varepsilon_0 + 2\langle J\rangle\left(1 - \frac{\langle I^2\rangle}{2\langle J\rangle^2}\right)\cos p, \quad (2.44)$$

where $\langle I^2\rangle = \langle (J - \langle J\rangle)^2\rangle$ is the dispersion of the exchange integral. Secondly, the state of quasi-momentum $p$ begins to relax in time, the relaxation time $\tau$ being given by the formula

$$\tau_p^{-1} = \nu_p = \frac{\langle I^2\rangle}{|\langle J\rangle \sin p|}(1 + \cos^2 p). \quad (2.45)$$

Analysis of formula (2.45) shows that the results obtained from the perturbation theory are correct at sufficiently low dispersions:

$$\langle I^2\rangle \ll \langle J\rangle^2. \quad (2.46)$$

To give more real significance to the condition (2.46), we can attempt a calculation, assuming that $J(R) \sim e^{-R/R_0}$. We shall also assume that correlation operates only between the positions of the two nearest atoms in the liquid. Without explicitly stating the form of $\Phi(R)$, we shall assume that the deviation of $R$ from its average value is small and of the order of $l$. Condition (2.46) then reduces to the requirement that

$$l \ll R_0. \quad (2.47)$$

In practice, the following condition must also be satisfied:

$$p^2 \gg \frac{\langle I^2\rangle}{\langle J\rangle^2}. \quad (2.48)$$

The inequality (2.48) follows directly from (2.43) and (2.45). This condition means that the theory of perturbations is not applicable near the band edge[30]. Using an improved form of the perturbation theory, it can be shown that a shift of the old band edge in the direction of expansion does in fact occur, and that the form of the spectrum in the region of the new band edge is as shown in Fig. 3 (dotted line close to the new band edge):

$$E(p) \simeq \varepsilon_0 + 2\langle J\rangle\left\{1 + \left(\frac{\langle I^2\rangle}{\sqrt{2}\langle J\rangle^2}\right)^{2/3} - \frac{p^2}{3}\right\}, \quad p^2 \ll \frac{\langle I^2\rangle}{\langle J\rangle^2}. \quad (2.49)$$

It follows from this formula that the average width of the band increases, due to the presence of dispersion, by an amount of the order of $(\langle I^2\rangle/\langle J\rangle^2)^{2/3}$, and that the

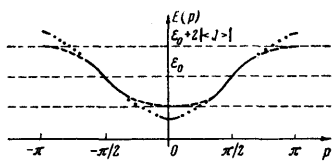



Fig. 3.

effective mass in the new band differs from the mass calculated for the old band by formula (2.43):

$$m_{\text{eff}} = \frac{3}{2} m^0_{\text{eff}}. \qquad (2.50)$$

The factor 3/2 in this formula appears because of the non-analytical variation of $E(p)$ with the small parameter $\epsilon = \langle I^2\rangle/\langle J\rangle^2$ [$E(p) \sim \epsilon^{2/3}$].

The most interesting case is, of course, that of large dispersion of the exchange integral [see Eqn. (2.47)]:

$$l \gg R_0. \qquad (2.51)$$

In this case perturbation theory is already inapplicable, but it has been possible to carry out a partial summation in the expression for the Green function. Retaining the most significant terms, the following equation for the electron spectrum was obtained:

$$E(p) - \varepsilon_0 = 2(E(p) - \varepsilon_0)\left\langle \frac{J^2(R)}{(E(p)-\varepsilon_0)^2 - J^2(R)} \right\rangle + 2(E(p) - \varepsilon_0)^2 \left\langle \frac{J(R)}{(E(p)-\varepsilon_0)^2 - J^2(R)} \right\rangle \cos p. \qquad (2.52)$$

This equation also was derived on the assumption that all the exchange integrals are uncorrelated, but the parameter $\epsilon = \langle I^2\rangle/\langle J\rangle^2$ was treated as much larger than unity. Eqn. (2.52) can be solved only if the binary distribution function of the atoms of the liquid is known. To arrive at the final expressions, we have used the simple model

$$\Phi(R) = \begin{cases} 0, & |R-a| > l, \\ \dfrac{1}{2l}, & |R-a| < l, \end{cases}$$

where $a$ is the average distance between the atoms of the liquid. The result was the following formula for the spectrum:

$$E_u(p) = \varepsilon_0 + |J_m|\left(1 \pm e^{-\frac{R_0}{2l(1-\cos p)}}\right),$$
$$E_l(p) = \varepsilon_0 - |J_m|\left(1 \pm e^{-\frac{R_0}{2l(1+\cos p)}}\right), \qquad (2.53)$$

where $E_u$ and $E_l$ apply to the upper and the lower band (see full line in Fig. 4), and $J_m$ denotes the maximum value of the exchange integral, corresponding to the minimum distance between the atoms, $R_{\min} = a - l$. In the derivation of (2.53) it was assumed that $J(R) \sim e^{-R/R_0}$.

It follows from (2.53) that the distance between the centres of the upper and the lower band is $2|J_m|$, and the width of both bands is $2|J(a)|$, i.e. the value of the exchange integral calculated for an average distance $a$. To make clear the physical significance of the result, we can compare formulae (2.53) with the spectrum calculated for the periodic chain shown in Fig. 5. This problem can be solved exactly, and the resulting form of the spectrum is (see broken curve in Fig. 4):

$$E^0_u = \varepsilon_0 + \sqrt{(J_1 + J_0)^2 - 4J_1J_0\cos^2 p},$$
$$E^0 = \varepsilon_0 - \sqrt{(J_1 + J_0)^2 - 4J_1J_0\cos^2 p}. \qquad (2.54)$$

Here $J_1$ is the exchange integral for particles 1 and 2, $J_0$ for particles 2 and 3 (see Fig. 5). The distance between the centres of the bands $E^0_u$ and $E^0_l$ is $2\sqrt{J_1^2 + J_0^2} \simeq 2|J_1|$, since $|J_1| \gg |J_0|$, and the width of each of the bands is $2|J_0|$. We see by inspection of formulae (2.53) and (2.54) that the major contribution to the average spectrum of the electron at high dispersions is given by the

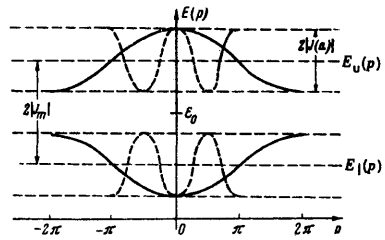



Fig. 4.

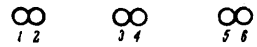



Fig. 5.

configurations of the atoms in which the closest approach of two atoms of the liquid occurs. This situation is reminiscent of the fact that in the calculation of mobility it is just these configurations which are the most important. This somehow corresponds to an electronic jump between two atoms. It is not hard to see that the temperature dependence of the mobility is also in qualitative agreement with the case of small polarons, discussed earlier in this Section. Thus (2.45) requires that a low temperatures the dispersion increases with increase of temperature, whilst $\tau_p$ decreases; consequently, the mobility $u \sim e\tau_p/m_{\text{eff}}$ also decreases. On the other hand, at high dispersions an increase in temperature must obviously increase the frequency of the jumps, and therefore the mobility.

## III. THEORY OF OXIDATION-REDUCTION REACTIONS

The simplest electrode reactions from the point of view of a theoretical study are of the form

$$A^z + e\,(\text{in the electrode}) \rightarrow A^{z-1}, \qquad (*)$$

where $A^z$ and $A^{z-1}$ are ions of charge $z$ and $z$ - 1 respectively

An electrode process involves several steps. In what follows, we shall be concerned exclusively with processes in which the slow (and therefore the rate-determining) step is discharge of the ion at the electrode. The phenomenological theory of slow discharge for reactions of the type (*) at a metal electrode was developed by Frumkin[31].

In the work of Levich, Vdovin, and Myamlin[32,33], the phenomenological slow discharge theory is extended to cover reactions at semiconductor electrodes. The earliest attempts at deriving a microscopic theory of oxidation-reduction reactions of the type (*) are due to Randles[35] and Hush[36]. Gerischer[37] had discussed heterogeneous reactions involving negligible changes in the inner coordination sphere of the ion. In his studies of oxidation-reduction reactions at metal and semiconductor electrodes, Gerischer has suggested that the activation energy arises mainly from the displacement of the atoms in the first coordination sphere of the ion. This approach gives the correct physical picture, but it failed to provide quantitative results.

Many more quantitative results were obtained by examining heterogeneous oxidation–reduction reactions not involving adsorption of reagents, formation or breaking of chemical bonds, and proceeding without any changes in the first coordination sphere of the ion. This review will deal exclusively with reactions of this type. The theory of these reactions has been developed in papers by Marcus[38-40], and Dogonadze, Chizmadzhev, and Kuznetsov[41-49]. As was stated at the beginning of this article, Marcus used the thermodynamic method, which offers several advantages coupled with the disadvantage of not allowing calculation of the exchange current.

In our previous papers[41-49] we have used the approach followed in the discussion of homogeneous reactions (see Section II). The main results of this work will now be described.

## 1. Calculation of the Fundamental Ion-Discharge Step at an Electrode and General Kinetic Relations

We shall consider a system consisting of an electrode, a polar solvent, an ion $A^z$, and an electron which can be associated either with the electrode or with the ion. The probability of electron transfer in this problem is determined by formula (2.19), in which $V$ is to be intepreted as an exchange integral and $J_s$ and $J_f$ are given by the following expressions

$$J_s = \varepsilon_{z-1} - e\varphi(R) - \frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int D^2_{0z-1}\,dv, \tag{3.1}$$

$$J_f = \varepsilon_f - e\varphi_e - U_0 - \frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int D^2_{0z}\,dv, \tag{3.2}$$

where $\epsilon_{z-1}$ is the energy of the electron in the isolated ion $A^{z-1}$, $\varphi(R)$ is the potential at the point where the ion undergoing discharge is located, $\varphi_e$ is the potential of the electrode, $U_0$ is the depth of the potential well for the electron in the electrode (see Fig. 6), $J_f$ is the level of the electron in the electrode, and $D_{0z}$ ($D_{0z-1}$) are the inductions of the ions $A^z$ ($A^{z-1}$). The quantities $\epsilon_s$ and $J_f$ have the same meaning as in the case of homogeneous reactions (Section II), but when dealing with heterogeneous reactions we must include in $J_s$ the energy of the interaction of the electron with the electronic polarisation of the solvent, since this is not included in $J_f$ and is not retained in the electron transfer process. In Eqns. (3.1) and (3.2) the subscript $s$ indicates that the electron is in the solution whilst $f$ indicates that the electron is in the electrode at the energy level $\epsilon_f$.

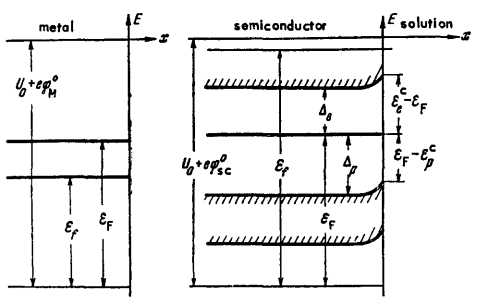



Fig. 6.

These expressions for the probability of electron transfer allow us to calculate the current flowing in the electrode–solution system. The current density can be expressed in the form

$$i = i_a - i_c,$$

where $i_a$ is the anodic current, generated by the passage of the electron from the solution into the electrode, and $i_c$ is the cathodic current. We shall invariably assume that all the ions are discharged at the electrode independently of each other. This implies that an expression for (say) the anodic current can be obtained as follows. The probability of electron transfer from the solution to the energy level $\epsilon_f$ of the electrode is multiplied by the concentration of the appropriate ions, $c_{z-1}(x)$, at the particular point in the solution, and by the probability of finding the energy level of the electrode unoccupied, $1 - n(\epsilon_f)$. The resulting expression must then be integrated over all possible states of the electron in the electrode and with respect to all the coordinates of the ion in the solution. An expression for $i_c$ can be obtained by a similar procedure:

$$i_a = e\int_0^\infty c_{z-1}(x)\,dx \int w_{sf}(x)\,[1 - n(\varepsilon_f)]\,\rho_f\,d\varepsilon_f, \tag{3.3}$$

$$i_c = e\int_0^\infty c_z(x)\,dx \int w_{fs}\,n(\varepsilon_f)\,\rho_f d\varepsilon_f, \tag{3.4}$$

where $n(\epsilon_f)$ is the distribution function of the electrons over the energy levels in the electrode, and $\rho_f$ is the density of energy states in the electrode. It must be noted that the problem of calculating the current really consists of two separate problems: the first problem is to find the probability of an ion being at a distance $x$ from the electrode, i.e. to evaluate $c_z(x)$ and $c_{z-1}(x)$; the second problem is to find $w_{sf}$ ($w_{fs}$). The solution of the second problem has been discussed in the previous paragraph. To find the probability that an ion approaches to a given distance from the electrode is a complex statistical problem which is still not finally solved. We shall therefore have to resort to one of the approximate theories, such as the Gouy–Stern theory. Within the framework of the theory developed in Section II, 2 it can be shown that the probability of the forward transition is related to the probability of the reverse transition by the expression $w_{sf} = w_{fs}\exp[(J_s - J_f)/kT]$. By using this expression, the resulting current can be written in the form[44]

$$i = e\int_0^\infty dx \int d\varepsilon_f \rho_f n(\varepsilon_f)\, c_z w_{fs}(x)\left\{\frac{c_{z-1}(x)}{c_z(x)}\,\frac{1 - n(\varepsilon_f)}{n(\varepsilon_f)}\,e^{\frac{J_s - J_f}{kT}} - 1\right\} \tag{3.5}$$

To simplify the subsequent calculations, we shall assume that the currents are not large, so that the Boltzmann equilibrium distribution can be used to express $c_{z-1}$ and $c_z$. For the same reason, we shall ignore departures from equilibrium within the electrode and use the normal Fermi distribution function for $n(\epsilon_f)$. This procedure is always justifiable for metals and intrinsic semiconductors at low current densities, and it can also be applied to impurity semiconductors if the current of minority carriers through the semiconductor interface is smaller than the limiting diffusion current of minority carriers. The formulae can be easily generalised to allow for departures from equilibrium in a semiconductor[45,49], which can be quite large at high currents and especially if

the semiconductor is illuminated (see also III, 5). In the light of these assumptions, Eqn. (3.5) can be rewritten

$$i = i_c\left(\exp\left\{\frac{e\varphi_e - (\alpha_{z-1}-\alpha_z) + \varepsilon_{z-1} - (\varepsilon_F - U_0) - kT\ln\frac{c_z}{c_{z-1}}}{kT}\right\} - 1\right), \quad (3.6)$$

where $\epsilon_F$ is the Fermi level in the electrode and $c_z$ and $c_{z-1}$ are the concentrations of the ions $A^z$ and $A^{z-1}$ respectively in the bulk of the solution at $x \to \infty$; the potential of the solution is taken to be zero. The quantity $\alpha_{z,z-1} = \frac{\epsilon_S - 1}{8\pi\epsilon_S}\int D^2_{0z,z-1}dv$ is the hydration energy of the ions $A^{z,z-1}$ in the Born approximation[50].

Using (3.6), it is easy to derive an expression for the equilibrium Galvani potential difference at the semiconductor–solution interface[44] from the condition that the total current must vanish:

$$e\varphi^0_e = (\alpha_{z-1}-\alpha_z) - \varepsilon_{z-1} + (\varepsilon_F - U_0) + kT\ln\frac{c_z}{c_{z-1}}. \quad (3.7)$$

It is evident from (3.7) that the equilibrium Galvani potential depends on properties of the electrode ($\epsilon_F - U_0$), on properties of the ions ($\epsilon_{z-1}$, $\Delta\alpha$), on the concentration of the ions, and on the properties of the solvent ($\Delta\alpha$).

An expression for $\varphi^0_e$ can be obtained also by using a thermodynamic cycle[42]. The various stages of the cycle are shown in Fig. 7. Under equilibrium conditions the work done in stages 1, 5, and 7 is zero. The work done in stages 2 and 4 is

$$\bar{\mu}_{z-1} = \psi_{z-1} + kT\ln c_{z-1};\quad \bar{\mu}_z = \psi_z + kT\ln c_z, \quad (3.8)$$

where $\psi_{z-1} = kT\ln N + \alpha_{z-1}$; $\psi_z = kT\ln N + \alpha_z$; $N$ is the number of solvent particles.

Denoting by $\alpha^e_m = e_e\varphi_0 + U_0 - \epsilon_F$ the work of extraction of the electron from the electrode, and equating to zero the work expended in the entire cycle, we obtain

$$-\bar{\mu}_{z-1} - \varepsilon_{z-1} + \bar{\mu}_z - e\varphi^0_V - \alpha^e_m = 0, \quad (3.9)$$

where $_e\varphi_0$ is the potential jump at the electrode–gas boundary and $\varphi^0_V$ is the equilibrium Volta potential of the electrode. The equilibrium Galvani potential at the electrode–solution interface is

$$\varphi^0_e = \varphi^0_V - {}_e\varphi_0. \quad (3.10)$$

Formulae (3.8), (3.9), and (3.10) lead to the expression (3.7).

We now introduce the overvoltage $\eta$ defined as

$$\eta = \varphi_e - \varphi^0_e. \quad (3.11)$$

Eqn. (3.6) can therefore be rewritten

$$i = i_c(e^{\frac{e\eta}{kT}} - 1). \quad (3.12)$$

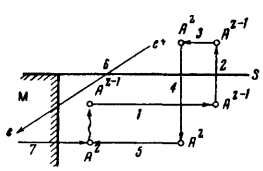



Fig. 7.

Furthermore, it follows from (3.12) that

$$i_a = i_c e^{\frac{e\eta}{kT}}. \quad (3.13)$$

It is obvious from the derivation of formulae (3.7), (3.12), and (3.13) that these expressions are applicable both to metal and to semiconductor electrodes.

The formulae derived here are quite general. To obtain more concrete expressions, we make the following approximation: the transition probability decreases very steeply as the distance from the ion to the electrode increases. The concept of an effective reaction region of thickness $l$, within which discharge occurs, thus arises quite naturally. The integral with respect to distance in formulae (3.3) and (3.4) can then be approximated by the product of $l$ by the value of the integrand function at some intermediate point $x = \delta$, which can be thought of as the most probable distance over which discharge occurs. In practice, the quantity $\delta$ can, of course, be identified with the thickness of the Helmholtz layer.

## 2. Kinetics at Metal Electrodes

To obtain concrete expressions for the current at a metallic electrode, it is necessary to carry out the integration with respect to the electronic states in the metal in expressions (3.3) and (3.4). Since in a metal all the states lying below the Fermi level are occupied, and all those lying above the Fermi level are empty, the integration in (3.3) must be performed between the limits $\epsilon_F$ and $U_0$, and that in (3.4) between 0 and $\epsilon_F$. Calculation leads[42] to the following expression for the anodic current

$$i_a = \left(\frac{\pi e^2 kT}{\hbar^2 E_s}\right)^{1/2}\cdot \rho_f c_{z-1}(\delta)\, l\,|V|^2 \exp\left\{-\frac{\left(e\varphi(\delta) + kT\ln\frac{c_{z-1}}{c_z} + E_s - e\eta\right)^2}{4E_s kT}\right\}, \quad (3.14)$$

where $\varphi(\delta)$ is the potential in the solution at the point $\delta$ (in practice, the $\psi_1$-potential). A similar calculation gives $i_c$.

Eqn. (3.14) shows that the variation of $\ln i_a$ with $\eta$ is not, in general, of the Tafel form. However, if $e\eta$ is small compared with $E_S$, the squared expression in brackets can be expanded and small terms of the second order can be ignored (the quantity $e\varphi'(\delta) + kT\ln\frac{c_{z-1}}{c_z}$ is usually much smaller than $E_S$). The expression for the total current then takes the Tafel form (provided that the potential jump $\varphi'(\delta)$ has its equilibrium value):

$$i = i_0(e^{\frac{e\eta}{2kT}} - e^{-\frac{e\eta}{2kT}}), \quad (3.15)$$

where the exchange current is equal to

$$i_0 = \left(\frac{\pi e^2 kT}{\hbar^2 E_s}\right)^{1/2}\rho_f l\,|V|^2\sqrt{c_{z-1}(\infty)\,c_z(\infty)}\,e^{-\frac{E_s}{4kT} - \frac{(2z-1)e\varphi'(\delta)}{2kT}} \quad (3.16)$$

In this case the transfer coefficient $\alpha$, defined by the expression

$$\alpha = -\frac{kT}{e}\frac{d\ln i_c}{d\eta}, \quad (3.17)$$

equals 1/2.

Brønsted's rule. The Tafel formula is usually derived by invoking a semi-empirical rule due to Brønsted[31], according to which

$$E^{\neq}(\eta) - E^{\neq}(\eta = 0) = -\beta[\Delta J(\eta) - \Delta J(\eta = 0)]$$

where $E^{\neq}$ is the activation energy and $\Delta J$ is the heat of the reaction (in our case $\Delta J$ is the difference between the minima of the potential energy curves of the system in its initial and final states). This expression is the equivalent of Polanyi's rule;[34], formulated for gas-phase reactions. In the theory discussed here, Brønsted's rule applies[44,47,49] for $e\eta < \sqrt{4E_S kT}$, the constant $\beta$ having the value 1/2 for a metallic electrode. It must be noted, however, that Brønsted's rule is obeyed by our system only at low enough overvoltages. When the overvoltage is appreciable, the rule ceases to apply, because the current–voltage characteristic deviates from the Tafel relation.

It is interesting to compare these theoretical results with experimental data obtained relatively recently by Frumkin and his coworkers[63]. Those workers investigated the electrolytic reduction of anions at metallic electrodes, and observed departures from the Tafel relation. Of all the reactions investigated, only the reduction of $Fe(CN)_6^{3-}$ behaves as required by the theory, but the qualitative nature of the agreement is evident from Fig. 8. The theoretical curve is smoother than the experimental curve. The greatest discrepancy between the two curves occurs in the region of potentials where other effects can become appreciable (for example, ion-pair formation). The particular feature of this reaction is that the $Fe(CN)_6^{3-}$ ion is fairly large, whereas $E_S$ is relatively small. Therefore, according to the theoretical predictions, deviations from Tafel's formula should set in at not very high overvoltages, as is indeed found to be the case in practice.

We must stress that the equilibrium potential does not appear in the expressions for the current which have been obtained: only departures from the equilibrium potential. In other words, the formulae for the current do not include quantities depending on the work function of the metal, and therefore the reaction rate in this sense is independent of the work function of the metal. Different electrodes are characterised by their density of states and by the exchange integral $V$ rather than by their work function.

The expressions (3.14)–(3.16) for the current are derived for reactions proceeding non-adiabatically. The study of adiabatic electrode reactions involves a number of difficulties arising from the presence of a continuous spectrum of states in the solid. However, we may suggest (without as yet any real proof) that these formulae will be applicable to the adiabatic case with the usual substitution of $V$ by $V_\sigma$ [see for example Eqn. (2.21)].

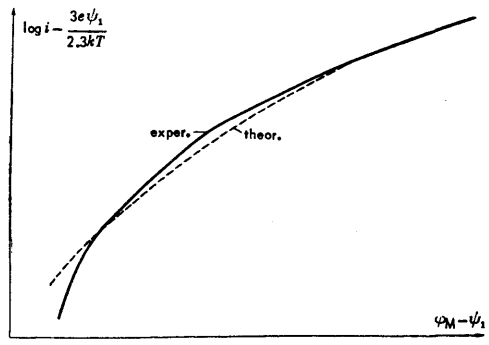



Fig. 8.

## 3. Kinetics at Semiconductor Electrodes

The basic physical mechanism of current flow at a semiconductor electrode is the same as for a metallic electrode. The most characteristic features of semiconductor electrodes are that the Fermi level in a semiconductor is situated in the forbidden gap, and that the filling of energy levels by electrons is a sensitive function of temperature and of the distribution of potential in the system. A consequence of the first characteristic is that the integration in (3.3) and (3.4) must be carried out over both the conduction and the valence band of the semiconductor. The resulting expressions will be called the electron current ($i^e$) and the hole current ($i^p$) respectively. From the second characteristic, it follows that in a semiconductor the variation of current with potential and with temperature will be determined not exclusively (or even mainly) by the effect of these parameters on the transition probability, but rather by their effect on the concentration of free carriers.

We can point out immediately that the procedure used to derive formulae (3.12) and (3.13) makes it obvious that the formulae are applicable to each of the components (electrons and holes) of the total current[44,49]. We shall therefore quote only the expressions for cathodic currents. The expressions for anodic currents are easily obtained by using the formulae given above.

Semiconductor with non-degenerate surface. We shall assume that the Fermi level does not extend into either band, i.e. that the following condition is satisfied (see Fig. 6):

$$\Delta_{e,p} - e|\varphi_{sc} - \varphi_c| > 4\,kT. \tag{3.18}$$

In this case the integration in (3.4) gives[47,49]

$$i_c^p = i_0^p \exp\left\{-\beta_p \frac{e(\eta_c - \eta_d)}{kT}\right\} \exp\left\{-\frac{ze\eta_d}{kT}\right\}; \tag{3.19}$$

$$i_c^e = i_0^e \exp\left\{-\beta_e \frac{e(\eta_c - \eta_d)}{kT}\right\} \exp\left\{-\frac{ze\eta_d}{kT}\right\} \exp\left\{-\frac{e(\eta - \eta_c)}{kT}\right\}. \tag{3.20}$$

where $i_0^e$ and $i_0^p$ are the electron and hole exchange currents,

$$\beta_p = \frac{1}{2} - \frac{\varepsilon_p^c - \varepsilon_F}{2E_s};\ \varepsilon_p^c - \varepsilon_F = -(\Delta_p - e(\varphi_{sc}^0 - \varphi_c^0)); \tag{3.21}$$

$$\beta_e = \frac{1}{2} - \frac{\varepsilon_e^c - \varepsilon_F}{2E_s};\ \varepsilon_e^c - \varepsilon_F = \Delta_e + e(\varphi_{sc}^0 - \varphi_c^0). \tag{3.22}$$

The remaining symbols are illustrated in Figs. 6 and 9.

The second terms in (3.19) and (3.20) give the potential dependence of the probability of electronic transition. Of course, this quantity depends only on the difference in potential between the electrode surface and the point where the ion undergoing discharge is situated. The third terms describe the potential dependence of the concentration of ions in the reaction region ($\psi_1$-effect). Lastly, the third term in (3.20) describes the potential variation of the concentration of electrons close to the semiconductor surface.

Brønsted's rule. It can be shown[44,47,49] that with semiconductor electrodes Brønsted's rule can only be

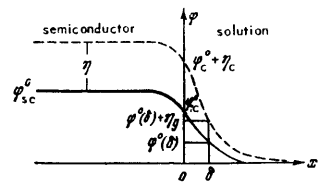



Fig. 9.

applied, generally speaking, to the electron and the hole current separately. The $\beta$ coefficients are given by formulae (3.21) and (3.22), and are not usually the same. In a semiconductor with a non-degenerate surface, the inequalities $\beta_e \leqslant \frac{1}{2} \leqslant \beta_p$ are always satisfied. Only when $E_S$ is large enough do we find $\beta_e = \beta_p = \frac{1}{2}$ (i.e. just as in the case of a metal electrode).

It is interesting to note that, in principle, the values $\beta_p \geqslant 1$ and $\beta_e \leqslant 0$ are possible. The cases of strict inequality correspond to the distribution of energy levels shown in Fig. 10). The cases of equality denote that the corresponding level is non-activated. These situations can evidently be realised in the discharge of large ions, for which the transpolarisation energy $E_S$ is relatively small, and when the equilibrium bending of the bands is large. Let us examine in greater detail the expressions for the currents $i^e$ and $i^p$. To simplify matters, we shall ignore the $\psi_1$-effect and assume that $\eta_g = 0$. The quantity $\eta_k$ is determined by the properties of the semiconductor surface. However, if the concentration of surface states is large, we find[44,50] that $\eta_k \simeq \eta$. This is precisely the case of interest when the situation $\beta_p > 1$ and $\beta_e < 0$ occurs, because an unusual current–voltage relation is observed. Thus, for $\eta_k = \eta$, say, the expression for $i^p$ takes the form

$$i^p = i_0^p \left\{ e^{\frac{e(1-\beta_p)\eta}{kT}} - e^{-\frac{e\beta_p\eta}{kT}} \right\}, \qquad (3.23)$$

and if $\beta_p > 1$ the current $i^p$ initially increases with increase of $\eta$, but reaches a maximum and then begins to fall off. It should be noted, however, that a curve of this type, showing a maximum, can only be obtained if for any reason the electron current vanishes or is very small. In the opposite case the electron current can mask the effect, since it will usually show a normal potential variation (it is very unlikely that the inequalities $\beta_p > 1$ and $\beta_e < 0$ can both be satisfied at the same time). A similar effect can take place for $\beta_e < 0$. The possibility of a maximum in the electron or the hole current was envisaged in a qualitative argument by Gerischer[51]. However, Gerischer considers that this can occur only if the semiconductor surface is degenerate. He gives[51] only a qualitative discussion, and does not derive the $\beta$ coefficients.

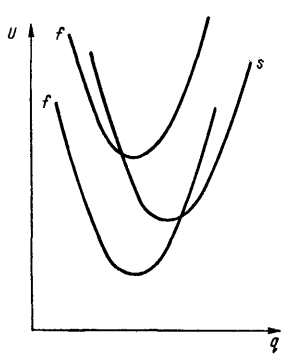



Fig. 10.

Transfer coefficients. The coefficient $\alpha$, introduced by formula (3.17), is indistinguishable from $\beta$ for a metallic electrode (in the absence of the $\psi_1$-effect). Such is not the case with a semiconductor. When the system comprises a semiconductor electrode, the following relations apply:

$$\alpha^e = 1 - (1 - \beta_e)\, d\eta_k/d\eta, \qquad (3.24)$$

$$\alpha^p = \beta_p\, d\eta_k/d\eta. \qquad (3.25)$$

In the absence of surface states, $d\eta_k/d\eta \ll 1$ and $\alpha^e$ and $\alpha^p$ are equal to 1 and 0 respectively[43,44]. Surface states can, on the one hand, affect the potential distribution in the system and thus influence the electron exchange between the solution and the bands of the semiconductor, and, on the other hand, they can themselves exchange electrons with the solution and thus contribute to the current. The former effect can make the transfer coefficients differ appreciably from 1 and 0, and be a function of the overvoltage, which should lead to departures from the Tafel relation[47,49]. The latter effect leads to a change in the nature of the current–potential relationship[47,49] (from electronic to hole current) as the surface states become gradually filled, if the concentration of surface states is high.

Exchange currents. The general expressions for the exchange currents are extremely cumbersome[44,47,49], and there is no simple relation, in general, between $i_0^p$ and $i_0^e$. However, if the condition $|\Delta_p, e \pm e(\varphi_{sc} - \varphi_c)| \ll E_S$ is satisfied, the two exchange currents are related by the simple expression[47]

$$i_0^e = i_0^p \exp\left\{ -(1 + \Delta_0/E_s)\, \frac{e\,(\varphi_{sc}^0 - \varphi_c^0) - (\Delta_p - \Delta e)/2}{kT} \right\}, \qquad (3.26)$$

where $\Delta_0$ is the half-width of the forbidden gap. This expression coincides with the formula given by Dewald[52]. It is evident from (3.26) that, in the absence of surface states, the ratio of exchange currents is independent of the impurity concentration in the semiconductor over a wide range. If a large density of surface states is present, the quantity $\varphi_{sc}^0 - \varphi_c^0$ is practically constant, and the ratio of currents becomes a function of impurity concentration.

Degenerate surface. If the Fermi level intersects either of the bands, the surface of the semiconductor assumes metallic properties. In this case the expression for the current is similar to the analogous expression for a metallic electrode, and the major part of the current is carried by electrons located close to the Fermi level[44,49].

In conclusion, we should stress the fact that the use of semiconductors as electrodes in the study of electron transfer processes between an electrode and a solution offers some definite advantages over metallic electrodes. The current at a semiconductor electrode is a function of semiconductor parameters such as the position of the Fermi level in the forbidden gap, the equilibrium bending of the bands, and the width of the forbidden gap. These parameters can be varied over wide limits, either by working with different semiconductors or by controlling the bending

of the bands for the same semiconductors. Therefore, a semiconductor offers very wide possibilities for research in this field. However, one serious disadvantage of semiconductors in this respect is that it is not always possible to determine unambiguously some of the semiconductor characteristics, and this can make the interpretation of experimental results very difficult.

## 4. Kinetics of Electrochemical Reactions in the Metal–Semiconducting Film–Electrolyte Solution System

In the study of various processes at metal surfaces one often has to deal with metals whose surface is covered with a natural oxide film. A considerable number of experimental and theoretical papers[53-59] have been devoted to oxide films on metal surfaces. The interest in studies of this type springs from the profound effect of oxide films on the course of many catalytic, corrosion, and electrochemical processes. Most contemporary workers consider that the semiconductor nature of oxide films must be taken into account when discussing the effect of these films on the above processes. Since we share this view, we have examined[46,49] a number of electrochemical processes in the metal–semiconducting film–electrolyte solution system.

In our discussion of the kinetics at a clean metallic electrode (III, 2) and at a clean semiconductor electrode (III, 3), we showed that there is an essential difference between these systems as regards their electrochemical behaviour. In a mixed metal–semiconductor–solution system we can expect to find properties both of the metallic and of the semiconductor electrode. Real oxide films are very complex structures, and are difficult to discuss theoretically. We have therefore considered[46,49] a highly idealised model, which, however, allows a qualitative study of some of the properties of these systems.

The film is treated as a uniform semiconductor to which the normal band theory can be applied. This limitation excludes very thin films from our discussion. An oxidation–reduction reaction of the type (*), satisfying all the conditions laid down at the beginning of this chapter, is proceeding at the surface of the film. It is assumed that the composition of the film does not change during the reaction, i.e. that the material of the film does not take part in the reaction.

A direct study of the kinetics of reaction (*) has shown[46] that the expressions obtained for a semiconductor electrode are quite general and can be modified for the present system by allowing for the difference between the energy diagram of this system (Fig. 11) and that of the semiconductor–solution system. The potential distribution in the two systems is also different, so that different quantitative results can be expected.

The expressions for the hole and the electron current are given, as before, by formulae (3.19) and (3.20), with the proviso that the values of $\epsilon_F - \epsilon_p^s$ and $\epsilon_e^c - \epsilon_F$ now take the form

$$\varepsilon_F - \varepsilon_p^c = \Delta_p - e(\varphi_M^0 - \varphi_c^0) + \chi_{sc}^0 - \chi_M^0, \qquad (3.27)$$

$$\varepsilon_e^c - \varepsilon_F = \Delta_e + e(\varphi_M^0 - \varphi_c^0) - \chi^0 + \chi_M^0, \qquad (3.28)$$

where $\chi_{sc}^0$ and $\chi_M^0$ are the work functions of the isolated semiconductor and metal respectively, and $\varphi_c^0$ is the equilibrium potential at the film–solution interface.

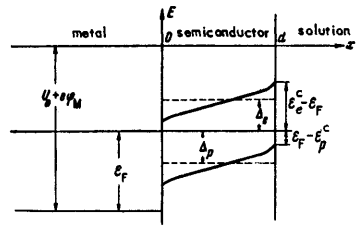



Fig. 11.

It follows from (3.27) and (3.28) that the properties of the system depend on the potential distribution (values of $\varphi_M^0 - \varphi_c^0$, $\eta_c$, $\eta_g$) and on the work function of the metal and the semiconductor ($\chi_M^0$ and $\chi_{sc}^0$). The whole of the above treatment is applicable to a uniform semiconductor under conditions of small departures from equilibrium in the semiconductor. The formulae can be generalised to include significant departures from equilibrium[48,49]. With weakly non-uniform semiconductors the general expressions remain valid, but the position of the bands at the interface with the solution with respect to the Fermi level ($\epsilon_{p,e}^s - \epsilon_F$) ceases to be defined by formulae (3.27) and (3.28), and becomes a function of the physical structure of the film.

The most significant feature of this system is that the parameters which determine the current–voltage characteristic (exchange currents and transfer coefficients) depend on the thickness of the film. In fact, the transfer coefficients [see Eqns. (3.21) and (3.22)] and the exchange currents depend on $\epsilon_{p,e}^s - \epsilon_F$. The latter quantity is a function of the potential distribution in the system and therefore of the thickness of the film. For a uniform semiconductor, it is possible to investigate in a general way the variation of the exchange currents with film thickness[46,49]. The expressions obtained[46,49] for the exchange currents show that the hole exchange current decreases and the electron exchange current increases with increase of $\varphi_c^0$ potential. Therefore, the problem becomes one of determining the variation of $\varphi_c^0$ with film thickness at a fixed value of $\varphi_M^0$. This relationship was investigated in Ref. 53, where the potential distribution in the film is examined under different conditions.

1. Consider the case of a uniform potential gradient in the film, with $\varphi_c^0 < \varphi_M^0$. As the thickness of the film decreases, $\varphi_c^0$ increases and approaches the value of $\varphi_M^0$, so that the hole exchange current decreases while the electron current increases. If $\varphi_c^0 > \varphi_M^0$, the reverse is true.

2. If the fall of potential in the film is not monotonic, the variation of $\varphi_c^0$ (and therefore also of $i_0^p$ and of $i_0^e$) with film thickness may or may not be monotonic[49]. Not surprisingly, the behaviour of the total exchange current $i_0 = i_0^p + i_0^e$ will be very complex, depending on the relative values of the individual exchange currents. We must stress that all the above effects will be appreciable only with film thicknesses smaller than the Debye length in the semiconductor.

The variation of the exchange currents and of the transfer coefficients with film thickness becomes particularly simple if the fall of potential in the film is linear. To make the problem concrete, let $\varphi_M > \varphi_c$, and also

$|\epsilon_{p,e}^{c} - \epsilon_F| \ll 2\sqrt{E_S kT}$. The exchange currents and the transfer coefficients are then given by[46]

$$\ln i_0^{p,e} = (\text{const})^{p,e} \mp (\chi_{sc}^0 - \chi_M^0) \pm e\varphi_M^0 \frac{1}{1 + \frac{\delta}{d}\frac{\epsilon_{sc}}{\epsilon_H}}, \quad (3.29)$$

$$\alpha_p = \frac{1}{2}\frac{1}{1 + \frac{d}{\delta}\frac{\epsilon_H}{\epsilon_{sc}}}; \alpha_e = 1 - \alpha_p, \quad (3.30)$$

where $d$ is the film thickness, $\delta$ is the thickness of the Helmholtz layer, $\epsilon_{sc}$ and $\epsilon_H$ are the dielectric constants of the semiconductor and of the Helmholtz layer. It is obvious that for large film thicknesses ($d \gg \delta\epsilon_{sc}/\epsilon_H$) $\alpha_p$ and $\alpha_e$ will approach 0 and 1 respectively, i.e. the film behaves as an ordinary semiconductor. As the thickness decreases, $\alpha_p$ increases and $\alpha_e$ decreases. In the limit of $d = 0$ we obtain $\alpha_{p,e} = 1/2$, i.e. the same result as for a metallic electrode. The condition of linear potential gradient in the film for small values of $\varphi_M$ ($e\varphi_M \ll kT$) leads to $\varkappa d \ll 1$, where $\varkappa$ is the Debye screening length in the semiconductor. If $\varphi_M$ is large, this condition becomes insufficient, and one must proceed with some care.

It follows from what has been said that the current–voltage characteristics of these systems are determined by the energy diagram of the system and by the potential distribution. Therefore, to obtain the variation of current with voltage for any system we must know the energy diagram and the potential distribution for the system. On the other hand, it is possible to form an opinion of the electronic structure of the film by comparing the theoretical relations derived from a definite model of the system with experimental results.

## 5. Stationary Photoeffect in the Semiconductor–Electrolyte Solution System

Methods relying on illumination of the electrode are widely used in studies of electrochemical processes at the semiconductor–solution interface. There are also theoretical papers devoted to the photoeffect at the semiconductor–solution interface. The influence of illumination on the potential of a semiconductor electrode has been examined[60,61] by a combination of a thermodynamic argument and of the Tafel formula. This method leads to a number of relationships containing experimentally determinable parameters. The stationary photoeffect, considered in the light of the above adiabatic theory of electron transfer reactions, is of interest in this context.

Consider a reaction of the type of (*), proceeding at a semiconductor electrode. In the absence of illumination, both the net current in the external circuit and the individual hole and electron currents must be equal to zero at equilibrium. When the semiconductor is illuminated, the latter requirement ceases to apply. The increase in electron and hole concentration in the semiconductor resulting from illumination produces an increase in the currents of both electron and hole transfer into the solution at a given potential. Therefore the potentials $\varphi_p^0$ and $\varphi_e^0$ at which the hole and the electron current respectively vanish are not equal to each other or to the equilibrium potential of the system $\varphi_{sc}^0$. When the semiconductor is illuminated, a steady state which we shall call a quasi-equilibrium state is established: in other words, we assume that the quasi-Fermi levels for electrons ($\Phi_e$) and for holes ($\Phi_p$) are constant over the entire space-charge region. Proceeding as in the derivation of formula (3.12), it is possible to obtain[45,47,49] the following expressions for the currents in a semiconductor with a non-degenerate surface not at equilibrium:

$$i^{e,p} = i_c^{e,p}\left[\exp\left\{\frac{e(\varphi - \varphi_{sc}^0) + \varepsilon_F - \Phi_{e,p}}{kT}\right\} - 1\right]. \quad (3.31)$$

It follows that the potentials $\varphi_p^0$ and $\varphi_e^0$ are related to the quasi-Fermi levels by the expressions

$$e\varphi_{p,e}^0 = e\varphi_{sc}^0 + \Phi_{p,e} - \varepsilon_F. \quad (3.32)$$

This result agrees with that obtained thermodynamically by Brattain and Garrett[60]. When there is no net current in the system (open circuit), a potential $\varphi_{st}$ is set up for which (see Fig. 12).

$$i^p = -i^e. \quad (3.33)$$

Since the quasi-Fermi level for electrons lies above the Fermi level when the semiconductor is illuminated, we have $\varphi_e^0 > \varphi_{sc}^0$. For holes, $\varphi_p^0 < \varphi_{sc}^0$. The quasi-Fermi levels for electrons and holes are related by the expression[62]

$$\left[\exp\left(\frac{\varepsilon_F - \Phi_p}{kT}\right) - 1\right]\left[\exp\left(-\frac{\varepsilon_F - \Phi_e}{kT}\right) - 1\right]^{-1} = n_0/p_0, \quad (3.34)$$

where $n_0$ and $p_0$ are the electron and hole concentrations in the bulk of the semiconductor.

The solution of the electrostatic problem taking account of Eqns. (3.33) and (3.34) determines the deviation of the potential from its equilibrium value in terms of the positions of the quasi-Fermi levels for electrons and holes. To find the variation of the steady-state potential $\varphi_{st}$ with the intensity of illumination $S$, we have to introduce an expression relating the position of the quasi-Fermi level to $S$. We shall assume that the semiconductor is illuminated with light in the fundamental absorption region and that the light is absorbed over a distance which is small compared with the diffusion length of minority carriers but not necessarily smaller than the Debye length: we assume, in other words, that the diffusion length of minority carriers is much greater than the Debye length. Taking an $n$-type semiconductor as a concrete example, we can write[62]

$$I - i_r^p = I_s^p\left[\exp\left(\frac{\varepsilon_F - \Phi_p}{kT}\right) - 1\right], \quad (3.35)$$

where $I$ is the number of hole–electron pairs generated by the light in unit time and per cm² of semiconductor surface ( a quantity proportional to $S$), $I_S^p = ep_0[D_p/L_p + v_S^p]$, $D_p$ and $L_p$ are the diffusion coefficient and diffusion length of holes, and $v_S^p$ is the surface recombination velocity.

At small departures from equilibrium, solution of Eqn. (3.33) gives

$$\frac{e(\varphi_{st} - \varphi_{sc}^0)}{kT} \simeq \frac{I}{I_s^p}\left[\frac{p_0}{n_0} - \exp\left\{\left(1 + \frac{\Delta_0}{E_s}\right)\frac{e(\varphi_{sc}^0 - \varphi_c^0) - (\Delta_p - \Delta_e)/2}{kT}\right\}\right] \text{ for } i_0^p \ll I_s^p. \quad (3.36)$$

It is evident from Eqn. (3.36) that the photoeffect can have either sign, according to the relative values of $\varphi_{sc}^0 - \varphi_c^0$ and $\Delta_p - \Delta_e$. In particular, the photoeffect vanishes at $e(\varphi_{sc}^0 - \varphi_c^0) \simeq (\Delta_e - \Delta_p)/2$ (since $\Delta_0 \ll E_S$). If $e(\varphi_{sc}^0 - \varphi_c^0) < (\Delta_e - \Delta_p)/2$, the photoeffect is positive. If the opposite is true, the photoeffect is negative. Analogous expressions can be written for a $p$-type semiconductor.

If the potential drop in the solution is ignored, expressions for $\varphi_{st}$ can be obtained also for the case of high illumination intensities[48,49] ($I \simeq I_S^p$). To simplify the problem, we shall assume that the condition $i^p \ll I_S^p$ holds true. Several different cases are possible.

1. $(i_0^p/i_0^e)^{1/2} \gg 1$.

$$e(\varphi_{st} - \varphi_{sc}^0)/kT \simeq -\ln(1 + I/I_s^p) = (\Phi_p - \varepsilon_F)/kT, \qquad (3.37)$$

i.e. the potential is shifted by the same amount as the quasi-Fermi level $\Phi_p$.

2. $(i_0^p/i_0^e)^{1/2} \ll 1$.

$$e(\varphi_{st} - \varphi_{sc}^0)/kT \simeq \ln(1 + p_0 I/n_0 I_s^p) \simeq (\Phi_e - \varepsilon_F)/kT, \qquad (3.38)$$

i.e. the potential shifts by the same amount at $\Phi_e$.

3. $i_0^p \simeq i_0^e$.

$$e(\varphi_{st} - \varphi_{sc}^0) \simeq [\Phi_e - \varepsilon_F + \Phi_p - \varepsilon_F]/2. \qquad (3.39)$$

These results are readily understood by reference to Fig. 12. The exchange currents determine the slope of the lines with respect to the $\varphi$ axis. In case 1 the left-hand line is very steep and the right-hand line is shallow. Thus their intersection is close to $\varphi_p^0$. In the second case the opposite situation occurs and the straight lines intersect close to $\varphi_e^0$. In the third case the picture is symmetrical and the lines intersect in the middle.

Let us now consider, in a sense, the opposite problem. We shall examine the variation of the current in the system under illumination at a given potential. It is easy to show that, for small light intensities [$e(\varphi_{st} - \varphi_{sc}^0) \ll kT$] and small values of $\varphi - \varphi_{st}$, the current varies linearly with $\varphi - \varphi_{st}$, and the exchange current is equal to its dark value. For appreciable intensities of illumination ($I \simeq I_S^p$), the expression for the total current is of the form[48,49]

$$i = i_0^{eff}[\exp\{e(\varphi - \varphi_{st})/kT\} - \exp\{-e(\varphi - \varphi_{st})/kT\}]. \qquad (3.40)$$

This expression is correct only for small deviations of the potential from $\varphi_{st}$. The effective exchange current is

$$i_0^{eff} = \sqrt{i_0^p i_0^e}\,\exp[e(\Phi_e - \Phi_p)/2kT]. \qquad (3.41)$$

It is evident from (3.41) that at high light intensities the exchange current is greater than the dark exchange current. This is not surprising, since the effective exchange current is the current flowing in one direction in the absence of net current in the external circuit. Under illumination this current can be very significantly higher than the dark exchange current.

The stationary photoeffect shows a distinct similarity to other steady-state processes: two oxidation–reduction reactions occur simultaneously at the semiconductor electrode under conditions such that the concentrations of the oxidised and the reduced form of both the first and the second species remain constant in the bulk of the solution. When the semiconductor is illuminated, the potentials $\varphi_p^0$ and $\varphi_e^0$ (at which the electron and the hole currents vanish) take on different values because the quasi-Fermi levels for electrons and holes no longer coincide. As a result, a steady state in which the total current is zero but the individual hole and electron currents are finite is established in the system. In a similar way, in a two-reaction system the potentials $\varphi_1^0$ and $\varphi_2^0$ ($\varphi_1^0 > \varphi_2^0$, say) at which the currents of the first and the second reaction go through zero do not coincide. (Of course, this difference does not arise from the difference in quasi-Fermi levels in the semiconductor, but is due to differences in the concentration and in the nature of the ions.) Therefore, we can again observe a state of zero net current but finite currents of the first and the second reaction:

$$i_1 = -i_2.$$

The solution of this equation defines the stationary potential $\varphi_{st}$ of the system. We shall not reproduce all the equations (see Refs. 48 and 49); they are similar to the corresponding equations for the stationary photoeffect. For small values of $\varphi_1^0 - \varphi_2^0$ and $\varphi - \varphi_{st}$, the variation of the current with $\varphi - \varphi_{st}$ is linear, and the exchange current equals the sum of the exchange currents of the first and the second reaction. If $\varphi_1^0 - \varphi_2^0$ is large, the expressions obtained are similar to (3.40) and (3.41) except for the replacement of $\Phi_e$ by $\varphi_1^0$, $\Phi_p$ by $\varphi_2^0$, and $\sqrt{i_0^p i_0^e}$ by $\sqrt{i_{20}^p i_{10}^e}$.

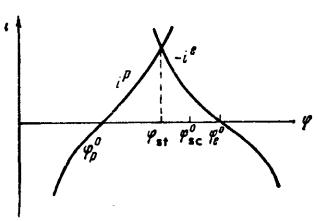



Fig. 12.


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# ELECTROCHEMICAL IMPLANTATION OF ALKALI METALS

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## I. INTRODUCTION

The alkali metals are deposited on cathodes at potentials so negative that hydrogen evolution makes them inaccessible in aqueous solutions, even when the electrodes consist of metals with a high hydrogen overvoltage such as lead or mercury. The highest potentials attainable under ordinary experimental conditions are more positive than the equilibrium potentials of the alkali metals by about 1 V. However, if liquid mercury is used as cathode, the alkali metals can be discharged at not too negative potentials because the discharge potential is shifted towards more positive values. This phenomenon is well known, and has been used in industry for a long time and has been investigated by physical chemists for over a hundred years. The cause of this shift is the strong chemical interaction between the alkali metals and mercury, with formation of amalgams. Electrolysis of aqueous solutions has produced amalgams not only of the alkali and alkaline earth metals, but also of ammonium and of some organic cations such as tetramethylammonium [1,2].

The large free energy change accompanying amalgam formation is the basic factor which enables alkali metal ions to be discharged on mercury from aqueous solutions. The high hydrogen overvoltage of mercury, which increases the fraction of the current carried by alkali metal deposition, and the rapid convective transport of the alkali metal towards the deeper layers of the liquid cathode (coupled with the high rate of formation of the amalgam), favour the discharge of alkali metal cations and enable the process to be used in practice. For this reason, the process has effectively been studied only at a liquid mercury cathode.

Numerous experimental studies have shown that the rate of discharge of alkali metal ions on mercury is very high[3-9]. Only recently have such measurements been made possible by the use of the Faradaic impedance[10] and the Faradaic rectification method[11]. Exchange current densities of the alkali metal ions have been found to be of the order of 0.1–0.2 A $cm^{-2}$ on these amalgams.

## II. THERMODYNAMIC POSSIBILITY OF DISCHARGING ALKALI METAL IONS

Strong chemical interactions with alkali metals are not an exclusive property of mercury. It is well known that the alkali metals, which occupy the first subgroup of the Periodic Table, react energetically with many elements, the reactivity increasing with increasing non-metallic character of the elements in question. We must remember that the overriding factor in the formation of intermetallic compounds is not, in general, the energy of interaction between the atoms involved in compound formation, but other factors such as the dimensional relationship between the reacting atoms or the concentration of free electrons in the resulting metallic compound. However, if the atoms from which the compound is formed show a strong interaction (as in the case of gold and an alkali metal) this interaction is found, as a rule, to be the major factor which determines the structure and properties of the intermetallic compound[12]. This accounts for the formation of stable intermetallic compounds, similar to amalgams in their properties, between the alkali metals and many other metals.

The behaviour of atoms towards compound formation can be characterised, for example, by the Pauling electronegativity concept[13]. The greater the electronegativity difference between two atoms, the more strongly the atoms will interact, and the greater the percentage ionicity of the resulting bond. Electronegativity values, taken from Ref. 14, are listed in Table 1. Most of these values were obtained by thermochemical methods.

It is evident from the table that the electronegativity of mercury is no greater than that of many other metals. Therefore, these metals should interact with the alkali metals at least as strongly as mercury.

TABLE 1.

| Elements | Li | Na | K | Rb | Cs | Cu | Ag | Au | Zn | Cd |
|---|---|---|---|---|---|---|---|---|---|---|
| Electronegativity | 0.95 | 0.9 | 0.8 | 0.8 | 0.75 | 1.8 | 1.9 | 2.3 | 1.6 | 1.7 |
| Elements | Hg | $Sn^{2+}$ | $Sn^{4+}$ | $Pb^{2+}$ | $Pb^{4+}$ | Bi | | | | |
| Electronegativity | 1.8 | 1.7 | 1.8 | 1.6 | 1.8 | 1.8 | | | | |

TABLE 2.

| | Cd | Sn | Pb | Zn |
|---|---|---|---|---|
| Na | 1.4 | 1.2 | 1.5 | 1 |
| K | 1.8 | 1.2 | 1.5 | 1.1 |

Many experimental investigations have been aimed at the interactions between alkali metals and other metals. They include measurements of the e.m.f. of a cell consisting of an alloy of the alkali metal and of one of the components of this alloy. However, this work was done mostly at high temperatures, above the melting point of the alloys. Hauffe and Vierk[15,16], and also Alabyshev, Morachevskii, and others[17-20], examined a large group of metals (Cd, Tl, Hg, Sn, Pb, etc.). Their experimental results indicate that at temperatures of 300–600° some of the metals (e.g. Cd, Tl) react with the alkali metals more strongly than does mercury, whilst others (e.g. Sn, Pb) show an interaction comparable to that of mercury or somewhat weaker. In order to extrapolate from these experimental data to the interaction at room temperature, we must know the temperature variation of the specific heats of the alloys. No such data are available at the present time. It must also be remembered that compounds which would form at room temperature may dissociate at higher temperatures. Hence, no firm conclusions as to the likely value of the interaction energy between these metals at room temperature can be drawn from these and other similar investigations.

Two series of relatively old papers (by the schools of Haber[21,22] and Kremann[23-29]) are concerned with studies of the potentials of alloys of the alkali metals. The work was carried out in solutions of electrolytes in organic solvents at room temperature and below. The results of these two series of papers are in good agreement, but the measurements of Kremann and his coworkers are the more accurate, and include a greater variety of metals. Some of the results obtained by Kremann's school are reproduced in Table 2, which lists the potentials of the most noble of the intermetallic compounds examined by those workers. The potentials are referred to the pure alkali metal, and are therefore equivalent to the maximum positive shift of the potential for cathodic deposition of the alkali metal on the particular electrode.

The table shows that the discharge potential of Na and K on Sn, Pb, Zn, and Cd electrodes is lowered by more than 1 V, which suggests that the deposition of alkali metals from aqueous solutions on these electrodes is apparently quite feasible.

Thus, we may conclude from these data that mercury has no thermodynamic advantage over a number of other metals. The discharge of alkali metal ions from aqueous solutions can be expected to occur also on other metals under suitable conditions.

## III. EXPLANATION OF SOME OBSCURE PHENOMENA BY MEANS OF THE IMPLANTATION CONCEPT

Until quite recently, there had been no experimental papers giving a direct demonstration of the possibility of discharging alkali metal ions on solid electrodes from aqueous solutions. There was some indirect evidence, however, that the process should be possible. Some

remarkable electrochemical phenomena have been observed during cathodic polarisation of solid electrodes in aqueous solutions containing alkali metal ions. A satisfactory explanation of these phenomena necessitates the assumption that the alkali atoms can be implanted into solid electrodes. The deposition of alkali metals on solid metal electrodes with formation of intermetallic compounds accompanied by penetration of the alkali metal into the bulk of the electrode has been termed[30] electrochemical implantation of alkali metals.

At the turn of the century Bredig and Haber[31,32] discovered and investigated the cathodic disintegration of lead, tin, mercury, thallium, and bismuth. They showed that the process can be reproduced satisfactorily only if the electrolyte contains alkali metal ions. In all cases, loosening of the electrode occurs before disintegration. The cathodic disintegration of lead and tin was later examined in more detail by Haber and Sack[21], and by Sack[22]. These workers explained the phenomenon by postulating the possibility of discharge of alkali metal ions at the electrode, but their discussion of the mechanism of this process is rather superficial.

After the work of Haber and Sack, not a single paper on the cathodic disintegration of lead appeared for almost half a century, and it was not until 1953 that Salzberg[33-35] again investigated the features of this process. He also found that cathodic disintegration proceeds stably and reproducibly only when alkali metal cations are present in solution, but he was unable to give the correct explanation of the phenomenon. Angerstein[36] showed that the disintegration of lead in acids, observed in some experiments both by Haber's school and by Salzberg, is due to the presence of alkali metal impurities in the solution.

Kabanov and his coworkers[37-39] observed the cathodic superactivation of aluminium and magnesium in alkalis, and explained it by assuming cathodic formation of a surface compound of Al or Mg with an alkali metal. This hypothesis was based on the dependence of superactivation upon the nature of the cation (from lithium to tetramethylammonium). In their study of the electrolytic reduction of acetone in alkaline solutions, Antropov and his coworkers[40] observed anomalous current yields on a number of solid cathodes. The anomalies were similar to those resulting from the use of amalgam cathodes. To explain their results, the authors suggested that intermetallic compounds are formed between an alkali metal and the cathode metal when lead, tin, zinc, and cadmium electrodes are cathodically polarised.

Turomshina and Stender[41] studied the electrodeposition of zinc from sulphuric acid solutions, and found that the current efficiency of zinc deposition drops when alkali metal ions are present in solution. They ascribe this behaviour to incipient co-deposition of alkali metal ion with the zinc ions†, with formation of the appropriate intermetallic compounds.

There are many reports of unexplained phenomena, noticed during measurements of the hydrogen overvoltage of various metals: slow changes in overvoltage with time, hysteresis, abnormally high slopes of the linear plots of overvoltage against the logarithm of current density[42-45]. The absolute values of the overvoltage (or the rates of hydrogen evolution at a given potential) in alkaline solutions are often very sensitive to elusive differences in experimental conditions. These surprising phenomena have not always been described in the published papers (unless of course they had a direct bearing on the main topic of the paper) because they were thought to arise from trivial, random causes. In some cases these phenomena are explicitly ascribed to the influence of random factors[43-45]. Thus, Kaptsan and Iofa have retracted the electrochemical mechanism of decomposition of amalgams[46] put forward in their previous papers, believing it to be due to random factors, and early measurements of the hydrogen overvoltage of mercury and of dilute amalgams in alkaline solutions have recently been re-examined[47-49], but no explanation has been given why the difficulties encountered in alkalis do not arise to the same extent when working in acid solutions. In some cases the change of overvoltage with time is explained by postulating the formation of surface hydrides.

The idea of alkali metal implantation was first put forward a few years ago[30] to explain the very startling hydrogen overvoltage curves obtained for zinc in alkalis. The explanation was later extended to other cases of hydrogen evolution on solid metals in alkaline solutions.

The shape of the plot of hydrogen evolution potential against the logarithm of current density is very sensitive to the conditions of measurement. Under certain conditions we find satisfactorily reproducible linear plots with a slope of 0.11–0.12 V. The requirements are that the cathodic potential of the electrode is not allowed to exceed a certain value, and that the measurements are made in a sufficiently short time. When the curve is plotted slowly, the potential begins to increase with time upon reaching a certain value (Fig. 1). After a few tens of minutes the electrode potential has shifted by 0.2–0.3 V in the negative direction. After this cathodic polarisation the slope of the curve is very much higher, and hysteresis is observed. If the curve is now plotted in the reverse direction (from high towards low polarisations), the potential is found to decrease with time at constant current when the polarisation of the electrode has been reduced by a sufficient amount.

We put forward the hypothesis that the time variation of the hydrogen evolution potential is associated with the formation (by implantation) or with the decomposition at the cathode surface of intermetallic compounds formed by the cathode metal with alkali metal atoms. The hydrogen overvoltage at the surface of these compounds is higher, as a rule, than on the pure metal (probably because of the lower hydrogen adsorption energy). The properties of the intermetallic compounds formed depend on the nature of the cation. Thus, the hydrogen overvoltage in alkalis is a

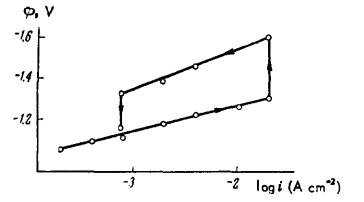



Fig. 1. Polarisation curves for hydrogen evolution on silver in 1 *N* NaOH.

† Since co-deposition of alkali metal ions with zinc ions is involved, rather than penetration of the alkali metal into the zinc cathode, this phenomenon is of minor relevance to our problem.

function of the nature of the alkali metal cation. The overvoltage increases with increasing ionic radius of the non-hydrated cation. After strong cathodic prepolarisation, the potential of the silver electrode at a current density of $10^{-2}$ A $cm^{-2}$ corresponds to -1.42, -1.54, -1.56, -1.68, and -1.72 V for the cations $Li^+$, $Na^+$, $K^+$, $Cs^+$, and $(CH_3)_4N^+$ respectively.

The observed dependence of hydrogen overvoltage upon the nature of the cation can be explained in terms of the variation of the adsorption properties of the intermetallic compounds towards hydrogen atoms when the cation is varied.

On the other hand, the implantation of the alkali metal is easier and faster, the smaller the intrinsic ionic radius, i.e. the faster the diffusion of the cation into the electrode metal. For this reason, lithium is implanted faster than any other alkali metal, and the lithium intermetallic compounds decompose more rapidly than others. This conclusion was drawn from measurements of the time needed to establish a constant electrode potential in hydrogen evolution experiments. The time was found to be shorter for the cations of smaller radius.

Recently, the structural changes of the surface of silver and zinc electrodes have been examined by electron microscopy after cathodic polarisation in solutions containing alkali metal ions[30,50]. Fig. 2 shows the structure of a silver electrode surface after weak polarisation lasting 3 h, Fig. 3 shows the same surface after strong polarisation. It is easy to see that strong polarisation causes loosening of the electrode surface. Similar changes take place on the surface of strongly polarised zinc electrodes. It was interesting to find that silver electrodes are embrittled only when their surface is etched in concentrated $HNO_3$ before polarisation. Electrodes whose surface has been cleaned with glass powder or mechanically polished before polarisation are not loosened under these conditions.

To detect structural changes in the deeper layers of the electrode, electron diffraction studies were made on silver films prepared by vacuum evaporation and cathodically polarised in a solution of sodium sulphate. It was found

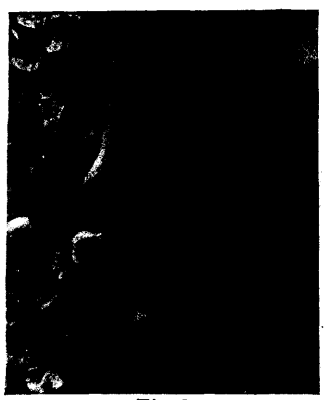


Fig. 2.

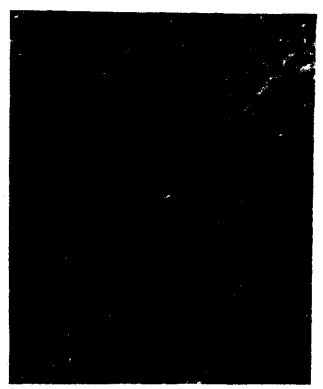


Fig. 3.

Figs. 2 and 3. Electron micrographs (×15 000) of the surface of a silver electrode after polarisation in 1 *N* NaOH:
Fig. 2 — at $\varphi$ = -1.1 V relative to the normal hydrogen electrode (n.h.e.); Fig. 3 — at $\varphi$ = -1.5 V (n.h.e.).

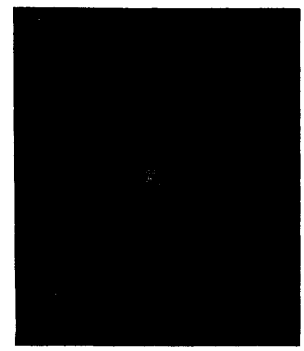


Fig. 4.

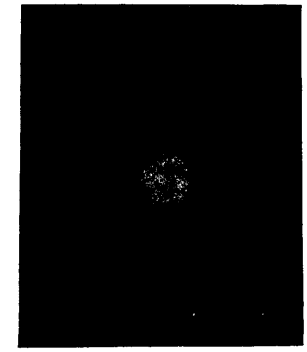


Fig. 5.

Figs. 4 and 5. Electron diffraction pattern of a thin silver film after polarisation in 1 *N* $Na_2SO_4$:
Fig. 4 — at $\varphi$ = -1.1 V (n.h.e.); Fig. 5 — at $\varphi$ = -1.4 V (n.h.e.).

that weakly polarised films give a fairly sharp electron diffraction pattern with narrow lines (Fig. 4). After strong cathodic polarisation the lines become diffuse (Fig. 5), showing that the films tend towards an amorphous structure as a result of polarisation.

Thus the implantation of alkali metals causes both loosening of the electrode surface and also, in some cases, a structural change in a layer adjacent to the surface. This phenomenon should no longer be ignored by electrochemists working with alkaline solutions.

However, none of these explanations was entirely satisfactory, because the implantation process itself was not understood owing to the many and serious contradictions. The most important one is the sharp difference between the small experimentally observed rate of penetration of the alkali metal and the large rates expected from various theoretical considerations and obtained experimentally for the amalgam formation process. Before attempting to explain this difference, we shall deal with the methods for investigating the implantation of alkali metals into solid metallic electrodes, and with the experiments on which was based the assertion that alkali metal implantation is possible.

## IV. EXPERIMENTAL STUDY OF IMPLANTATION

The electrochemical membrane method[50] is one of the techniques which have been applied to the study of alkali metal implantation into electrodes.

In this method the alkali metal is passed through a zinc foil membrane, polarised on one side. Double electrochemical cells are used, similar to the cells used in electrochemical studies of hydrogen diffusion through a metallic membrane (Fig. 6). On one side of the membrane the alkaline solution is placed, and cathodic polarisation is applied for a long time at various current densities, and on the other side is placed a dilute solution of $K_2SO_4$, and the pH of this solution is monitored. The results of diffusion measurements of lithium, potassium, caesium, and tetramethylammonium ions through a membrane 30 $\mu$m thick indicate that the rate of implantation of the first two ions is in inverse proportion to the crystallographic radius of the ions, whereas caesium and tetramethylammonium ions

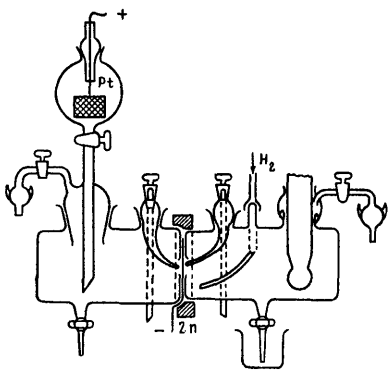



Fig. 6. Cell for measuring the diffusion of an alkali metal through a zinc membrane.

do not in fact diffuse through the membrane. These results are in qualitative agreement with the measurements of the rate of implantation of various ions from the time needed to establish a constant hydrogen evolution potential[42].

The diffusion coefficient of potassium through the zinc membrane was evaluated from the measured time dependence of the rate of diffusion, and found to be of the same order of magnitude as the coefficient for the self-diffusion of zinc along crystal grain boundaries.

The variation of the rate of implantation with electrode potential was investigated in the particular case of penetration of potassium into zinc. In Fig. 7 the polarisation potential of the membrane is plotted horizontally, and the logarithm of the amount of potassium diffusing through the membrane in 22 h is plotted vertically. The membrane thickness was 20 $\mu$m. It can be seen that the rate of implantation increases exponentially with increasing membrane potential. A negative shift in membrane potential of 0.35 V raises the implantation rate by nearly a factor of 100.

Implantation is a complicated, inadequately investigated type of diffusion: it involves reactive diffusion, during which the diffusing substance interacts with the medium. In particular, nothing is known about the difference between bulk and grain-boundary reactive diffusion of the alkali metals in other metals. It is known, however,[51,52]

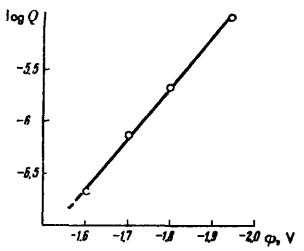



Fig. 7. Variation of the amount ($Q$) of potassium diffusing in 22 h through a zinc membrane 20 $\mu$m thick with polarisation potential of the membrane in 1 $N$ KOH.

that the rate of bulk self-diffusion in zinc at room temperature is smaller by a factor of about $5 \times 10^5$ than the rate of boundary self-diffusion. Most often, the bulk and boundary heterodiffusion rates differ by at least as much as the rates of self-diffusion, since the difference is caused primarily by the difference in structure between the crystal grain boundaries and the bulk phase. Therefore, the transport of the alkali metal through the membrane at room temperature can be expected to occur exclusively along crystal grain boundaries. Thus, when comparing measurements of the rate of implantation by diffusion of alkali metal ions through a membrane with measurements based on the time needed to reach a steady potential during hydrogen evolution, it is important to remember that diffusion measurements characterise only the rate of penetration at the outcrop of grain boundaries on the electrode surface. Since the grain boundaries occupy only a small fraction of the electrode surface, clearly, this process cannot give rise to a significant increase in hydrogen overvoltage. The coverage of the whole surface of the electrode by the intermetallic compound and the consequent establishment of a high hydrogen overvoltage arise from penetration of the alkali metal into the surface of the crystal grains (albeit to a very small depth). The rates of these two penetration processes are expected to be vastly different.

The experiments show that loosening of the surface takes place during the actual polarisation. This makes it very difficult to analyse the results of hydrogen overvoltage measurements on solid electrodes, if the solutions contain alkali metal cations, since at least two opposing factors are always operative. On the one hand, the formation of an intermetallic compound raises the electrode potential at constant current density, and, on the other hand, the loosening of the electrode surface lowers the hydrogen overvoltage. There have been reports of a decrease (rather than an increase) of potential resulting from implantation, and the process responsible for this change in potential could not be unambiguously identified. In any case, we cannot exclude the possibility of the hydrogen overvoltage at some intermetallic compounds being lower (rather than higher) than at the pure metal.

The direct study of the implantation process and the study of the properties of the resulting intermetallic compounds meet with a host of difficulties. We must first of all point out that cathodic implantation of an alkali metal in aqueous solutions is invariably accompanied by hydrogen evolution, the rate of the latter process being higher than that of the former by several orders of magnitude. Yet another difficulty attending the study of these systems is the fact that the compounds which are formed are often unstable, and are rapidly attacked by water when the electrode polarisation is removed. For this reason, they cannot be studied by conventional analytical methods. The most appropriate method for the purpose has been found to be one based on oscillographic recording of $\varphi-t$ (potential–time) curves, or charging curves[53].

The $\varphi-t$ curve allows the change in electrode potential to be monitored after an interruption or a reversal of the current. From the type of curve obtained, one can deduce whether or not a certain process operates at the electrode in a given potential region.

It was found that, when a $\varphi-t$ curve is measured without preliminary cathodic polarisation of the electrode in alkaline solutions, the potential suffers a steep, monotonic change, and the electrode capacity calculated from

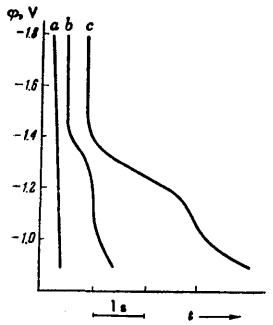



Fig. 8. Anodic potential–time curves for Pb in 1 *N* NaOH; $i_a = 5 \times 10^{-5}$ A cm$^{-2}$: *a*) $t_c$ = 1 min; *b*) $t_c$ = 15 min; *c*) $t_c$ = 30 min

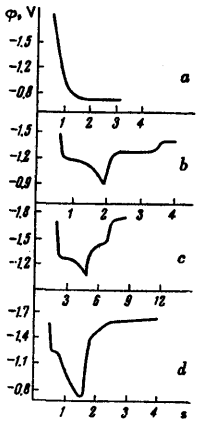



Fig. 9. Anodic and cathodic potential–time curves in 1 *N* LiOH after polarisation at $\varphi_c$ = -1.6 V: *a*) Cd, $t_c$ = 1 min; *b*), *c*), and *d*) Ag, Cd, Pb, $t_c$ = 30 min.

this curve is equal to the double-layer capacity. If, however, the electrode is cathodically polarised during 30 min in the alkaline solution at a potential of, say, -1.6 V, before plotting the $\varphi$–$t$ curve, an arrest is observed on the anodic $\varphi$–$t$ curve (Fig. 8). If the cathodic polarisation is once again applied, it is possible to observe a curve for the growth of cathodic polarisation which also has a plateau (potential arrest). Typical anodic and cathodic $\varphi$–$t$ curves are shown in Fig. 9: the arrests in the fall and in the growth of potential are clearly visible. Arrests on the cathodic $\varphi$–$t$ curves are normally ascribed to the formation of intermetallic compounds, whereas arrests on the anodic curves are ascribed to their decomposition. From the position of the arrests, we can determine an important characteristic of the intermetallic compounds: their equilibrium potential. The equilibrium potential values are intermediate between those corresponding to the onset of the anodic and of the cathodic arrests. Table 3 lists the measured potentials of the arrests, and the equilibrium potentials of the intermetallic compounds of silver, cadmium, lead, and zinc with lithium[53].

TABLE 3.

| Potential | Ag | Cb | Pb | Zn |
|---|---|---|---|---|
| Cathodic arrest | −1.30 | −1.40 | −1.40 | −1.45 |
| Anodic arrest | −1.28 | −1.27 | −1.28 | (−1.35) |
| Equilibrium | −1.29 | −1.33 | −1.34 | (−1.40) |

The presence of arrests on the $\varphi$–$t$ curves is indisputable evidence that electrochemical processes occur at the electrode when these potentials are reached. It remains to be proved, however, that these processes are in fact the formation and decomposition of intermetallic compounds, and that the equilibrium potentials observed are those of the intermetallic compounds. Charging curves alone are not enough to justify this assertion. Cathodic polarisation may be expected to give rise also to compound formation between the electrode metal and hydrogen (hydrides)[54].

On metals (such as iron and nickel) which show a strong tendency to adsorb hydrogen, electrochemical formation of surface hydrides is a definite possibility. However, zinc, cadmium, and lead are metals for which no hydrides are known. Metals from which hydrogen is evolved with a large overvoltage, such as mercury, are known to adsorb very small amounts of atomic hydrogen on their surface[55]. Cathodic formation of hydrides in appreciable quantities is unlikely in this case, and amounts of the order of a monolayer are out of the question. Conversely, intermetallic compounds of lead, zinc, cadmium, and silver with alkali metals are well known, and can be prepared chemically or by electrolysis in molten salts with liquid cathodes.

A direct proof that these arrests are associated with the formation and decomposition of intermetallic compounds was obtained by comparing the equilibrium potentials calculated from the arrests with the potentials of genuine intermetallic compounds, prepared by fusing the elements together. This test was applied to a number of compounds, both in aqueous and in non-aqueous solutions. It was found, for example, that the equilibrium potential of $NaPb_3$ prepared by fusing lead with sodium is the same as the equilibrium potential read off the charging curve of lead in a solution of NaOH. Thus the identity of intermetallic compounds obtained by thermal synthesis with those formed by cathodic polarisation was demonstrated.

Anodic curves sometimes show two or three arrests instead of a single one. This indicates that several intermetallic compounds of different composition can be obtained on the electrode under cathodic polarisation.

Assuming that each molecule of the resulting intermetallic compound contains one alkali metal atom, and knowing the standard potentials of the compounds, we can calculate their standard free energies $\Delta G^\circ$ of formation by the implantation reaction

$$nM + Li^+ + e = LiM_n$$

and the free energy of these compounds.

TABLE 4.

| Composition | $\varphi^\circ$ | $\Delta G^\circ$ | $G^\circ_{LiM_n}$ | Composition | $\varphi^\circ$ | $\Delta G^\circ$ | $G^\circ_{LiM_n}$ |
|---|---|---|---|---|---|---|---|
| $LiAg_n$ | −1.29 | 30 | −40 | $LiZn_n$ | (−1.4) | (32) | −38 |
| $LiCd_n$ | −1.33 | 30.5 | −39.5 | $NaHg_8$ | −1.92 | 44.2 | −18.35 |
| $LiPb_n$ | −1.34 | 31 | −39 | $NaHg_8$ | −2.0 | 46 | −16.48 |

Table 4 lists the free energies of the lithium compounds calculated in this way; for comparison, the values for $NaHg_6$ and $NaHg_2$ are also given.

## V. MECHANISM OF IMPLANTATION

### 1. Implantation Overvoltage

Despite the conclusive evidence discussed above for the existence of alkali metal implantation into solid electrodes in aqueous solutions, all attempts at explaining the behaviour of electrodes in alkalis in terms of implantation failed until the inconsistencies mentioned above (mostly concerning the high implantation overvoltage) were overcome. It was difficult to visualise the cause of the high overvoltage for the deposition of alkali metals, since these metals are deposited on mercury cathodes in alkaline chloride solutions with negligible overvoltage, and they are deposited even more readily in melts. Table 4 shows that implantation into solid metals gives rise to compounds which are more stable than the alkali metal amalgams. Thus we can expect the electrochemical stage of the implantation reaction to proceed at least as fast as the electrochemical amalgam formation reaction. But if implantation into solid metals is fast and exceeds (as in the case of mercury) the rate of hydrogen evolution, we would expect not one monolayer but $10^5$ or more monolayers to form in 30–60 min. Furthermore, when the cathodic polarisation is lowered the compound decomposes very rapidly (hundreds of thousands of times faster than implantation into the pure metal).

Using the observed increase of hydrogen overvoltage with time, we can obtain some information on the rate of the cathodic implantation reaction. If we assume that the achievement of a limiting hydrogen overvoltage denotes the completion of a monolayer of the compound, we can evaluate the mean rate of implantation on a fresh electrode. Clearly, this calculation can give no more than the order of magnitude of the reaction rate. The hydrogen overvoltage of lead in 1 *N* CsOH reaches a limiting value after 60 min cathodic polarisation (Fig. 10). The extrapolated mean current density of alkali metal implantation into pure lead at $\varphi$ = -1.3 V is of the order of $10^{-10}$ A cm$^{-2}$. This means that implantation proceeds with an extremely high overvoltage. The fact that, after brief cathodic polarisation of the electrode, the anodic oscillographic charging curve does not show an arrest is further evidence of the slowness of implantation. An anodic arrest can be observed only after lengthy cathodic polarisation (30 min, say)[53,56].

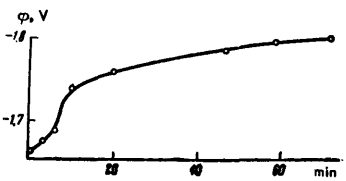



Fig. 10. Growth of the hydrogen overvoltage of lead in 1 *N* CsOH at constant current density $i_c = 3 \times 10^{-3}$ A cm$^{-2}$.

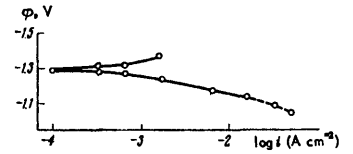



Fig. 11. Polarisation curve for the decomposition of an intermetallic compound, measured for a prepared alloy in 1 *N* NaOH.

The plot of overvoltage curves ($\varphi$–log $i$) is one of the methods used in electrochemistry to measure reaction rates. For the alkali metal implantation reaction, these curves were plotted using the lead–sodium compound obtained by thermal synthesis (Fig. 11). The exchange current of sodium over the alloy was found to be of the order of $10^{-3}$ A cm$^{-2}$.

For an electrode of pure metallic cadmium, the variation with potential of the rate of the anodic decomposition of the intermetallic compound produced by previous cathodic polarisation was measured from a series of anodic charging curves, taken over a range of anodic current densities between $10^{-4}$ and $10^{-2}$ A cm$^{-2}$. The potential of the anodic arrest varied with anodic current density. These results were used to construct a $\varphi$–log $i$ curve for the reaction at a cadmium electrode (Fig. 12). The exchange current was again found to be $\sim 10^{-3}$ A cm$^{-2}$.

Thus, even allowing for the very rough approximation made in the estimation of the rate of the implantation reaction on lead, we can say that the rates of implantation into a fresh lead electrode and into cathodically polarised lead or an alloy of lead with sodium differ very substantially (by approximately seven orders of magnitude).

We concluded earlier, on the basis of published data, that from the point of view of thermodynamics and of electrochemical kinetics mercury should be in no way superior to a number of other metals. It seems reasonable to suppose that the major obstacle to the rapid deposition of alkali metals on solid electrodes is the structural difference between liquid and solid metals. Thus, when alkali metal ions are discharged at a liquid mercury cathode the free volume which exists between atoms in the liquid ensures that the penetration of the alkali metal ions into the cathode is unhindered. Solid metals (lead, silver, zinc, etc.) are composed of closely packed atoms. All the intermetallic compounds which they form with alkali metals are of the substitutional type. Diffusion in these metals and in the intermetallic compounds occurs by exchange between a metal atom and a vacancy in the crystal lattice.




Fig. 12. Polarisation curve for the decomposition of an intermetallic compound, measured for cadmium in 1 *N* NaOH.

Therefore, the diffusion of an alkali metal into the bulk of a solid electrode can only occur by the vacancy mechanism [56].

On the other hand, if we assume, as is often done, that the interaction energy of an ion in the metal with its surroundings is proportional to the coordination number of the ion, it turns out that the most energetically favourable process is the transition of the alkali metal ion undergoing discharge to a vacancy on the electrode surface, since its coordination number then takes the value 9. For comparison we might point out that the coordination number of an ion falling on the plane surface of the electrode is 3, and the coordination number of an ion falling onto the edge of a step (incomplete crystal plane) or of a screw dislocation is 5 or 6. Since the equilibrium potentials of the alkali metals are approximately 1.5 V more negative than the electrode potential during implantation of alkali metals, it is evident that any alkali metal ion falling on the plane surface of the solid electrode will have a higher probability of going back into the solution than of remaining on the electrode surface or of diffusing along the surface until it meets a site where the number of bonds between the ion and the atoms of the electrode is a maximum. Such a site, as was said above, is a surface vacancy. Of course, there is a finite probability that an alkali metal ion falling on a vacancy will also go back into the solution, but the average residence time of the ion on the electrode will be greater the stronger the binding to the electrode. Therefore, an ion falling on a vacancy has the highest probability of exchanging places with another vacancy diffusing outwards from the bulk of the electrode, thus penetrating further into the electrode, instead of going back into the solution.

We have already remarked that the electrochemical stage of the implantation reaction should be a fast one, and cannot therefore determine the rate of the overall reaction. It follows that, even at potentials slightly more negative than the equilibrium potential of the intermetallic compound, all the vacancies present at the electrode surface should be occupied by the alkali metal. Hence, the phenomena taking place at a solid electrode undergoing alkali metal ion implantation are determined by the interplay of two factors. On the one hand, we have the increased concentration of the alkali metal in the surface layer of the electrode due to ion implantation. The rate of this process is determined by the number of vacancies at the electrode surface, which may depend (as we shall see below) on the potential of the electrode. On the other hand, we have the diffusion of alkali metal to the interior of the electrode at a rate which can be very sensitive to the structure of the electrode. Therefore, the course of the overall process of alkali metal implantation is determined (unlike the course of the majority of electrochemical reactions) not only by processes taking place at the electrode surface itself but also (and to a considerable extent) by the structural peculiarities of the electrode metal. As long as the rate of diffusion of the alkali metal towards the interior of the electrode remains smaller than the rate of implantation into the surface, the concentration of alkali metal in the surface layer of the electrode will increase. At first, a solid solution of the intermetallic compound in the electrode metal is formed, and later, when the concentration of alkali metal reaches a value corresponding to the composition of the intermetallic compound, reorganisation of the crystal lattice occurs at a definite rate. With further increase in concentration, a solid solution of the alkali metal (or of a compound richer in the alkali metal) in the intermetallic compound first formed is obtained. In time, the alkali metal diffuses to the interior of the electrode, and the thickness of the layer of intermetallic compound increases [50].

## 2. Loosening and Disintegration of Cathodes

The well-known phenomenon of cathodic loosening and disintegration of metals is intimately associated with diffusion of an alkali metal into the bulk of the electrode. The mechanism responsible for surface loosening of electrodes during implantation is not completely understood. Some authors believe the loosening to result from decomposition of an intermetallic compound formed at the surface [21,22,30,36,50]. Decomposition of the compound present in intercrystalline layers probably plays an important part. It is possible that the compound decomposes as a result of changing polarisation conditions at a given locality on the electrode, for example, by the formation of a hydrogen bubble which screens the surface. A significant accumulation of alkali metal must obviously be present in the surface layer of the electrode to produce loosening. This can happen if the alkali metal penetrating into the electrode cannot reach the interior rapidly enough. Disintegration is possibly connected with the fact that implantation occurs mainly along grain boundaries. If the rapid penetration of alkali metal gives rise to stresses tending to weaken the mutual binding of the grains, separate grains of the metal can break loose and float away with hydrogen bubbles.

Silver electrodes which have been mechanically polished or cleaned with glass powder have a surface layer of heavily deformed metal (cold working) showing enhanced permeability towards diffusion processes. The alkali metal rapidly penetrates to the interior of the electrode, the surface layer cannot become supersaturated with alkali metal, and as a result the electrode does not disintegrate. Etching the electrode in $HNO_3$ dissolves the cold-worked layer, and the electrode disintegrates upon subsequent cathodic polarisation.

Since all the surface vacancies are occupied by the alkali metal even at potentials very little different from the equilibrium potential for the implantation reaction, the observed relationship between the rate of implantation and potential suggests that the concentration of vacancies at the electrode surface increases with increasing potential. Polukarov [57] tried to explain the dependence of the structural peculiarities of the metallic electrode on the electrode potential by suggesting that the change in surface tension of the metal with potential is responsible for the variation with potential of the rate of disappearance of defects in the electrolytic deposit. Similar ideas were used to explain the implantation process [50]. The energy of formation of vacancies depends on the surface tension of the metal, and the relationship can be taken to be linear to a first approximation. The lower the surface tension, the lower will be the energy of formation of vacancies. According to the laws of electrocapillarity, an increase in cathodic potential lowers the surface tension of the electrode metal, lowers the energy of formation of vacancies, raises the surface concentration of vacancies, and therefore increases the rate of implantation. This explanation of the potential dependence of the rate of implantation cannot, of course, be advanced as the only possible one, since it must be remembered that in aqueous solutions a much more intensive process — hydrogen evolution — occurs

in parallel with the implantation of alkali metal and can also affect the energy of formation of vacancies.

The conversion of deposited silver films into an amorphous state by cathodic polarisation in a solution containing alkali metal ions, mentioned above, can be ascribed to the excess of vacancies left behind when alkali metal is implanted and subsequently diffuses outwards.

The number of vacancies at the surface is a function of their rate of formation and of their rate of arrival from the underlying layers of the metal. Lead, unlike silver, has a low melting point and a relatively large self-diffusion coefficient, which allows recrystallisation to occur at room temperature. A concentration of vacancies in excess of the thermodynamic equilibrium value is therefore unlikely to exist at room temperature within the crystal grains of a lead electrode. The main sources of vacancies in this case are the surface, the grain boundaries, and the dislocations.

As we have already pointed out, progressive coverage of the electrode surface by a layer of intermetallic compound is accompanied by an increase in hydrogen overvoltage. The overvoltage reaches its limiting value, in all probability, when the surface is completely covered. Upon further polarisation the layer of intermetallic compound on the electrode surface gradually thickens, whilst at the same time the compound penetrates more rapidly into the core of the electrode along grain boundaries. If during cathodic polarisation the intermetallic compound was formed not merely as a surface monatomic layer, but was allowed to penetrate to the adjacent layer of the metal, and was then decomposed at the surface by passing anodic current, a vastly increased number of vacancies will appear not only at the surface, but also in a small volume immediately below the surface (mainly along grain boundaries and near the intermetallic phase remaining undecomposed below the surface). Such an electrode is said to be "worked". Its high vacancy concentration facilitates the discharge of alkali metal cations with formation of an intermetallic compound, and increases the rate of diffusion. As a result, the overall rate of the process is increased by several orders of magnitude [56].

The electrode can retain its "worked" condition for only a limited time, until the excess vacancies have diffused to the sites which act as sinks for vacancies. Thereafter, the electrode regains the properties characteristic of the pure metal rather than of the compound, and the rate of the process once again becomes very small.

The following experiments confirm the mechanism described for the implantation process. An electrode was polarised for 90 min, and its anodic $\varphi$–$t$ curve was recorded. Without delay, the electrode was again cathodically polarised for 0.5 s and the anodic polarisation curve was again recorded, followed by further brief cathodic polarisation and so on. It was found that after the 90 min polarisation it was possible to plot a number of anodic curves in succession, showing a gradual decrease in the length of the potential arrest, by applying brief periods of cathodic polarisation. The explanation of this is that the rate of diffusion of sodium from the bulk of the electrode is not high enough to give rise to a single large arrest at $\varphi$ = = -1.3 V for the particular anodic current density employed. However, the layer of compound on the surface can become partly reduced after 0.5 s cathodic polarisation, due to the discharge of sodium ions and to the diffusion of sodium from the interior. After 20 min cathodic polarisation, only one anodic arrest can be detected, and the next anodic charging curve does not show any potential arrest. This indicates that even after 20 min a sufficiently thick layer of intermetallic compound has not had time to form.

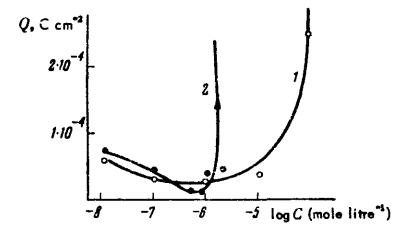



Fig. 13. Variation of the length of the anodic arrest with concentration of $As_2O_3$ (1) and HgO (2) in 1 *N* NaOH.

The anodic decomposition of the resulting intermetallic compound is characterised by the diffusion of sodium atoms from the interior of the electrode to the surface through a layer of intermetallic compound, both for a "worked" lead electrode and for an electrode of the intermetallic compound, prepared by alloying in a separate experiment. We have already pointed out that this type of diffusion should be much faster than the diffusion of the same atoms in the pure electrode metal. The experimental results show that, in fact, on a fresh lead electrode (but not on the alloy) the cathodic formation of intermetallic compound is slower by several orders of magnitude than the anodic decomposition of the intermetallic compound formed by cathodic polarisation. Similar results have been obtained with other electrode metals and other alkali metals [56].

These experiments made it clear that "equilibrium" vacancies, generated at the surface of a metallic electrode or diffusing from the bulk, can give rise to implantation but only at extremely low rates, typically $10^{-10}$ A cm$^{-2}$ for the case of lead. Implantation can occur at appreciable rates only in the presence of a number of vacancies greatly in excess of the "equilibrium" concentration, supplied to the surface from the deeper layers of the electrode. Hence, the essential characteristic of the implantation process is rate control by the state of the metal in the bulk (but close to the surface), a situation not often found in electrochemistry. Of course, factors affecting only the state of the surface can play a part in this case also. However, their effect is incomparably smaller than the effect of structural changes in the bulk of the electrode. Anodic polishing and etching activate the surface and significantly assist implantation. The rate is affected also by the presence of arsenic, mercury, and tellurium on the electrode surface, the effect being a function of the concentration of these elements in solution. At concentrations of $10^{-8}$–$10^{-6}$ M, these impurities inhibit implantation, but when present in greater amounts they assist the process by being co-deposited with the alkali metal (Fig. 13).

Thus, the rate of implantation of an alkali metal into an electrode is determined by the concentration of defects in the bulk of the cathode metal, whilst factors affecting only the electrode surface, such as adsorption of poisons, polishing, and etching, have a vastly smaller effect on the rate of the process [56].

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We may conclude as follows. Electrochemists working at the turn of the century suggested that implantation of alkali metals into electrode metals can occur in aqueous solutions, but they were unable to demonstrate the phenomenon experimentally, and the majority of electrochemists rejected the suggestion. In later years there were occasional indications of the reality of alkali metal implantation, since a number of phenomena observed during cathodic polarisation with alkali metal cations in the solution could not otherwise be explained. These included the cathodic disintegration of metals, the cathodic superactivation of aluminium and magnesium in alkalis, the anomalous behaviour of lead, tin, zinc, and cadmium electrodes during cathodic reduction of acetone, anomalies in hydrogen overvoltage in alkalis, certain phenomena in electroplating, and others. Many departures from the expected behaviour for cathodic processes in alkaline and in neutral solutions were disguised by introducing empirical coefficients, and practical methods of preparation of electrodes failed to attract the attention of electrochemical analysts, for example. Of course, a related phenomenon can often accompany implantation in analytical electrochemistry, in electro-hydrometallurgy, and in electroplating; the co-deposition of alkali metals with other metals such as Zn, Pb, Cd, Ag, and others. However, the most striking feature of implantation — an extremely high initial overvoltage — does not manifest itself. This overvoltage is responsible for the apparent lack of reproducibility of the phenomenon, which compelled most electrochemists of the first half of the present century to abandon their attempts to substantiate the idea of cathodic formation of intermetallic compounds between alkali metals and various electrode metals, and to establish its mechanism. Haber and others tried to investigate this phenomenon 60 years ago, but they did not progress far towards an explanation of the mechanism. In very recent years considerable progress has been made in this direction, and the remarkable features of alkali metal implantation into electrodes have been revealed and explained to some extent; we owe this to the rapid developments in electrochemistry, to the very high level reached by the theory of electrochemistry and of electrochemical methods (due in large measure to the fundamental researches of A. N. Frumkin), and lastly to progress in solid state physics.

It now remains to develop in more detail and to substantiate the theory of electrochemical implantation, and to broaden its experimental foundations.

We cannot exclude the possibility that this process takes place also on metals of Group VIII, say, although hardly any intermetallic compounds have so far been reported between these metals and alkali or alkaline-earth metals.


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# BARRIERLESS ELECTRODE PROCESSES

L. I. Krishtalik

The slow discharge theory, developed and substantiated by the work of Frumkin and his school, satisfactorily describes the basic features of a large number of electrochemical processes (see, for example, Ref. 1). The concepts which had been originally used to describe the discharge of hydrogen ions were shown to be widely applicable to all types of reaction, such as the electrochemical desorption of adsorbed hydrogen, the reduction of anions and neutral molecules, etc. In recent years it has been shown that the basic ideas of the slow discharge theory imply the existence (in a few limiting cases) of new types of electrode reactions showing a number of interesting features [2-4]. The present review article aims to discuss these limiting cases.

The most distinguishing feature of electrochemical reactions is the variation of their activation energy with potential: as the electrode departs from its equilibrium potential in the cathodic (or the anodic) direction, the activation energy of the corresponding electrode process decreases. This behaviour is most conveniently described by the relation

$$A = A_0 - \alpha\eta F, \qquad (1)$$

where $A$ is the activation energy at an overvoltage $\eta$ (real activation energy values [5] will be used throughout), and $A_0$ is the activation energy at the equilibrium potential. The transfer coefficient $\alpha$ is found experimentally to be constant over a range of potentials, and its value is often close to 1/2.

If the activation energy of the forward reaction decreases with increase of overvoltage, the activation energy for the reverse reaction must increase

$$A' = A_0' + \beta\eta F. \qquad (2)$$

It can be shown thermodynamically† that at a given potential $\alpha + \beta = 1$.

Relationships involving activation energy values are conveniently visualised with the help of a potential energy diagram. Fig. 1 shows a cross-section of the potential energy surface along the reaction coordinate. Curve *2* corresponds to a higher potential than curve *1*. Since the energy of the activated transition state increases more slowly with potential than does the energy of the initial state, the difference between the two, i.e. the activation energy, decreases.

Consider a discharge reaction (cathodic, say). Since its activation energy is finite at any given potential, and since it decreases with increase of overvoltage, it must ultimately tend to zero at a high enough overvoltage. Under these conditions the reaction rate will be a maximum, and further increase in potential will not affect the current. In other words, for a non-activated process such as this we can write $\alpha = 0$. But for the reverse ionisation reaction we find $\beta = 1$ at these potentials. The potential curves for this case are shown in Fig. 1 as curves *3* and *4* .

Imagine now that the overvoltage is decreased. This raises the activation energy for discharge, but at the same time the activation energy for ionisation is lowered. At a sufficiently low cathodic (i.e. at a sufficiently high anodic) potential the activation energy vanishes. Under these conditions $\beta = 0$ and $\alpha = 1$. The shape of the corresponding potential energy diagram is shown by curves *5* and *6* of Fig. 1.

Unlike non-activated processes, the processes for which $\alpha = 1$ (or $\beta = 1$) require a considerable activation energy. However, and in contrast to normal discharge processes, this activation energy is equal to the heat of the fundamental reaction step, and the activation energy for the reverse processes is zero‡. On a potential diagram this process does not show the familiar hump of the

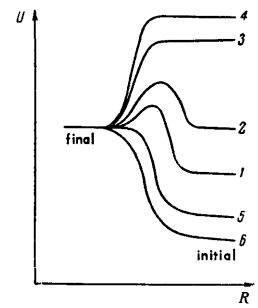



Fig. 1. Potential energy diagram for normal (curves 1 and 2), non-activated (curves 3 and 4), and barrierless discharge (curves 5 and 6).

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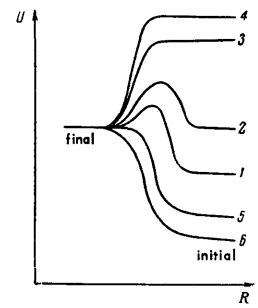



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activational barrier, and therefore we have introduced the term "barrierless" to describe processes of this type[2].

Thus, every electrode process can be expected, in principle, to occur in three forms: barrierless, normal, and non-activated. The polarisation curve, ignoring complications resulting from other stages of the reaction, should have the shape shown in Fig. 2.

Whether or not a current–voltage relation of this form can be observed in practice depends first and foremost on the position of the curve in Fig. 2 with respect to the equilibrium potential. Thus, if the transition from $\alpha = 1$ to $\alpha = 1/2$ occurs below the equilibrium potential (the case denoted by the letter *a* in Fig. 2), barrierless discharge cannot be observed since the reverse (ionisation) reaction predominates below the equilibrium potential. This case appears to be a very common one. However, if the break in the polarisation curve occurs above the equilibrium potential (case *b* of Fig. 2) barrierless discharge becomes accessible to direct observation.

To carry out a barrierless process it is essential that the fundamental reaction step be accompanied by heat absorption, because an activation energy is essentially a positive quantity. In other words, the energy level of the final state must lie above that of the initial state.

It follows that for the slow discharge of hydrogen ions, say, a barrierless process can in principle be observed only with metals which adsorb hydrogen poorly. This is because for these cathodes the energy level of the final state of the slow step — adsorbed hydrogen and a water molecule on the electrode surface — lies well above the energy level corresponding to molecular $H_2$ in the gas phase and water in the bulk. At the equilibrium potential this latter state is practically at the same level as the initial state — $H_3O^+$ ions in the double layer. (As before, we are ignoring the latent equilibrium heat of the process.) These energy relations are illustrated in Fig. 3.

On the other hand, for the slow electrochemical desorption of hydrogen the barrierless process is possible in principle only if the energy of the metal–hydrogen bond is large. In this case the final state is a physically adsorbed $H_2$ molecule, whose energy level is close to that of gaseous hydrogen, and the energy of the initial state (which includes an adsorbed H atom) is lower, the higher the heat of adsorption of hydrogen.

In addition to the above criterion for the realisation of a barrierless process, it is essential that the activation barrier in the normal discharge region should not be too

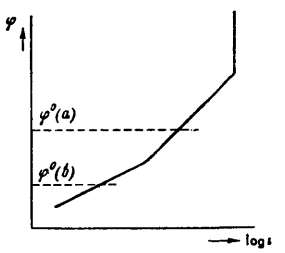



Fig. 2. Idealised polarisation curve (the current corresponding to reaction in one direction only is plotted as abscissa).

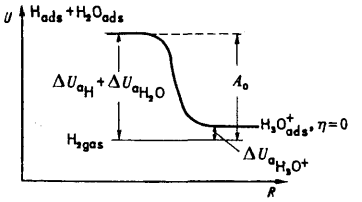



Fig. 3. Potential energy profile for barrierless discharge of $H_3O^+$ ions at the equilibrium potential; $\Delta U_a$ is the adsorption energy of the species indicated, and $A_0$ is the apparent real activation energy at the equilibrium potential; the horizontal line denotes the energy level corresponding to gaseous $H_2$.

high, i.e. that the activation energy of the reverse reaction should vanish before the potential has decreased too much. Earlier tentative calculations[6] of the height of activation barriers justify the belief that the barrierless process should be observable on metals with a high hydrogen overvoltage. A comparison of activation energy data for normal discharge on mercury with plausible values for the heat of adsorption of hydrogen on this cathode leads to the same conclusion.

These were the basic considerations used in formulating an experimental study of the hydrogen overvoltage of mercury under conditions likely to lead to barrierless discharge. However, before proceeding to a discussion of the experimental results, it may not be out of place to consider the characteristic features of the kinetics of this new type of electrode reaction.

The rate of discharge of hydrogen ions at constant potential and constant double-layer structure is proportional to their concentration (or activity, see below). This statement is, of course, applicable to any discharge process, ordinary as well as barrierless. However, if we compare the processes at constant overvoltage rather than at constant potential an entirely different set of relations applies. An increase in the concentration of species undergoing discharge, e.g. $H_3O^+$ ions, lowers the equilibrium potential, and therefore the rate at constant overvoltage increases as $C_{H_3O^+}^{1-\alpha}$ instead of as $C_{H_3O^+}$. For normal discharge $\alpha = 1/2$, and the current density is proportional to $C_{H_3O^+}^{1/2}$. For barrierless discharge, however, $\alpha = 1$, and the rate of reaction at constant overvoltage becomes independent of concentration: the accelerating effect on the reaction of the greater number of species undergoing discharge is exactly compensated by the retardation due to the lowering of the equilibrium potential.

A similar situation exists as regards the effect of the $\psi_1$-potential. A negative shift of the $\psi_1$-potential accelerates the discharge, on the one hand, due to the increased surface concentration of $H_3O^+$ ions, but, on the other hand, it retards the discharge by decreasing the potential jump across the dense part of the double layer. In normal discharge the former effect predominates, because the $\psi_1$-potential appears with the coefficient $\alpha = 1/2$ in the expression for the retarding effect. In barrierless discharge $\alpha = 1$, and these two effects exactly compensate each other.

Whereas the conclusion that overvoltage is independent of concentration of the discharging species applies equally

to the discharge of ions and to the oxidation–reduction of molecules, exact compensation of the $\psi_1$-effects can occur only in the reduction of a singly charged cation (or in the oxidation of a singly charged anion). In other cases the effects of the $\psi_1$-potential on the surface concentration and on the potential jump may not be mutually compensating.

We should stress that lack of dependence of the overvoltage on $C_{H_3O^+}$ and on the structure of the double layer is not at all inconsistent with the assumption of a slow discharge step. Thus, if we examine the rate of hydrogen evolution at constant potential we find that it is proportional to the concentration of $H_3O^+$ ions. But if it were possible to compare overvoltages in different solutions at constant surface concentration of hydrogen ions, the effect of the $\psi_1$-potential would be very clearly revealed.

The features of barrierless discharge discussed above can be described by the following equation, which we had previously derived[2] on the basis of the theory of absolute reaction rates:

$$i = \varepsilon \frac{kT}{h} \frac{\varkappa}{\gamma^{\neq}} 10^{18} a_{H_2O} P_{H_2}^{1/2} (1-\theta) \exp\left\{-\frac{1}{RT}\left[\Delta H_{a_H} + \right.\right.$$
$$\left.\left. + \Delta H_{a_{H_2O}} + T\left(\frac{1}{2} S^0_{H_2} - \Delta S^0_{a_{H_2O}}\right) - \eta F\right]\right\} \quad (3)$$

Here $\epsilon$ is the electronic charge, $\varkappa$ is the transmission coefficient, $\gamma^{\neq}$ is the activity coefficient of the activated complex, $a_{H_2O}$ is the activity of water, $\theta$ is the coverage of the surface by adsorbed hydrogen (for mercury $\theta \ll 1$), the subscript $a$ after $\Delta H$ and $\Delta S$ indicates that these quantities refer to the adsorption process, and the superscript 0 denotes standard values. The remaining symbols have their usual meaning.

We shall now introduce some refinements into this equation.

It follows from the above discussion and from Eqn. (3) that the overvoltage under conditions of barrierless discharge is practically independent of the composition of the solution: this, as well as $\alpha = 1$ (i.e. $b = 59$ mV), is the most characteristic criterion of slow barrierless discharge. For normal discharge, we know that the overvoltage can be very sensitive to the composition of the solution.

The lower the polarisation curve for normal discharge, the higher is the current density and the overvoltage at which it intersects the branch corresponding to barrierless discharge, i.e. the more easily can the phenomenon be demonstrated experimentally. We have therefore examined the hydrogen overvoltage of mercury in concentrated solutions of salts having a strongly adsorbable anion (iodide and bromide), because the overvoltage for normal discharge is lowest in solutions of this type.

The experimental procedure has already been described in detail[3]. Since it was essential that the results at low current densities be reliable and not distorted by effects such as depolarisation by oxygen, special care had to be taken in the purification of materials and solutions. To improve the efficiency of the electrolytic purification of the solution, we used a relatively thin layer of liquid which was vigorously stirred. This procedure enabled us to obtain satisfactorily reproducible polarisation curves free from depolarisation drift down to current densities of $10^{-7}$, $10^{-7.5}$, and $10^{-8}$ A cm$^{-2}$ for iodide, bromide, and chloride solutions respectively.

Some typical polarisation curves are shown in Fig. 4. Their shape is entirely in keeping with the suggested

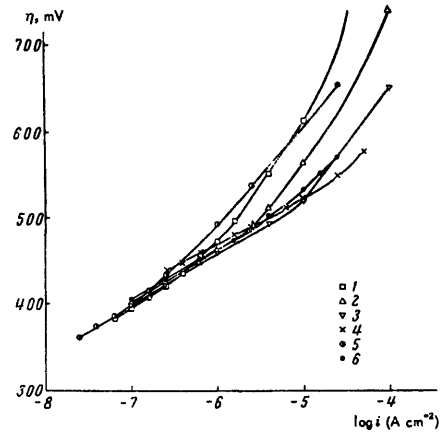



Fig. 4. Polarisation curves for solutions of the following composition (M):
1) 3.2 KI, 0.15 HCl; 2) 3.2 KI, 0.45 HCl; 3) 6 KI, 0.55 HCl; 4) 3 KI, 0.9 HCl, $1.3 \times 10^{-3}$ $N(Bu)_4Br$; 5) 6.6 NaBr, 0.85 HCl; 6) 11.8 LiBr, 0.1 HCl.

theory of the transition from barrierless to normal discharge§. The sharp inflection of the curves and the transition to a lower value of $b$ have been shown[3] to be not due to any conceivable experimental error, and can be taken as a firmly established fact.

The situation described above has been observed in 23 solutions of KI of different composition, covering a range of KI concentration from 0.8 to 6.0 M and a range of HCl concentration from 0.1 to 1.2 M, three of which contained tetrabutylammonium salts in concentration $10^{-4}$–$1.3 \times 10^{-3}$ M. Three solutions contained 6.5–11.8 M LiBr and 0.1–0.9 M HCl; two solutions contained 6.6 and 7 M NaBr and 0.85 M HCl. In every case the $b$ coefficient for the lower branch of the curve was close to 60 mV: the lowest value observed was 52 mV, the highest 63 mV, and in 21 out of 28 experiments $b$ varied between 55 and 60 mV. The average value for all the experiments was $b = 58.5$ mV, which effectively coincides with the theoretical value of 59.1 mV.

In the upper part of the curves (the region of normal discharge) we observe a strong dependence of the overvoltage upon solution composition, including acid concentration, concentration of the adsorbable anion, and concentration of added tetrabutylammonium salt¶. For the range of solution compositions examined in our work, the difference in overvoltage over this region can be 200 mV or higher. On the other hand, in the region where $b = 60$ mV all the curves lie within a band of about 20 mV, and 18 out of the 28 curves lie within 10 mV. There is no apparent relationship between the overvoltage and the composition of the solution. The scatter of the curves obtained with different solutions is of the same order of magnitude as the scatter of the curves obtained in different experiments for a solution of a given composition. We can conclude,

§ The high slope of the top part of some of the curves in iodide solutions is due to the well-known, large shift of the $\psi_1$-potential in these solutions on approaching the point of zero charge.

¶ This has been shown[7] to intensify the adsorption of $I^-$ very considerably when the surface is positively charged.

therefore, that in the region where $b \simeq 60$ mV the overvoltage is effectively independent of the composition of the solution.

The value $b$ = 58.5 mV and the lack of dependence of the overvoltage on solution composition are in complete agreement with the predictions of the theory, and enable us to state that slow barrierless discharge of $H_3O^+$ ions takes place on mercury at low current densities.

Various authors have observed slopes of the order of 60 mV in their semilogarithmic plots for different cathodes. However, their interpretations (which are not strictly substantiated even for their particular systems) are clearly not applicable to the mercury cathode.

Thus, Thomas[8] ascribes this slope to a logarithmic hydrogen adsorption isotherm, which is clearly not the case for mercury. Equally improbable (for the case of mercury) is the assumption of slow surface diffusion of the adsorbed hydrogen or slow detachment of the hydrogen from stable adsorption sites[9]. A different explanation, put forward by Bockris and coworkers[9], associates the appearance of a low value of $b$ with a change in $\psi_1$-potential near the point of zero charge. This argument is unconvincing on general grounds[10], and in our particular system it is refuted also by the fact that the inflection in the curve occurs well away from the point of zero charge (up to 0.4 V in concentrated HCl, see Ref. 4), and in a region where the shape of the polarisation curve for normal discharge has already become stabilised (see Fig. 4).

We had previously shown[11] that a slope of 59 mV should be observed if the slow step is non-activated electrochemical desorption, and discharge and ionisation are effectively at equilibrium. However, this explanation does not apply to the present problem, since it predicts a strong dependence of the overvoltage on solution composition.

Thus, of all the mechanisms discussed in the literature which predict $b$ = 59 mV, the barrierless discharge mechanism alone accounts for the whole of the experimental data.

The value $\alpha$ = 1 implies that over the same region of potential $\beta$ = 0, i.e. the ionisation proceeds as a non-activated process. Therefore, although no direct demonstration has yet been given of non-activated electrochemical processes, the present results can be taken as an indirect proof of the existence of such processes. It follows that the general kinetic features of any arbitrary electrode reaction can be expressed, in all probability, by a curve of the type given in Fig. 2. Whether or not any particular portion of the curve is experimentally accessible, however, depends on the quantitative aspects of each individual case.

An important feature of the barrierless discharge of hydrogen ions, the fact that its rate is independent of the concentration of $H_3O^+$ and of the $\psi_1$-potential, enables us to use this phenomenon to solve certain general problems not otherwise readily handled.

There has been some discussion[12] of the screening effect of tetraalkylammonium cations on the discharge of other ions. In normal discharge, the strong influence of these cations on the $\psi_1$-potential (and therefore on the overvoltage) can mask their screening effect if, of course, this effect is not very large. In barrierless discharge $\psi_1$-effects are absent, but any screening effects should make themselves felt as in normal discharge. According to our results, addition of tetrabutylammonium salts has practically no effect on the overvoltage. There is, in fact, a very small increase in potential, particularly at the lowest current densities, but it is of the order of 10–15 mV and therefore borders on experimental error. This question needs further study, but it is clear in any case that the screening effect in the discharge of hydrogen ions is relatively small.

A more interesting problem is that of the kinetic activity factor. Frumkin and Iofa[13] found that the overvoltage attending hydrogen evolution from concentrated acid solutions of chlorides at constant concentration of acid and $Cl^-$ ions (i.e., according to those workers[13], under conditions of practically constant $\psi_1$-potential) remains unchanged when the $Li^+$ cations are replaced by $K^+$, in spite of the large difference in the activity coefficient of $H_3O^+$ ($\gamma_{H_3O^+}$) in these solutions. They concluded that, as $\gamma_{H_3O^+}$ changes, the activity coefficient of the activated complex ($\gamma^{\neq}$) also changes so as to produce compensation. The ratio $\gamma^{\beta}_{H_3O^+}/\gamma^{\neq}$, which appears in the equation for normal slow discharge, was thus found to be equal to unity.

However, strictly speaking, the kinetic activity factor is not confined to the ratio $\gamma^{\beta}_{H_3O^+}/\gamma^{\neq}$. The equation for discharge, both normal and barrierless, includes also the activity of water raised to the power $\alpha$†, so that the full expression for the kinetic activity factor should be $\gamma^{\beta}_{H_3O^+}\gamma^{\alpha}_{H_2O}/\gamma^{\neq}$. Usually $\gamma_{H_2O}$ is close to unity, and this correction has no significant effect on the precision of the kinetic activity factor. It is very important in principle, however, because the results of Frumkin and Iofa have been generalised by Temkin[14] to include temperature variation (see below).

A rigid experimental evaluation of the effects associated with the activity of water is practically out of the question for normal discharge. Thus, appreciable departures of $\gamma_{H_2O}$ from unity occur only in very concentrated solutions, in which the error in estimating the $\psi_1$-effect due to specific adsorption is obviously much greater than any likely potential shift arising from water activity effects. In barrierless discharge, on the other hand, where no $\psi_1$-effect occurs, the conditions for demonstrating the effect of the activity of water are quite favourable.

To this end, we have studied the overvoltage in very concentrated, acidified solutions of LiBr in which the activity of water was very low (0.1 or less) although the mole fraction was higher than 0.6. If the overvoltage had been directly determined by the activity of water, we should have expected the overvoltage under these conditions to be 50–60 mV higher than in the 3–4 $N$ solutions of KI. In fact, as Fig. 4 shows, the two sets of curves are indistinguishable within experimental error. If, on the other hand, we expect to find only an effect determined by the mole fraction of water, the resulting increase in overvoltage is only 6–8 mV, i.e. a quantity of the order of the experimental error and therefore difficult to observe. Thus, we may conclude that the activity coefficient of water has no effect on hydrogen overvoltage under conditions of barrierless discharge. Hence, following Frumkin and Iofa, we state that $\gamma_{H_2O}/\gamma^{\neq} = 1$. Extending this result, and that of Frumkin and Iofa, to any arbitrary hydrogen ion discharge process, we can write the following approximate equation:

$$\gamma^{\neq} = \gamma^{\beta}_{H_3O^+}\gamma^{\alpha}_{H_2O} \quad \text{or} \quad RT \ln \gamma^{\neq} = \beta RT \ln \gamma_{H_3O^+} + \alpha RT \ln \gamma_{H_2O}. \qquad (4)$$

† This factor allows for the effect of the activity of water on the equilibrium potential.

For barrierless discharge it is easy to verify that $\gamma^{\neq} \simeq \gamma_{H_2O}$. Thus, the distinguishing feature of barrierless discharge is that the activated and the final states are identical: the highest point of the potential energy profile occurs just at the final state. The final state for the discharge of oxonium ions consists of an adsorbed hydrogen atom and a water molecule in the double layer. The activity coefficient of the adsorbed hydrogen is unity (small $\theta$), and therefore the activity coefficient of adsorbed water ($\gamma_{H_2O ads} \simeq \gamma_{H_2O}$) must be adopted as the activity coefficient of the transition state. Thus, the identity of the final and activated state have led us to the same conclusion as the experimental data on overvoltage in very concentration solutions.

Temkin[14], using the analogy between the transfer of a species from a concentrated to a dilute solution and the transfer of a species from one solution to another, and treating water at two not very different temperatures as two distinct solvents, found the entropy of the activated complex. According to Frumkin and Iofa[13], $RT\ln\gamma^{\neq} \simeq \beta RT\ln\gamma_{H_3O^+}$, i.e. $\Delta G^{\neq} \simeq \beta\Delta G^0_{H_3O^+}$, where $\Delta G$ is the change in standard Gibbs free energy attending the transfer of the species from the ideal to the real solution. Assuming that this relationship applies also to transfer from one temperature to another, dividing by $\Delta T$, and letting $\Delta T \to 0$, we obtain

$$S^{\neq} \simeq \beta S^0_{H_3O^+}. \quad (5)$$

An analogous argument for barrierless discharge, based on the equality $\gamma^{\neq} \simeq \gamma_{H_2O}$, leads to

$$S^{\neq} \simeq S^0_{H_2O}. \quad (6)$$

An expression of the type of (6) can also be obtained by an alternative approach, without resorting to the above approximation for the activity coefficients or to the analogy between change of temperature and change of solvent. As we have already pointed out, the activated complex for barrierless discharge coincides with the final state, i.e. with an adsorbed H atom and $H_2O$ molecule. Hence

$$S^{\neq} = S^0_{H_{ads}} + S^0_{H_2O_{ads}}. \quad (7)$$

$S^0_{H_{ads}}$ includes only the vibrational contribution. Since the vibrational frequencies of practically all chemical H bonds are fairly high‡, the corresponding partition function is close to unity and $S^0_{H_{ads}}$ is almost zero. Therefore

$$S^{\neq} = S^0_{H_2O_{ads}}. \quad (7a)$$

Since $\Delta S^0_{\alpha_{H_2O}}$ is not large§,

$$S^{\neq} \simeq S^0_{H_2O}. \quad (6)$$

‡ We shall show below that the energy of the adsorption bond is of the order of 30 kcal, which corresponds to a vibrational frequency of $\sim 1100\ cm^{-1}$, i.e. $S^0_{H_{ads}} \simeq 0.06$ e.u.

§ $\Delta G^0_{\alpha_{H_2O}}$ can be calculated as $10^{-15}N(\sigma_{Hg/H_2O} - \sigma_{Hg})$, where $N$ is Avogadro's number, $10^{-15}$ is the area in $cm^2$ occupied by a water molecule in the surface layer, $\sigma_{Hg/H_2O}$ is the mercury–water interfacial tension, and $\sigma_{Hg}$ is the surface tension of mercury. On differentiating this expression with respect to temperature, we find $\Delta S^0_{\alpha_{H_2O}}$. Using data on the temperature dependence of the surface tension of mercury[15] and of the interfacial tension at the electrocapillary maximum[16], we obtained $\Delta S^0_{\alpha_{H_2O}} = -1.15$ e.u. One could justifiably question how accurately this value, which applies to the adsorption of water at the potential of the point of zero charge, describes the state of the water molecule formed on discharge of an $H_3O^+$ ion. However, the order of magnitude is undoubtedly correct, and $\Delta S^0_{\alpha_{H_2O}}$ is much smaller than $S^0_{H_2O} = 16.72$ e.u.[17]

We have pointed out that the relationships between the activity coefficients found experimentally for normal and for barrierless discharge can be generalised in the form of Eqn. (4). Applying the same treatment to this generalised form, we find

$$S^{\neq} \simeq \beta S^0_{H_3O^+} + \alpha S^0_{H_2O}. \quad (8)$$

Eqn. (8) differs from Temkin's Eqn. (5) by a term containing the entropy of water. As was stated above, the starting expression for $\gamma^{\neq}$ used by Temkin makes no allowance for the activity coefficient of water, which is practically equal to unity in most cases. Allowing for this factor introduces an additional term into the expression for the entropy of the activated complex. In fact, Eqn. (8) states that the entropy of the activated complex has a value intermediate between the entropies of the initial ($H_3O^+ + e_{met}$) and of the final ($H_2O + H_{ads}$) states. (It is assumed that $Se_{met} \simeq 0$ and $S_{H_{ads}} \simeq 0$.) This conclusion appears reasonable, since the activated complex corresponds to a configuration intermediate between the initial and the final state. It is well known that the entropy of an activated complex is not in general equal to the mean of the entropies of the initial and the final states. However, in the present case [as pointed out by Temkin[14] in connection with Eqn. (5)] the entropy terms associated with the vibrational partition functions for the activated complex and for species in the initial and in the final state are quite small, and the entropy of the activated complex is almost entirely determined by its interaction with the solvent, as expressed by Eqn. (8).

If the entropy of the activated complex is taken to be the mean of the corresponding values for the initial and the final state, it is more correct to write Eqn. (8) in the form

$$S^{\neq} = \beta S^0_{H_2O^+_{ads}} + \alpha S^0_{H_2O_{ads}}. \quad (8a)$$

For $\alpha = 1$ and $\beta = 0$, this expression reverts to (7a), i.e. the expression obtained directly for the entropy of the activated complex under conditions of barrierless discharge.

For non-activated discharge, the transition state coincides with the initial state, whence it follows that

$$S^{\neq} = S^0_{H_2O^+_{ads}}. \quad (9)$$

But Eqn. (9) can also be obtained directly from (8a) by putting $\alpha = 0$ and $\beta = 1$.

The fact that Eqn. (8a) gives the right results, verified by an independent method, in the limiting cases, leads us to believe that the generalisation of experimental results used in its derivation is also reasonable, and that Eqn. (8a) can also be used in the case of $\alpha = \beta = 1/2$, i.e. for normal discharge.

In the derivation of the kinetic Eqn. (3) given above we took account of the identity of the activated and the final state[2], in particular as regards the value of the entropy of the activated complex [according to (7a)], but we had not brought out the significance of the kinetic activity factor. After introduction of the necessary refinements, the equation takes the following form (the ratio $\gamma_{H_2O}/\gamma_{H_2O\,ads}$ is assumed to be unity):

$$i = e\frac{kT}{h} \varkappa 10^{15} x_{H_2O} p_{H_2}^{1/2} (1-\theta) \exp\left\{-\frac{1}{RT}\left[\Delta H_{a_{H_2O}} + \Delta H_{a_H} + T\left(\frac{1}{2}S^0_{H_2} - \Delta S^0_{aH_2O}\right) - \eta F\right]\right\}. \quad (10)$$

The real activation energy $A$ is determined from the slope of the plot of $\ln i$ against $1/T$ at constant overvoltage [5]¶.

The corresponding expression for $A$ is obtained by differentiating Eqn. (10):

$$A = -R\left(\frac{\partial \ln i}{\partial 1/T}\right)_{\eta} = \Delta H_{a_{H_2O}} + \Delta H_{a_H} - \eta F + RT. \qquad (11)$$

From (10) and (11) we find the real pre-exponential factor $K$:

$$K = \varepsilon \frac{kT}{h} e\varkappa\, 10^{15} x_{H_2O} p_{H_2}^{1/2} (1-\theta) \exp\left(-\frac{{}^1/_2 S^0_{H_2} - \Delta S^0_{a_{H_2O}}}{R}\right). \qquad (12)$$

Fig. 5, in which a number of typical plots of $\log i$ against $1/T$ are shown for different solutions, satisfactorily confirms that the linear relationship is obeyed. Values of $K$ and $A$ were obtained from the experimental linear plots. These values were recalculated by means of Eqn. (1) for the equilibrium potential, i.e. for $\eta = 0$. In all, we obtained 16 independent sets of data: one for a solution of LiBr, two for NaBr, and the rest for KI (two of them with addition of tetrabutylammonium salts). The mean of all the experimental values is $\log K = 3.0\ (\pm 0.4)$ and $A_0 = 22.9\ (\pm 0.5)$ kcal × × mole$^{-1}$. (The figures in brackets denote the mean deviations from the average.)

Eqn. (12) allows us to calculate the pre-exponential term if we make the usual assumption of a transmission coefficient $\varkappa = 1$ (adiabatic process). All the necessary constants are known, and $\Delta S_{H_2O}$ has been evaluated above. (Even if the error in this estimate is of the same order of magnitude as the value itself, the error introduced into the calculation of $K$ is smaller than the experimental error.) The result of this calculation is $\log K = 5.7$. Thus we must record a discrepancy between theory and experiment in excess of the experimental error.

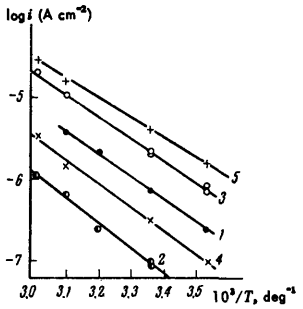



Fig. 5. Temperature variation of the current at constant overvoltage for solutions of different composition (M): 1) 11.8 LiBr, 0.1 HCl, $\eta$ = 460 mV; 2) 7 NaBr, 0.85 HCl, $\eta$ = 400 mV; 3) 4.2 KI, 0.45 HCl, $\eta$ = 470 mV; 4) 3 KI, 0.9 HCl, $1.3 \times 10^{-3}$ N$(Bu)_4$Br, $\eta$ = 500 mV; 5) same solution, $\eta$ = 440 mV.

For normal discharge, Temkin [14] found $\log K = 2.6-3.3$ (for two different solutions) from the data of Iofa and Mikulin [18]; using the data of Post and Hiskey [19], he obtained $\log K = 4$. Thus, the pre-exponential factor for normal discharge is not very different from the value obtained by us for barrierless discharge (the difference being of the order of magnitude of the experimental error).

Temkin's calculation [14] gave $\log K = 5$, the agreement between this and the experimental value being thought fully satisfactory. The small discrepancy was ascribed, with some reservations, to the effect of tunnelling by the proton. If, however, we use Eqns. (8) or (8a) to calculate the pre-exponential factor instead of the expression used by Temkin [Eqn. (5)], a procedure which we now believe to be more justifiable, the pre-exponential term becomes much larger, and $\log K$ takes the value 6.7–6.8. The value of $K$ obtained by this calculation is an order of magnitude larger than the theoretical value for barrierless discharge.

Thus, the discrepancy between theory and experiment is very significant both for normal and for barrierless discharge. It cannot be ascribed to the tunnel effect, since under conditions of barrierless discharge there is no potential barrier through which a proton could penetrate. The tunnel effect may possibly occur to some extent in normal discharge — the disagreement between theory and experiment is perhaps somewhat more serious in this case — but it is quite impossible to draw any definite conclusions from the data which have been discussed.

It should be noted that at least in barrierless discharge the discrepancy between theory and experiment is not associated with any assumptions made in the evaluation of the properties of the activated complex: in this case exact calculation was possible without any need for additional hypotheses. The cause of the discrepancy must be sought, therefore, in the approximations which underlie the theory of absolute reaction rates.

We have reported above our value ($A_0 = 22.9$ kcal × × mole$^{-1}$) for the activation energy for barrierless discharge at the equilibrium potential. As shown by Eqn. (11), and by the potential diagram of Fig. 3, this value enables us to calculate the adsorption energy of hydrogen, a quantity which has not so far been experimentally accessible because of the very low adsorbability of hydrogen on mercury.

Eqn. (11) includes the quantity $\Delta H_{a_{H_2O}}$. This can be found from the data on $\sigma_{Hg/H_2O}$ and $\sigma_{Hg}$ and their temperature variation, used above to evaluate $\Delta S^0_{a_{H_2O}}$. The result is $\Delta H_{a_{H_2O}} = -1.0$ kcal mole$^{-1}$, and the error in this value has little effect on any subsequent conclusions.

Using the experimental value of $A_0$ and the above estimate of $\Delta H_{a_{H_2O}}$, we find $\Delta H_{a_H} = 23.3$ kcal mole$^{-1}$. The error is hardly more than 1.5 kcal (assuming that the error in $\Delta H_{a_{H_2O}}$ is of the order of magnitude of the value itself). From a knowledge of the heat of adsorption of hydrogen and of its heat of dissociation [17], we can calculate the energy of the Hg–H adsorption bond. This turns out to be 29 kcal, a value close to a previous estimate based on a number of analogies and tentative calculations [2, 6, 20].

A case of great interest is that in which neutral molecules rather than $H_3O^+$ ions undergo barrierless discharge. We noted the phenomenon [4] in the evolution of hydrogen on

¶ Since the comparison of $i$ at different temperatures is made at constant concentration of $H_3O^+$ in the bulk (but not at the surface), the activation energy determined in this way is termed apparent, and does not include a term for the adsorption energy of $H_3O^+$ (see Fig. 3).

mercury from concentrated solutions of HCl and strongly acidified, concentrated solutions of KI.[4] Under these conditions the discharge of neutral molecules of the acid is predominant. The composition of the solution now has a significant effect: as was said at the beginning of this article, the effects of the $\psi_1$-potential on the potential drop across the fixed part of the double layer and on the surface concentration of reducible species are mutually compensating only in the case of singly charged cations. With neutral molecules the second factor is not operative. It is evident from Fig. 6 that the addition of tetrabutylammonium ions, which assist the action of $I^-$, raises the overvoltage quite significantly in the barrierless discharge region, as should be the case for the discharge of neutral molecules. In weakly acid solutions, however, where $H_3O^+$ ions are discharged, tetrabutylammonium ions have practically no effect on the overvoltage (Fig. 4). This example shows clearly that a change in the structure of the double layer affects the barrierless discharge process as much as any other discharge process, and that it is only because of the compensation of two opposing effects that the phenomenon is not directly observable in the barrierless discharge of hydrogen ions.

In addition to the evolution of hydrogen on mercury, considered here, there are other electrode reactions for which a barrierless process is likely.

Various authors[9,21-27] have observed a Tafel $b$ constant close to 60 mV, changing to a slope of over 100 mV at higher current densities, in the evolution of hydrogen from acid solutions at a silver cathode. The effect of solution composition on overvoltage was not studied in sufficient detail by those workers. Bockris and Conway[23] found that the overvoltage in pure 0.01 $N$ HCl and in a KCl (or $BaCl_2$) electrolyte is quite different over the region where $b \simeq 120$ mV, but is practically indistinguishable in the region of $b \simeq 60$ mV, as required by the barrierless discharge mechanism. Admittedly, the slope of $\sim 60$ mV was not detected in another series of experiments reported in the same paper. Disagreement at the top end of the curves, and exact agreement at the bottom end, has been reported also[9] for 0.1 $N$ and 0.4 $N$ HCl.

This reaction is being investigated by V. I. Bystrov in our laboratory. From preliminary results, it appears that change of pH has a powerful effect on hydrogen overvoltage in the region where $b \simeq 120$ mV, but at lower potentials ($b \simeq 60$ mV) the effect is very much weaker. On the whole, the situation seems to indicate slow barrierless discharge changing to normal discharge at higher potentials.

Even less is known about hydrogen evolution at cathodes of Au,[28] W,[9] and Mo,[28] and under certain conditions Pt [9] and Rh,[29] for which a slope of $b \simeq 60$ mV has also been reported. It is not possible to reach a firm conclusion, but only to point out that, with strongly hydrogen-adsorbing metals such as W and Mo, barrierless electrochemical desorption is most likely[2]. For the platinum metals we cannot exclude the possibility of an adsorption-electrochemical mechanism, in which the reaction rate is determined by the rate of electrochemical desorption of hydrogen atoms adsorbed on the cathode from the gas phase[11,30]. This electrochemical desorption could be barrierless[2].

Hydrogen evolution does not appear to be the only type of reaction in which the barrierless process is realised. Thus, the present writer and Rotenberg[31] have observed a perfectly sharp break in the polarisation curves for the anodic evolution of chlorine on graphite (see Fig. 7), the slope at the lower end of the curve corresponding to 60 mV. (The experimental slope is higher by a factor of two because of the peculiar current distribution in the porous electrode; the relation between the apparent and the true slope in porous electrodes is discussed, for example, in Ref. 32.) It is important to note that, in keeping with the theory, the addition of $SO_4^{2-}$ anions and $Fe^{3+}$ cations (both of which are adsorbed on graphite) has practically no effect on the lower part of the polarisation curves, whereas their effect in the region of $b \simeq 110$ mV, where we suppose that normal discharge is proceeding, is quite appreciable. Polarisation curves of similar shape have also been observed under somewhat different conditions[33,34].

The phenomena occurring during anodic evolution of oxygen are more obscure. Several authors[35-38] have

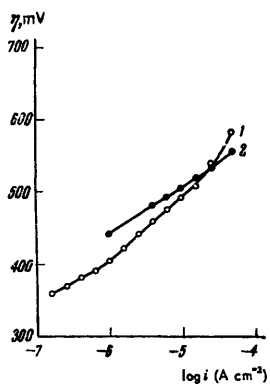



Fig. 6. Effect of tetrabutylammonium ions on the overvoltage in strongly acid KI solutions:
1) 2.2 M KI, 4 M HCl; 2) same solution, + $1 \times 10^{-3}$ M $N(Bu)_4Br$.

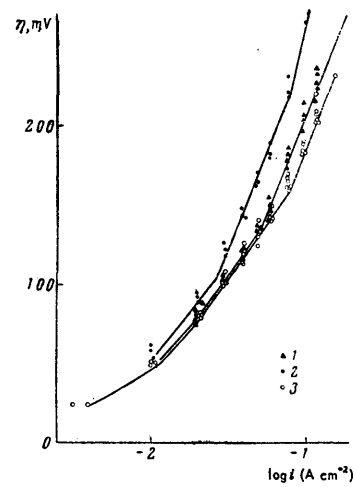



Fig. 7. Polarisation curves for the evolution of chlorine on graphite:
1) 4.4 M $Cl^-$, 1.5 M $H^+$; 2) solution 1 with addition of 0.2 M $Na_2SO_4$; 3) solution 1 with addition of 0.1 M $FeCl_3$.

reported slopes of the order of 60–70 mV on Au, Cu, and Co anodes, but an unambiguous discussion of these results is not possible as yet. Bardina[39] has obtained some interesting results in our laboratory on the anodic oxidation of high-temperature pyrolytic carbon below the equilibrium oxygen potential. We believe that these results can be most satisfactorily explained in terms of barrierless electrochemical desorption of $CO_2$ accompanying the discharge of $OH^-$ ions.

A slope of ~ 60 mV has been frequently observed in the anodic evolution of nitrogen from azide solutions on anodes of different materials[40-42]. The variation of potential with azide concentration[40,41] corresponds exactly with the requirements of barrierless discharge (or electrochemical desorption). However, another explanation is possible, based on the shape of the adsorption isotherm of nitrogen[42]. A choice between these possibilities must await further experimental work.

In conclusion, we can state that the existence of barrierless discharge in the evolution of hydrogen on mercury is a firmly established fact. A barrierless process offers the most plausible explanation of the features of hydrogen evolution on silver and chlorine evolution on graphite: we may hope that current investigations will finally resolve this problem. Furthermore, there are numerous data which justify the belief that many other electrode reactions can occur by the barrierless mechanism.


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# THEORY OF THE MACROSCOPIC KINETICS OF HETEROGENEOUS AND HOMOGENEOUS-HETEROGENEOUS SYSTEMS

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## 1. PRESENT STATE OF DEVELOPMENT OF MACROKINETICS

The term macroscopic kinetics usually denotes the kinetics of chemical changes in real systems in which the reaction rate is affected by mass-transfer and heat-transfer processes. Transfer processes take the form of molecular diffusion and thermal conduction, on the one hand, and of convective transfer phenomena, on the other hand. In the latter, substance (mass or energy) is transferred by the macroscopic motion of the medium.

Mass-transfer processes are especially important in heterogeneous chemical changes. It is often found that in heterogeneous changes the overall rate of the reaction is determined by the rate of access of the reactants to the reaction surface or by the rate of removal of the reaction products from the surface. In this case we say that the kinetics of the heterogeneous reaction are diffusion-controlled. Diffusional kinetics are most often rate-determining in fast heterogeneous reactions.

In processes attended by large absorption or evolution of heat the overall kinetics are determined by heat transfer. To simplify the terminology, we shall combine mass--transfer and heat-transfer processes under the term "transport phenomena", and we shall use the term macrokinetics to describe the kinetics of a reaction involving complicating transport phenomena.

To the chemist the supply or removal of reagents or heat to or from reaction surfaces, vessel walls, etc., is of little interest, and is merely an obstacle to an understanding of the true reaction mechanism. To the technologist these processes are the main barrier preventing the achievement of the optimum reaction conditions. This is why the mechanism of mass- and heat-transfer processes has long been ignored by chemists and technologists alike, who have confined their attention to ways of eliminating diffusional and thermal limitations. It soon became apparent that adequate convection of the liquid or gaseous medium was essential for this purpose. Hence, the problems of macrokinetics became tightly bound up with problems of hydrodynamics.

We can identify three stages in the development of the macroscopic kinetics of chemical reactions. The first goes back to the turn of the century, when the basic qualitative ideas underlying the transport of reacting species and of heat in reaction vessels and in mass-exchange apparatus were formulated. Nernst's hypothesis of the diffusion layer, Langmuir's film theory, etc., relate to this period.

In the 1930's to 1950's many workers (mostly chemical technologists and heat engineers) were forced to study transport phenomena in greater detail, because of the developments in the design of reactors and mass-exchange apparatus. Transport equations applicable to moving media were formulated. Since these could not be solved exactly, the methods of group similarity theory were applied with success to the description of mass and heat transport processes.

The development of the basic (distinguishing) similarity criteria and the numerical treatment of experimental results constitute the second stage of the development of macroscopic kinetics. This period is characterised by a large number of experimental studies. In some cases, a practical description of the transport phenomena in macrokinetics was achieved by establishing the numerical relationships.

However, it became clear in recent years that this partial description was inadequate and not always satisfactory. Furthermore, in many cases it was quite impossible to base a model on the equality of distinguishing criteria. This is particularly true of models of chemical reactors, in which the various criteria are often mutually incompatible.

With heterogeneous reactions, whose rates can vary over fairly wide limits, it is easily possible to cover the whole range of reaction rates (from the activation-controlled to the transport-controlled region) under constant conditions of stirring.

This case is most commonly met in electrochemistry. It is easy to vary the rate of an electronic reaction over quite wide limits by controlling the potential difference applied to an electrochemical cell.

It is usually found that the current–voltage characteristic has the form of a rising curve with a plateau, indicating that the rate of the process is independent of the applied e.m.f. Since the rate of the electrode reaction is essentially a function of the e.m.f., it follows that in the plateau region the process is controlled by mass transfer: the supply of ions to the electrode surface. This phenomenon has been called concentration polarisation.

A. N. Frumkin laid the foundations of the quantitative theory of concentration polarisation about 20 years ago[1,2]. A few years earlier, the quantitative theory of combustion processes in gases had begun to be developed intensively[3,4]. Lastly, the quantitative study of heat-transfer processes belongs to the same period[5]. The achievement of fast reactions and the enhancement of mass-transfer and heat--transfer processes in chemical engineering urgently need a formulation of the quantitative laws of macrokinetics, applicable to the complicated conditions which exist in chemical reactors and in mass-exchange apparatus. For this reason, disconnected investigations in these fields have begun to merge into a general theory of macrokinetics during the past ten years.

The third stage in the development of macroscopic kinetics is intimately concerned with the quantitative description of transport processes in moving media under conditions approaching those obtaining under realistic working conditions in chemical plant.

The mathematical calculation (or quantitative description) of the macroscopic kinetics under complicated conditions was made possible by two circumstances:

1. The study of the hydrodynamic, physicochemical, and kinetic processes which together characterise chemical change in real systems.

Important theoretical and experimental data have been obtained in recent years on the mechanism of convective mass and heat transfer. These apply to laminar and to turbulent flow, in liquids and in gases, at phase boundaries, under various geometries, and under stationary and non-stationary conditions.

2. The general application to the solution of complicated problems of modern computational methods, relying on the use of high-speed computers.

Studies of macroscopic kinetics can be classified into three basic stages: (a) the study of "fundamental" processes in transport and macrokinetic phenomena; (b) the study of transport processes in statistical systems, including a large number of random fundamental transport steps; (c) the study of transport processes in chemical plant.

Each of these stages has its own special features, but they are all combined into a single complex. We can explain this by a simple example. Mass transfer to the surface of a single bubble, freely rising in a liquid, is a fundamental process according to our terminology. A column of bubbles executing a collective motion is an example of a statistical system with mass transport. In an absorption apparatus it is necessary to consider the motion of a column of bubbles, complicated by a large number of specific factors arising from the design of the column, e.g. non-uniform distribution of the bubbles over the cross-section.

Equations for matter and heat transport can be formulated on the most general assumptions concerning the properties of the medium.

When dealing with bulk or surface (catalytic) reactions involving the absorption or evolution of heat, we are faced with a system of interdependent equations for mass and heat transfer. The coupling between the equations of motion of the medium and the transfer equations arises from changes in viscosity and density of the medium with temperature or from volume changes in gas-phase reactions. The system of equations resulting from all these factors defies both analytical and numerical solution.

Nevertheless, in chemical kinetics and in chemical engineering the velocity, concentration, and temperature distribution in the reaction volume must be known. It is very important, therefore, to establish at least qualitatively the analytical dependence of these distributions on the basic external parameters of the system (prescribed flow rates, initial composition, etc.).

Indeed, the assignment of the velocity, concentration, and temperature distribution is essential both in order to establish the true kinetics of homogeneous and heterogeneous reactions and in order to establish the mode of operation of large-scale reactors and mass exchange apparatus. Therefore, the subdivision of real processes into similar phases or stages, susceptible to analytical or numerical study, is a very important aspect of this stage in the development of macrokinetics.

In the following Sections we shall discuss the realisation of this programme by considering various examples.

## 2. MACROKINETICS AT AN IMMOBILE PHASE BOUNDARY, LAMINAR FLOW

We shall begin the discussion with the fundamental process of transport to the surface of a solid body. The hydrodynamic behaviour of liquids and gases near a solid surface is known in fair detail both for laminar and for turbulent flow.

Consider the case of laminar motion. Analysis of the equations of momentum transfer (hydrodynamic equations), energy transfer (heat-transfer equations),and mass transfer indicates that all these transport processes show some definite similarities.

We know[6-8] that at high Reynolds numbers the total flow can be divided into a main region and a hydrodynamic (or Prandtl) boundary layer. In the main region the velocity of the liquid (or gas) has the constant value $U_0$ over the entire cross-section of the flow. The whole of the velocity change from $U_0$ to zero (at the solid surface) takes place in a thin boundary layer whose thickness is given by the formula

$$\delta_0 \sim \sqrt{\frac{\overline{vx}}{U_0}}, \qquad (1)$$

where $x$ is the distance along the surface of a streamlined body. The shear stress under these conditions is of the order of magnitude

$$\tau \sim \mu \frac{U_0}{\delta_0}. \qquad (2)$$

In formulae (1) and (2) $\mu$ is the normal and $\nu = \mu/\rho$ is the kinematic viscosity.

A quantitative expression for the velocity distribution under steady-state flow can always be calculated for not too complicated geometries of the streamline surface.

In isothermal processes such as those associated with mass exchange the convective diffusion equation can always be solved if the velocity distribution is known.

For a planar or axially symmetrical interface, the convective diffusion equation can be written in the form[7]

$$\left(\frac{\partial c}{\partial x}\right)_{\psi} = D \frac{\partial}{\partial \psi}\left[v_x(x, \psi)\frac{\partial c}{\partial \psi}\right], \qquad (3)$$

where $\psi$ is the hydrodynamic stream function, simply related to the velocity components, and $v_x$ is the velocity component along the surface:

$$v_x = -\frac{\partial \psi}{\partial x}.$$

An entirely similar expression (with the diffusion constant replaced by the thermal diffusivity) applies to the temperature distribution if heat evolution resulting from viscous dissipation in the medium can be ignored. The usual boundary conditions are the given concentration $c_0$ or temperature $T_0$ at a point remote from the surface, the balance between the numbers of particles transported to the surface and of reacting particles, and also the temperature at or the heat flow to the reaction surface. From a mathematical point of view, Eqn. (3) is formally identical with the equation for non-stationary heat conduction in an immobile medium and with a thermal diffusivity depending on time and position:

$$\chi_{eff} = Dv_x. \qquad (4)$$

Eqn. (3) can be solved numerically in all cases for which the function $v_x(x, \psi)$ is known analytically or numerically.

Analytical solution of Eqn. (3) is possible for the case of a liquid phase. This is because of the very large value of the Prandtl number $Pr_D = \nu/D$, where $\nu$ is the kinetic viscosity of the medium. In liquids, where $D$ is small

compared with $\nu$, the Peclet number $Pe = RePr_D = U_0L/D$ (where $U_0$ is a characteristic flow velocity and $L$ is a characteristic length) is large even at a relatively small Reynolds number Re (down to $Re \simeq 10^{-1}$). Therefore, a diffusion boundary layer (within which the main concentration changes occur) is formed near the surface of the streamlined body (Fig. 1). Outside the diffusion layer, in the main region, convective transport ensures that the concentration of material is constant, $c \simeq c_0$. In the diffusion layer the concentration changes from $c_0$ to the value $c_S$ at the reaction surface. The thickness $\delta_{diff}$ of this layer is smaller than that of the characteristic region of velocity change. This allows the stream function in Eqn. (3) to be used directly in the neighbourhood of the surface. Thus, the ratio of the thicknesses of the diffusion and of the hydrodynamic boundary layers can be evaluated in the most general case:

$$\delta_{diff} \sim \delta_0 (Pr_D)^{-1/3}, \quad (5)$$

and there is a geometrical similarity between $\delta_{diff}$ and $\delta_0$, as shown in Fig. 1. The thickness of the diffusion layer decreases with increasing flow velocity. The order of magnitude of $\delta_{diff}$ in liquids is $\sim 10\%$ of $\delta_0$, and for normal velocities it lies between $10^{-2}$ and $10^{-4}$ cm. The whole of the diffusional resistance is confined within this narrow layer. In gases $\delta_{diff}$ is of the same order of magnitude as $\delta_0$.

In laminar flow the thickness of the diffusion layer is inversely proportional to the viscous shear stress $\tau$:

$$\delta_{diff} \sim \frac{|\operatorname{grad} \vec{v}|}{U_0} \sim \frac{\tau}{\mu U_0}. \quad (6)$$

If the surface has a small curvature the thickness of the diffusion boundary layer varies with the distance from the leading edge of the body according to the formula

$$\delta_{diff} \sim \sqrt{\frac{x}{U_0}} D^{1/3} \nu^{1/6}. \quad (7)$$

Thus the thickness $\delta_{diff}$ of the diffusional layer varies from point to point along the surface of the body. If the concentration at the surface is given (e.g. if the diffusing particles are used up by a fast reaction, or in the case of dissolution), the boundary condition at the reaction surface can be written in the form

$$c = c_S \text{ at the surface}, \quad (8)$$

where $c_S$ is the constant concentration at the reaction surface itself (equal to zero in the special case of a fast reaction).

The equation for convective diffusion in liquids with boundary condition (8) at the reaction surface and the condition $c \to c_0$ in the main stream has been integrated for many solid reaction surfaces.

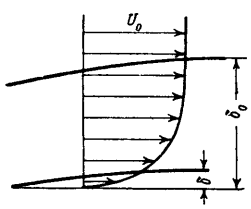



Fig. 1

Systems for which an analytical solution of the convective diffusion equation has been obtained are listed in the Table. Knowing the concentration distribution, we can find the diffusion flux accurately from the formula

$$j = D\left(\frac{\partial c}{\partial n}\right)_S, \quad (9)$$

where $\partial c/\partial n$ is the derivative along the normal to the surface $S$.

It has been shown that the diffusion flux is given, to the nearest order of magnitude, by the formula

$$j \simeq D\frac{\Delta c}{\delta_{diff}} = D\frac{c_0 - c_S}{\delta_{diff}}, \quad (10)$$

where $\Delta c$ is the total (fixed) concentration difference.

The significance of this result is as follows. In liquids the thickness $\delta_{diff}$ of the layer is so small that the concentration change from $c_0$ to $c_S$ can be satisfactorily approximated by a linear law. Formula (7) and the Table show that the diffusion flux varies along the reaction surface, increasing with velocity (for laminar flow) in proportion to $U_0^n$ (where $n \leqslant 1/2$), in proportion to the diffusion coefficient $D^m$ (where $m \leqslant 3/4$), and depending on the nature of the liquid. The dependence of $j$ on the diffusion coefficient $D$ is readily understood: molecular diffusion is a very slow process, and matter transport occurs mainly by convection. Under these conditions the slow stage of the transport process is the passage of matter through the thin layer of liquid adjacent to the solid surface, where its flux is determined by the viscosity.

The solution of the problem of convective diffusion in gases is somewhat more complicated than in liquids. In gases the diffusion coefficient is of the same order of magnitude as the kinematic viscosity, and therefore the thicknesses of the hydrodynamic and diffusion layers are of comparable magnitude. Consequently, we cannot use the approximate expression for the velocity close to the solid surface to solve the convective diffusion equation. The concentration distribution is best calculated numerically. However, the calculations have shown that in practice the concentration distribution can be again satisfactorily approximated by a linear law (over the thickness of the boundary diffusion layer).

The thickness of the diffusion layer in gases is given by the same expression as in the case of liquids, but with a different numerical coefficient (slightly dependent, strictly speaking, on the Prandtl number). The second difference between convective diffusion in gases and in liquids is that in the former the total pressure of the gaseous mixture can vary if the surface reaction is so fast that appreciable quantities of gas are generated (or consumed). The diffusion component of the gas mixture is also affected, since

TABLE.

| Regime | Type of surface | Refs. | Regime | Type of surface | Refs. |
|---|---|---|---|---|---|
| Laminar | rotating disc | 1,7 | Turbulent | semi-infinite plate | 7 |
| » | solid sphere | 7,9 | » | disc | 7 |
| » | semi-infinite plate | 7, 10–13 | » | inner surface of a tube | 7 |
| » | semi-infinite, non-uniform plate | 7,14 | » | rough surface | 7 |
| » | throttle | 6,7,15 | Natural convection | smooth vertical plate | 7 |
| » | inner surface of a tube | 1,7,16 | Turbulent | particle carried by a turbulent stream | 7 |

the total pressure of the gas should remain constant. These features can readily be allowed for in two-component gas mixtures, but they seriously complicate the calculations in multicomponent systems. However, they do not bring any qualitative changes into the general picture.

We shall now consider the case of a chemical reaction proceeding at the surface. Its rate depends on surface concentration, usually according to a power law:

$$Q = f(c_1) = kc_S^n. \tag{11}$$

In these circumstances boundary condition (8) no longer applies.

The boundary condition now imposed on the surface concentration is of the form

$$D\left(\frac{\partial c}{\partial n}\right)_S = f(c_S). \tag{12}$$

The convective diffusion problem is not amenable to analytical solution with boundary condition (12) if $f(c_S)$ is a non-linear function of its argument and the reaction surface has a complicated shape.

A solution of this boundary problem was found[7,14] only for the simplest case of $f = \kappa c_S$ at the surface of a semi-infinite sheet. The effective thickness of the diffusional stream turns out to be a complicated function of the distance $x$, and also of the rate constant of the reaction $k$, of the diffusion coefficient $D$, and of the flow velocity $U_0$. The variation of the effective thickness of the boundary diffusion layer with the rate constant ($k$) of the reaction is a clear indication of the arbitrariness of this concept.

The quantity most commonly measured is the total flux $J = \int j\,dS$, where the integration is carried out over the whole of the reaction surface. It is evident that, having measured $J$, we can find the coefficients $k$ and $n$ in the kinetic law (11) only by solving the corresponding integral equation. The integral equations can be formulated, and their solutions presented in series form, for the surface of a plate and for the interior of a tube[17,18].

If the shape of the reaction surface exposed to the flow is more complicated, great difficulty is encountered not only in solving but even in obtaining the integral equation. Therefore, the kinetic law of the reaction must be determined either by carrying out the reaction under activation control or by making the measurements on "uniformly accessible" surfaces, for which the current density or the thickness of the diffusion layer have a constant value all over the surface.

The first requirement is somewhat indeterminate. The value of the diffusion flux near the edge of the plate or at the mouth of the tube formally tends towards infinity. This means that in these regions the reaction is always activation-controlled. The relative contribution of activation control to the total diffusion flux over the entire surface depends on the size of the plate and on the kinetic law.

Conversely, the diffusion flux at the surface of a body of non-streamlined shape is always finite, and does not exceed the value $j \simeq \frac{D\Delta c}{\sqrt{\nu R/U_0}}$ if we take the leading part of a sphere as an example. (The trailing part is discussed below.) In any kind of stagnant region, such as depressions in the body, the diffusion flux is low, and the reaction can obey the laws of diffusion-controlled kinetics, whereas on the streamlined parts of the body activation control is possible. Hence, in order to find the true kinetic law of the surface reaction, it is advisable to carry out the measurements under conditions to which macrokinetic theory is applicable[19,20]. The work of Frumkin's school[21-23] on solid electrodes as well as on the dropping mercury electrode[24] offers a striking example of the successful use of developments in macrokinetic theory for the determination of the true kinetics of a surface reaction.

As was stated above, it is particularly desirable to carry out the kinetic measurements on a surface such that all points are equally accessible to diffusion.

For laminar flow of a liquid or a gas, only two surfaces of this type are available: (1) the surface of a rotating disc; (2) the inner surface of a pipe or crack, beyond the inlet section where diffusion occurs (whose length $L$ is approximately equal to 50 RePr).

The rotating disc was first used to study the kinetics of electrochemical reactions by Frumkin's school[25], and is now very widely applied in electrochemistry[26,27] and in studies of the kinetics of the dissolution of solids[28,29]. The investigations in which the rotating disc has been used are numbered in hundreds.

The thickness of the diffusion layer (as well as the flux density) is constant over the surface of the disc, and is given by

$$\delta_{\text{diff}} \simeq 1.61 \left(\frac{D}{\nu}\right)^{1/3} \sqrt{\frac{\nu}{\omega}}, \tag{13}$$

where $\omega$ is the angular velocity of rotation.

To determine the kinetic law, we only need to solve the transcendental algebraic equation[8]

$$kc_S^n + \frac{D}{\delta_{\text{diff}}}(c_S - c_0) = 0. \tag{14}$$

The function $j(\omega)$ for reactions with $n = 1$ and $n \ll 1$ is presented graphically in Fig. 2. These curves enable us to assess the degree of selectivity of surface reactions, falling in the region of mixed kinetics on going over from $n = 1$ (curve *1*) to $n \ll 1$ (curve *2*).

However, this unique, uniformly accessible surface has not as yet been used to any appreciable extent in the study of catalytic reactions. We know of only two investigations in which a rotating disc was used for catalytic measurements[30,31]. Yet, nothing short of a complete plot of $j$ against $\omega$ can provide a sufficiently accurate means of evaluating the constants $k$ and $n$ in the kinetic law (11). We believe that measurements of this type would be highly desirable.

Non-stationary processes can play an essential role in the study of the faster heterogeneous reactions. These processes have already found an extremely wide field of application in electrochemistry, where they can be very easily realised in practice by measurements of potential or current as a function of time[32]. In catalytic reactions meaningful measurements can be made on the surface of a disc by using pulsewise input of reactants or a variable surface temperature.

Kinetic studies on uniformly accessible surfaces are especially important when several competing or consecutive reactions take place. The theory of this type of process has also been worked out to a useful degree. In particular, the method of a disc with ring has been successfully applied by Frumkin and coworkers to reactions involving unstable intermediate products[22,23].

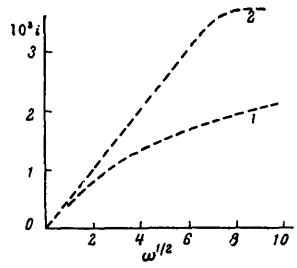



Fig.2.

The inner surface of a pipe cannot be used in liquid--phase processes, because the inlet section is very long in this case. It has been widely used, however, for reactions at the gas–liquid interface (see below).

In this context it is important to point out the relationship between the hydrodynamic theory of the boundary diffusion layer, discussed above, and the so-called "film theory", which has found very wide acceptance[33]. The underlying basis of this theory is the assumption that matter transport due to external convection is completely absent in a layer of thickness $d$, which is uniform over the reaction surface.

In liquids this is equivalent to assuming total absence of convective transport. Thus, the film theory in liquids coincides with Nernst's theory of the immobile diffusion layer.

In gases a somewhat different situation exists. In addition to convective transport, associated with the motion of the outer stream, we have a motion of the gas from (or towards) the reaction surface, due to the evolution (or absorption) of gas in the course of the reaction. The flow of gas arising from the removal or supply of particles from or to the surface is ignored in the film theory.

The main shortcoming of the film theory is the use of the arbitrary quantity $d$, which must be found by comparing the theory with measured mass fluxes. Yet, as the exact formula (7) shows, this thickness is in fact a function of the diffusion coefficient of the material (and therefore must be determined experimentally for each material), and also of the nature (viscosity) of the medium. Also, generally speaking, the thickness of the diffusion layer is variable from point to point along the reaction surface.

The attractions of the film theory are its relative simplicity and its ability to deal with complicated reaction kinetics. But these do not outweigh, in the writer's opinion, the drawbacks of this theory.

So far only mass transport phenomena have been considered. Heat transfer phenomena are no less important to the theory of macrokinetics. This is particularly true of gas reactions, which are frequently characterised by large heat changes.

The equations describing the transfer of energy (heat) in moving media are formally very similar to the corresponding equations for mass transfer. This circumstance, as already pointed out, justifies the use of the term transport phenomena.

Heat transfer phenomena have been studied in great detail in the physics of heat. However, as will be stressed below, heat-transfer problems in chemically reacting media have a number of specific features. In mobile media (liquids and gases) a thermal boundary layer, across which the main temperature drop occurs, is formed at the surface of a solid body maintained at a given temperature. This boundary layer is the analogue of the hydrodynamic and the diffusion layer.

The thermal Prandtl number $Pr_T = \nu/\chi$, where $\chi$ is the thermal diffusivity of the gas ($\chi = \varkappa/\rho c_p$, $\varkappa$ being the thermal conductivity), is of the order of 0.5–10 for gases and for most liquids alike. (The only exceptions appear to be some organic liquids and liquid metals[7].) The thicknesses of the boundary diffusion layer in a gas and of the thermal boundary layer in liquids are of the same order as the thickness of the hydrodynamic boundary layer. Therefore the equation for the temperature distribution must be solved by numerical methods.

Approximate methods of solution, such as Pohlhausen's method, have also found wide acceptance. In this method the distributions of velocity, concentration, or temperature in the boundary layer are described approximately by polynomials in powers of the distance from the surface[34]. There are also many other approximate methods, such as the method of integral moments[33]. The main disadvantage of these methods is that the error thereby introduced cannot be estimated quantitatively.

As regards the variation of concentration and temperature distribution in mobile media with the Prandtl number, the limitations of the analogy between mass transfer and heat (and also momentum) transfer must be borne in mind, particularly in the case of liquids. In gases the viscosity, thermal conductivity, and diffusion coefficients are relatively constant, so that the conditions under which the processes resemble each other are satisfied to a good approximation.

Non-isothermal reactions are very relevant to the study of the macrokinetics of heterogeneous chemical reactions. Non-isothermal processes are complicated by the interdependence of mass and heat transfer. In heterogeneous reactions this dependence is expressed not by the equations themselves, but by the boundary conditions, which take the following form at the reaction surface:

$$D\left(\frac{\partial c}{\partial n}\right)_S = kc_S^n e^{-\frac{E}{RT_S}} \quad \text{at the surface,}$$
$$\chi\left(\frac{\partial T}{\partial n}\right)_S = hkc_S^n e^{-\frac{E}{RT_S}} \quad \text{at the surface,} \qquad (15)$$

where $T_S$ is the surface temperature, $h$ is the heat of the heterogeneous reaction, and $E$ is the activation energy.

The experimental and the theoretical study of such reactions is also most conveniently carried out on a uniformly accessible surface, such as the surface of a rotating disc. In this case the surface temperature $T_S$ is constant along the surface, and simultaneous solution of the diffusion and thermal diffusivity equations involves the solution of a system of two transcendental algebraic equations.

By comparing the measured mass flux and surface temperature with experimental data, it is possible to determine the activation energy and the rate constant for a heterogeneous reaction.

Among other cases of diffusion-controlled kinetics at the boundary between a solid and a gas (or a liquid), diffusion to a porous catalyst particle deserves special mention.

Diffusion and heat transfer to a spherical particle from the external stream can be calculated. Departures from the spherical form merely introduce, in general, a different numerical coefficient.

In the case of isothermal reactions the problem of mass exchange in a pore can be solved for the general case. The main types of non-isothermal reaction, i.e. reactions of the first and of fractional orders, have been investigated in very recent years.

In this context, the so-called gradientless method of establishing the kinetics of catalytic reactions, which is now very widely applied, should be mentioned. In this method the main criterion of the presence of activation control is lack of dependence on the stirring rate. The method calls for three critical remarks.

1. Independence of the velocity of the external stream is a qualitative, but not a quantitative criterion of the transition to activation control.

2. The measured reaction rate is the combined result of the true chemical kinetics and of diffusional and thermal processes within the catalyst grains. The relation between these effects can be very complex, particularly in non-isothermal reactions. This can be demonstrated by calculations of non-isothermal reactions of zero, fractional[35], and first orders within the catalyst grain[36]. The presence of pores on whose surface the catalytic reaction proceeds is taken into account by introducing effective diffusion and thermal diffusivity coefficients for the particle. The effective activation energy $E_{eff}$ is related to $h$, $D$, and $\chi$ and can be very appreciably different from the true activation energy $E$: it can be either smaller or greater than $E$. Therefore, the constants in the kinetic equations obtained by this method have a somewhat indeterminate meaning.

3. The method of measurement requires that the reaction products be removed from the reactor. No allowance is made for the possibility of build up, or for the effect of other non-catalytic reactions during removal of the products.

For these reasons, the writer believes measurements on a uniformly accessible surface to be essential.

## 3. MACROKINETICS AT A MOBILE PHASE BOUNDARY (LIQUID–LIQUID OR LIQUID–GAS)

The interface between mobile phases will now be considered. There are several cases of "fundamental" processes in mobile media: near the surface of drops, of bubbles, jets, and liquid films on solid surfaces. It must be stressed that the hydrodynamics of systems with mobile interfaces have been examined very much less fully than the hydrodynamics of flow in the neighbourhood of a solid surface.

With a mobile interface mass transport occurs by two independent transport processes in each of the phases. In particular, mass transfer at the liquid–gas interface involves processes occurring in phases of vastly different hydrodynamic behaviour.

Very often the mass-transfer process is complicated by chemical reactions between the diffusing species. Mass transport towards the simplest surface from the hydrodynamic point of view, a single bubble or drop moving in a quiescent medium, has been most fully investigated. The diffusion flux towards a growing, immobile drop was calculated several years ago[37,38]. The use of the formula for the diffusion flux towards a growing mercury drop provided the quantitative foundation of the polarographic method.

Frumkin and his coworkers[24] have developed the quantitative theory of the macrokinetics of reactions from the theory of the growing drop, and this has led to important results on the kinetics of hydrogen ion discharge. More recently, the theory of convective diffusion from the external phase to the surface of a moving drop or bubble has been worked out, and in very recent years the author has arrived at the general macrokinetic theory for the surface of small drops and bubbles[39], with allowance for transport in both the external and the internal phase. He has also arrived at the theory for the diffusion flux towards the surface of large drops[40], which are subject to periodic oscillations during their motion.

The diffusion flux in this case is expressed by relatively cumbersome formulae. Their main feature is that the flux is proportional to the square root of the velocity, and is also a function of the exchange (partition) coefficient of the diffusing species between the phases, and of parameters of both phases.

The diffusion flux in the system consisting of "gas bubbles in a liquid" can be obtained from these formulae for the limiting case in which the density of the inner phase is much smaller than the density of the outer phase. With large bubbles, which are deformed during motion, the diffusion and thermal fluxes can be calculated to the nearest order of magnitude. It is useful to note that surface-active substances, which influence the hydrodynamic behaviour of drops and bubbles very considerably, must also affect the diffusion flux. Theoretical formulae for the diffusion and thermal fluxes towards the surface of a drop or bubble are in satisfactory agreement with experiment in the particular case of negligible mass transfer in the inner phase. However, the more general expressions for the flow, allowing for diffusion in the inner phase, have not yet been compared with experimental data, and neither have the formulae for large vibrating drops. The macrokinetics of the process in which species diffusing from the drop undergo chemical reaction in solution have been recently worked out[41]. Because of its practical importance, this process has been examined in a number of papers concerned with the so-called penetration theory.

According to this theory[42], the time needed for the diffusing substance to penetrate into the external phase is much smaller than the time during which its concentration profile is significantly modified by the non-uniform distribution of velocities in the stream. In other words, the theory assumes that the velocity at all points of the external phase which the diffusing particle can reach is equal to the velocity of the interface.

In fact, such is not the case at high Peclet numbers. Even a relatively small point-to-point variation in the velocity distribution in the external phase has a powerful influence on the transport conditions, since at high Peclet numbers convective transfer predominates over transport by molecular diffusion. Calculations show that the formulae of the penetration theory can be applied only over times so short that formation of the diffusion boundary layer has not gone to completion. This time is much smaller than the times involved in the transfer process under the realistic conditions of drops moving in extraction apparatus. Formulae suitable for long times have been obtained: these

give the diffusion flux both in the absence and in the presence of chemical reaction in the external phase.

The second case of flow with a mobile interface concerns thin liquid films flowing on a solid surface. The flow of very thin films is laminar, and the calculation of convective flux presents no difficulty. At somewhat greater thicknesses the flow becomes wavelike, and calculation shows that the diffusion or thermal flux increases by about 25% as compared with a smooth surface. However, we have no theory for convective diffusion in a film covered with ripples of relatively large amplitude. The successful experimental studies of convective diffusion in liquid films exposed to fast countercurrents of gas[43] are a further stimulus to the development of a theory. We also lack a theory for convective transfer in liquid or gaseous jets issuing into a quiescent medium from an orifice or a packed column. This list of important problems relating to "fundamental" transport processes at a mobile interface is far from complete.

However, the main achievement is that theoretical and experimental studies in recent years have provided a general picture of transport processes at a mobile boundary, and have explained their basic features.

## 4. TURBULENT FLOW

The flow of liquids and gases in practically all chemical reactors and mass-exchange apparatus is turbulent. Hence, the theory of mass transfer and heat transfer in the turbulent regime of flow of liquids and gases is at least as interesting as the theory of transport in the laminar regime. Modern theories of turbulence enable us to arrive to certain quantitative conclusions regarding the transport of mass and heat in a turbulent stream.

The most fully developed theory is that of local isotropic turbulence; the theory of a turbulent stream in the vicinity of a solid surface has been developed to a lesser extent.

The theory of turbulence near a mobile interface is in its initial stages of development. In the region of free turbulence, far from the interface, all the turbulence eddies transfer passive materials (solute, gaseous impurity, or heat). Agitation of the liquid, moving in a region of dimensions $L$, is caused by all eddies with velocities up to $\Delta U_0$ and characteristic length $L$. The effective turbulent diffusion coefficient $L_{\text{eff}} \simeq \chi_{\text{eff}} \simeq \Delta U_0 L$ is so large that the turbulence ensures concentration and temperature constancy over the whole of the volume except for a very thin turbulence boundary layer close to the interface.

Here the scale of the turbulence eddies $l$ decreases according to the law $l \propto y$, and at quite small distances according to the law $l \propto y^2$, where $y$ is the distance to the solid surface. At a distance $\delta_0$ from the solid surface, called the viscous sublayer, the turbulence eddies become so weak that momentum transfer in the liquid occurs by the molecular viscosity mechanism, and turbulence subsides. Nevertheless, the damped turbulence eddies are still able to transport mass and heat. At Prandtl numbers in excess of unity the molecular transfer mechanism begins to predominate over the convective mechanism in a liquid layer of thickness $\delta' \simeq \delta_0/\text{Pr}^{1/4}$, amounting to $10^{-4}$–$10^{-5}$ cm. This extremely thin layer is the diffusion boundary layer, within which is concentrated the major diffusional resistance. The concentration (or temperature) distribution in this layer is effectively linear. Under these conditions the flux is given by the expression[7]

$$j_{\text{turb}} \sim \sqrt{k_f} U_0 \text{Pr}^{-1/4} \Delta\varphi. \tag{16}$$

At low Prandtl numbers the molecular transport mechanism takes over from the convective mechanism in a layer of thickness

$$\delta'' \sim \frac{\delta_0}{\text{Pr}} \gg \delta_0, \tag{17}$$

and therefore[7]

$$j_{\text{turb}} \sim \frac{\sqrt{k_f} U_0 \Delta\varphi}{\ln \frac{L U_0 \sqrt{k_f}}{\nu} + \ln\text{Pr} - A}. \tag{18}$$

Here $\Delta\varphi$ is the concentration or temperature difference between the bulk and the layer of liquid close to the reacting or cooled surface, $k_f$ is the resistance coefficient, a slowly varying function of distance, and $U_0$ is the velocity.

For Prandtl numbers of the order of unity, we can write down interpolation formulae which combine both limiting laws, (16) and (18). These expressions agree satisfactorily with experiment[7,44].

It must be stressed that in a turbulent stream the exposed surface is not uniformly accessible owing to the dependence of $k_f$ on the coordinates, mentioned above. This is true, in particular, for the surface of a disc. The only geometries in which the surface is uniformly accessible are the inner surface of a tube (in the region beyond the inlet section), and the surface of a cylinder rotating about its axis and remote from the walls of the vessel. The resistance coefficient is constant over the entire length of the tube and the entire height of the cylinder. Therefore, what was said above regarding the surface of a disc under laminar flow applies to turbulent flow towards the surface of a tube and of a rotating cylinder.

A theoretical expression for the flow at high Prandtl numbers was derived by the writer for a smooth and a rough tube[7], and more recently for a cylinder.

Turbulent motion at a mobile interface has been investigated in far lesser detail. For the turbulent motion of a gas stream over a liquid surface, we can expect turbulence of an entirely different character to be set up in the gas and in the liquid.

Since the density of the liquid is much greater than that of the gas, turbulence near the liquid interface will be damped in much the same way as near a rough solid surface. This statement is correct if the mean gas velocity is greater than the maximum rate of propagation of the waves (given by $\sqrt[4]{4\sigma g/\rho}$, where $\sigma$ is the surface tension — 24 cm $s^{-1}$ for water). However, we still lack experimental data on the distribution of velocities in the gas close to a liquid surface, and particularly measurements of the mean amplitude as a function of stream velocity. There have been few systematic measurements of resistance coefficients for a gas stream at different depths of liquid layer, surface tensions, etc. These measurements would be very valuable.

Turbulence near a free liquid surface has been studied in fair detail in the context of wind-generated waves in deep liquids. A similar approach is permissible under the conditions encountered in chemical hydrodynamics. By

using the ordinary theory of turbulent transfer in conjunction with the hypothesis as to the scale of the eddies near the free surface

$$l \sim \bar{a} \tag{19}$$

where $\bar{a}$ is the average amplitude of the surface waves, we can obtain an expression for the density of the diffusional flow near the surface:

$$j \sim v_0 \Delta c. \tag{20}$$

Here $v_0$ is the characteristic velocity of the turbulence eddies in the stream, related to the mean flow velocity by the familiar expression

$$v_0 \sim \bar{U} \sqrt{k_f}.$$

The total diffusional flow is of the order of magnitude

$$J = jS$$

where $S = S_0(1 + \bar{a}^2)$ is the true area, and $S_0$ is the nominal area of the liquid surface. Neither the turbulence in the gas phase nor the turbulence in the liquid phase have in fact been studied close to a free boundary by the powerful experimental tools of modern hydrodynamics.

On the subject of the difficulties presented by mass transfer problems near a mobile surface, it may be pertinent to point out that many authors[45,46] have been forced by the complications and lack of understanding of these problems to put forward views not in keeping with modern developments in hydrodynamics. The surface renewal theory is typical of this approach.

In the surface renewal theory the concept of turbulent eddies used in the turbulence theory is replaced by unsubstantiated ideas involving the time of renewal of surface elements with an entirely arbitrary distribution function for these times. These quasi-hydrodynamic theories are almost valueless.

## 5. HOMOGENEOUS–HETEROGENEOUS SYSTEMS

In the study of radical reactions occurring in cracking, pyrolysis, and other reactions in fast moving liquids and gases the most important problem is that of the relations between reactions in the bulk and at the surface. The macrokinetics of such systems have been discussed for the idealised case of an immobile medium[47] or of a medium undergoing laminar flow in a tube[19,48].

The last few years have witnessed the development of a general hydrodynamic theory of the macrokinetics of systems comprising both homogeneous and heterogeneous reactions at very high flow rates (more precisely, streaming at high Reynolds numbers), as is almost invariably the case in practice[49].

Consider a tube in which a turbulent stream of a chemically active medium (liquid or gas) is moving, and assume that chemical reactions accompanied by absorption or evolution of heat are taking place in the bulk. The kinetics of homogeneous reactions are usually described by an expression of the type

$$Q_i = k_i c_i^{n_i} c_j^{n_j} \ldots e^{-E_i/RT}$$

where $Q_i$ is the rate of reaction of the $i$th component in the bulk phase, $c_i$ and $c_j$ are the bulk concentrations of the components, and $E_i$ is the activation energy.

In the presence of homogeneous reactions the convective transport equation becomes non-linear, and accurate analytical solutions cannot be obtained. At the surface of the tube heterogeneous reactions take place, and under steady-state conditions the number of species arriving at the surface from the bulk equals the rate of heterogeneous reactions. Since the kinetics of heterogeneous reactions are also expressed by non-linear laws, the boundary conditions at the surface of the tube are non-linear. At first sight it would appear that a system of non-linear partial differential equations with non-linear boundary conditions is too complex to permit analytical or numerical solution. However, in practice it is possible to apply the ideas of the boundary diffusion layer to this system.

The total flow can be subdivided into the main region and a thin diffusion (or thermal) layer adjacent to the surface. In the main region the turbulent mixing ensures that the distribution of velocities, concentrations, and temperature is close to the average over the cross-section. A significant change in concentration along the tube axis, resulting from chemical reactions, occurs on a scale comparable to the length $L$ of the reactor. If the change occurred over a shorter length one would simply shorten the reactor.

Surface reactions cause an appreciable change in concentration, from $c_S$ at the surface to $c_0$ in the bulk, over the very thin boundary layer $\delta'$.

It is clear, however, that in this thin layer we may ignore longitudinal changes in concentration of the main component at the outer limit of the boundary layer, and therefore we can also ignore the bulk reaction. The concentration change arising from the bulk reaction is significant at distances of the order of $L$, but not of the order of $\delta'$.

By coupling the solutions for the main region and for the boundary layer, we can arrive at the distribution of concentration, temperature, and reaction rate along the reactor.

In two real systems — the pyrolysis of ethane to ethylene and the radical–chain oxidation of hydrocarbons — the overall macrokinetics have been calculated. The rate of the characteristic deposition of side-products has been obtained for the former reaction, and the effect of the surface-to-volume ratio of the reactor has been obtained for the latter reaction.

## 6. STATISTICAL SYSTEMS

In the previous sections we have dealt with some simple "fundamental" mass- and heat-transfer processes. Their main characteristic is a simple and well defined set of geometrical conditions. Furthermore, the flow regimes were assumed to be fixed and uniform over the whole of the system, and random time-changes of regime or spatial variations in the properties of the system were not considered. In practice, one attempts to stir as intensively as possible in order to obtain high rates of transfer. In real situations the process usually occurs in a statistical system, composed of a set of "elementary" objects, rather than on a single object such as a solid reaction surface, a drop, etc. Therefore, in order to construct a physicochemical model of a real process we must, on the one hand, analyse the complex process into its individual stages (or fundamental steps), and, on the other hand, we

must make a particularly careful study of the simple stages, uncomplicated by incidental and random phenomena. We shall illustrate these statements by two examples.

Absorption is a very complicated phenomenon. Yet, it can be separated into a number of stages whose relative contributions to the overall process depend on the particular conditions. We can distinguish the following stages: (1) the gas jet emerges from the nozzle and breaks up; (2) the resulting bubbles are further broken down, or coalesce; (3) motion of individual bubbles; (4) motion of the system of bubbles; (5) mass transfer to a single bubble, taking account of external and internal diffusional resistance; (6) exhaustion of the solution with time; (7) non-uniform radial distribution of gas and liquid; (8) foaming; (9) mass transfer in the bubble walls of the foam.

Some of these stages are adequately characterised at the present time, others are insufficiently understood.

However, some of the stages play an insignificant part under actual process conditions. Thus, the overall process becomes very much simpler if the liquid layer is deep enough, if the proportion of gas is not too large, and if conditions are constant over the cross-section.

The bubbles of different sizes formed by the breaking up of gas jets are further comminuted (if they are coarse) and coalesce (if they are fine) relatively quickly. The main body of bubbles achieves an almost uniform size, and rises at a uniform rate. Their mutual effect can be estimated, and the speed at which they rise can be found[50].

The mass transport for bubbles of a given size and velocity is known; thus, all the above stages can be evaluated, and the operation of a gas bubbler under these conditions can also be evaluated. Obviously, however, the calculation has no meaning for bubblers of different design, which fail to satisfy the above assumptions.

A detailed experimental and theoretical study of all the stages listed above would give an indication of their relative importance in various types of apparatus.

For our second example, we shall consider a tubular reactor containing a granular, immobile layer of catalyst. In this case the fundamental stages are as follows.

1. The kinetics of the process. It is essential to know the overall mechanism, and sometimes also the true, detailed kinetic mechanism of the process, including true kinetic data such as the rate constant, the activation energy, the order of the reaction with respect to concentration, the heat of the reaction.

2. Diffusion and heat-transfer processes within the catalyst particles (as a function of catalyst structure, thermal conductivity, etc.). The effect of these processes on the kinetics.

3. Motion of a liquid or gas through the granular medium, convective diffusion and heat transfer in a porous medium, heat transfer in the catalyst skeleton. The influence of these processes on the kinetics has already been discussed. Convective transfer in a granular medium has not been adequately investigated. The longitudinal diffusion coefficient in a granular medium with stagnant regions has been recently calculated[51] on the basis of quite general assumptions as to the actual properties of the medium.

The radial convective diffusion and thermal conductivity coefficients must be very much smaller than the longitudinal coefficients; their dependence on velocity has been calculated from an unsatisfactory model[52]. Experimental results for $D_{\parallel}$ in porous media are in satisfactory agreement with theory, but $D_{\perp}$ is often found (experimentally) to be slightly dependent on velocity. Other results suggest that $D_{\perp}$ is proportional to $U_0$. The vast majority of the experiments refer to a porous, but not coarse-grained, structure. The large scatter of the values of $D_{\parallel}$ and $D_{\perp}$ obtained from experimental data indicates a dependence on the actual structure, packing density, etc. It must not be forgotten that the overall thermal conductivity of a granular medium includes the convective thermal conductivity and the thermal conductivity of the skeleton. Under these conditions the concentration and temperature distributions will show significant differences. The calculations which have been made up to now make no allowance for the difference between $D_{\parallel}$ and $D_{\perp}$ or for their dependence on velocity. The resulting error is not easy to assess.

4. Transition from a granular structure to a continuous medium. Many workers treat the granular medium filling the reactor as a continuous, porous medium.

In practice, very wide variations in the ratio of grain diameter to tube diameter are encountered. There is a need for more detailed studies as to the nature of the approximations made on going from a granular to a continuous medium: this is particularly important when a laboratory-scale process is transferred to industrial plant. Various models of a granular medium in a reactor with an immobile layer have been put forward: the cellular model[53], the cellular model with stagnant regions[54], the quasi-homogeneous model[55], etc. This in itself is a clear indication of the lack of a universal model applicable to real systems.

5. Simplification of the basic equations for mass and heat transfer in a porous medium within the framework of the quasi-homogeneous model.

6. Calculation of the average temperature distribution along the reactor.

7. Calculation of the stability of the operating conditions of the reactor.

8. Allowance for non-uniform gas flow over the cross-section of the reactor.

As in the previous example, we see that some of these stages have been investigated to a sufficient extent, whilst others are inadequately understood.

In conclusion it should be stressed that the complications of hydrodynamics and of mass- and heat-transfer processes in chemical reactors and mass-exchange apparatus are such that mathematical and experimental studies must be brought to bear on them jointly. The common aim of these studies should be to produce sound physicochemical approximations (models) which would serve as a basis for calculations on processes and apparatus. Calculations on reactors which allow for major factors but ignore second-order factors (usually called mathematical modelling) should always be compared with experiment in order to confirm that the approximations made are compatible with real processes in chemical plant.

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# THE ELECTROCHEMICAL EFFECT OF HIGH COVERAGE

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The inhibition of electrochemical reactions by adsorbed extraneous substances or reaction products is well recognised[1-8]. The basic causes underlying this phenomenon include blocking of the surface by an adsorption film, and the generation of an energy barrier opposing the reduction, through the adsorption of ions or polar molecules. In recent years, the inhibition of an electrochemical reaction by adsorbed reactant has been demonstrated by refined experimental techniques. This effect has been termed[9,10] the high-coverage effect.

Frumkin et al.[9] and Tedoradze and Dzhaparidze[10,11] were the first to compare the degree of coverage of the electrode surface by reactants, determined experimentally, with the rate of the electrochemical process, measured at the same potentials. They reported a decrease in current density with increase in coverage for the catalytic evolution of hydrogen from diphenylamine solutions. A qualitative explanation of the inhibition of the reduction of diphenylammonium ions at coverages of the electrode approaching unity has been given[9].

This article will describe the outward experimental symptoms of the high-coverage effect, and some possible causes. The reduction of organic substances at a mercury electrode, being the simplest case, will be treated in detail.

As long as the coverage of the surface by molecules of a reducible substance is not large, and interactions between these molecules (as well as the effect of adsorbed molecules of the product) can be ignored, the rate $i$ of an

electrochemical reaction is proportional to the surface concentration of the reducible substance ($\Gamma$), and is given to a first approximation by the expression

$$i = nF\Gamma k \exp\left[-\frac{\alpha nF}{RT}(\varphi - \psi_1)\right], \quad (1)$$

where $\varphi$ is the potential of the electrode, $\psi_1$ is the potential at the point in the electrical double layer occupied by the reacting site of the reducible substance, and $k$ is the value of the rate constant at $\varphi - \psi_1 = 0$. However, as Frumkin pointed out[12,13] in 1962, when the surface is largely covered with the reactant entirely different expressions should apply: formula (1), which assumes proportionality between the concentration of the activated complex and that of the reducible substance in its initial adsorbed state, is correct only for low and intermediate coverages of a uniform surface. At high coverages we can expect steric hindrance to oppose transition to the activated complex state, and the variation of the rate of the process with surface concentration may no longer be monotonic. Thus, the orientation of the adsorbate molecules on the surface may vary when the degree of coverage increases[14,15]. If this results in the reactive site of the molecule taking up a position remote from the electrode, we can assume that the formation of the activated complex will involve rotation of the adsorbed molecule on the electrode surface. At high coverages this reorientation can be impeded by neighbouring adsorbate molecules, and the probability of transition of a reacting molecule to the activated state is thereby decreased. However, this explanation of the high-coverage effect is not applicable to some substances. For example, the system of conjugated $\pi$-bonds allows motion of an electron along a molecule of dipyridylethylene, and it is impossible to choose an orientation of the reducible molecule on the electrode surface for which the steric hindrance effect is operative.

Transition to the activated complex state will also be hindered at high coverages if the activated complex occupies a greater area on the electrode surface than the molecule in its original adsorbed state[12,13]. The high-coverage effect observed[16-18] in the reduction of dipyridylethylene on mercury at pH values not far from neutrality appears to be a case in point.

It should be noted that a similar phenomenon has been reported[19-28] in the study of the reactions of organic substances in solution at high pressures: in some cases, formation of the activated complex involves an increase in the volume of the molecule (this is called the negative activation volume), and under these conditions increase in pressure inhibits the reaction. Cases are also known in which the activated complex is formed with a decrease in molecular volume (positive activation volume): the rate constant now increases with increase of pressure. One of the commonest causes of a change in volume by the molecule is identified, in the literature dealing with high-pressure chemistry, with unequal solvation of the initial state and the transition state. A difference in solvation can always be expected if the charge of the activated complex is different from that of the original molecule. In the examples which we shall consider, the volume of the activated complex may be greater than the volume of the adsorbed molecule in the initial state for yet other reasons, such as bond labilisation preceding bond rupture; replacement of a double bond by a single bond also causes an increase in volume, because double bonds are shorter than single bonds.

Phenomena reminiscent of the high-coverage effect can occur when two adsorbed species are involved[29] in the formation of the activated complex. If the difference in the adsorption energy of the two species is large, the surface concentration of the second component will be small at high coverages, and this will decrease the surface concentration of the activated complex and therefore also the rate of the electrochemical process.

The study of the variation of current density with surface concentration of (or coverage of the electrode by) the reducible substance is a direct and reliable method of observing high-coverage effects. To use this method, however, some serious experimental difficulties have to be overcome, because at least two surface-active substances are present on the electrode surface during the passage of Faradaic current, and their relative amounts depend on the duration of electrolysis. The method of differential capacity measurements, which is fairly accurate, gives only the total coverage of the electrode surface in this case. The electrocapillary curve method suffers from the same disadvantage, whereas the charging curve method, by which the surface concentration of reactant can be evaluated, is not accurate enough.

To measure the coverage of the surface by the reactant under conditions of Faradaic current flow through the cell, the differential electrode capacity method can be used if the product of the electrochemical reaction is not adsorbed on the electrode. The catalytic evolution of hydrogen on mercury is a reaction of this type. On the plot of the rate of reduction of the diphenylammonium ion against coverage, the high-coverage effect is shown by a current density maximum[9,11] at a $\Theta$ value close to 0.85. It should be noted that, if the current density–coverage curve goes through a maximum, the current density must also go through a maximum as a function of bulk concentration of the reducible substance. Bagotskii and Vasil'ev[30] have observed this type of variation. However, their maximum could be associated with inhibition of the electrode reaction by preferential adsorption of the reaction product on the electrode surface.

The influence of the reaction product on the rate of the electrode reaction will be minimal if the electrolysis is restricted to very short times and low current densities, so that the amount of product formed is insufficient to cause appreciable blocking of the surface. By constructing a family of plots of current density against surface coverage (or against bulk concentration of the reducible substance) at constant time, the inhibition caused by the reaction product can be separated from the high-coverage effect. These plots are most conveniently made on the basis of experimental $I-t$ curves.

Furthermore, the form of the $I-t$ curves can itself reveal the presence of a high-coverage effect. Thus, if the bulk concentration of the organic material is not very large (in practice, less than $10^{-3}$ M), the degree of coverage of the surface by the reactant reaches a value of the order of unity in a measurable time interval, determined by the diffusion of the organic molecules to the electrode surface [provided of course that the product $Bc$ in the adsorption isotherm equation $Bc = f(\Theta)$, where $B$ is a function of potential only, $c$ is the bulk concentration, and $\Theta$ is the coverage, is large enough to induce such a high coverage]. Therefore, we can expect to find that the reduction will proceed without high-coverage effects at short times, when the coverage is still low. As the lifetime of the drop increases, the surface coverage by the reactant will also

increase, and after a definite time the coverage may be sufficient to display the high-coverage effect. When this happens, the current must begin to fall off (because of the sharp decrease in the rate constant), and a maximum appears on the $I-t$ curve.

However, a maximum on the $I-t$ curve could have quite a different explanation: for example, adsorption of the reaction product, which blocks part of the surface. As shown by Koutecký and by Koryta[31,32], the $I-t$ curves begin to fall off due to this blocking effect at surface coverages of the order of 0.8–1 if the rate constant is large enough. If the fall of the $I-t$ curve due to adsorption of the reaction product is assumed to set in at that exact coverage of the electrode surface, the quantity of electricity $q_{max}$ which passes through the electrode up to the moment when the curve begins to fall off must be constant. The value of $q_{max}$ should be approximately equal to $nF\Gamma_\infty$, or larger than this quantity, since formation of the reaction product is invariably accompanied by desorption of the product into the solution: this is because the concentration of the product in the region adjacent to the electrode is close to zero.

If we increase the bulk concentration of the organic compound, the current at constant potential and constant time increases. Therefore the time corresponding to the maximum on the $I-t$ curve ($\tau_{max}$) will decrease, but $q_{max}$ will be practically unaffected by the bulk concentration of the reactant. The changes in potential of the electrode at constant bulk concentration lead to the same result. In this case an increase in potential causes an increase in current, but the value of $q_{max}$ remains independent of potential. However, the latter (and experimentally simpler) method is applicable only over a narrow range of potentials close to the potential of maximum adsorption of the reaction product. As we approach the potential of the desorption peak, $q_{max}$ and $\tau_{max}$ begin to increase rapidly because of the faster desorption of the products from the electrode. Thus, in order to eliminate the effect of the reaction product on the rate of the electrode process, it is enough to arrange for the measurements to be completed in times much shorter than $\tau_{max}$. The approximate constancy of $q_{max}$ with change of potential, for the fall in the curve induced by reaction products, was demonstrated by Levinson in her investigation of the reduction of $\alpha\alpha\alpha\omega$-tetrachloroalkanes (Fig. 1).

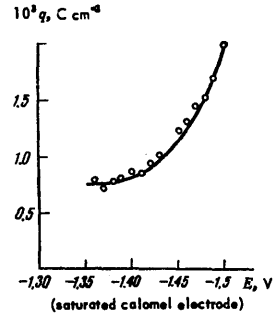



Fig. 1. Potential variation of the quantity of electricity passing through the electrode up to the onset of the fall of current in the reduction of $\alpha\alpha\alpha\omega$-tetrachlorononane; solution composition: 0.0031 M $CCl_3(CH_2)_7CH_2Cl$ + 70% $CH_3OH$ + + 0.25 M $Cs_2CO_3$; from data of I. M. Levison.

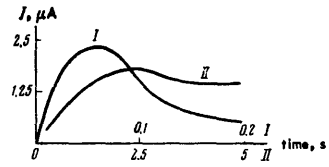



Fig. 2. Variation of the current with time in the reduction of dipyridylethylene; potential -0.83 V (s.c.e.); pH 5; concentration of reactant $2 \times 10^{-3}$ M; from Ref. 18.

In the high-coverage effect, on the other hand, if concentration polarisation is small, the instant when the current begins to fall off (at constant bulk concentration and near the potential of the adsorption maximum of the reactant) is independent of the current, since it is determined by entirely different factors. Provided $Bc$ is large enough, $\tau_{max}$ is independent of potential, and the value of $q_{max}$ increases as the electrode potential increases, but if the currents are much smaller than the limiting diffusion current $q_{max}$ can be significantly lower than $nF\Gamma_\infty$. Current falls of this type are found in the reduction of dipyridylethylene on mercury in aqueous solutions[17,18]. Curve *1* of Fig. 2 shows that $4 \times 10^{-5}$ C cm$^{-2}$ (including the charging current) have passed through the electrode up to the onset of current fall. Therefore, the whole of the reaction product can block no more than one-half of the electrode surface (assuming that the product takes up 46 Å$^2$ of the surface, i.e. the same area as the reducible compound[18]). We conclude that the current fall on the $I-t$ curve arises from the high-coverage effect.

In the case of the high-coverage effect, the value of $q_{max}$ should decrease with increase in the concentration of reactant. If the rate of adsorption of the organic compound is determined by the rate of diffusion to the dropping mercury electrode[33,34], the following equation will apply

$$0.74c\frac{\sqrt{D\tau_{max}}}{\Gamma_\infty}\left(1+3.4\frac{\sqrt{D\tau^{1/6}_{max}}}{\sqrt[3]{m}}\right)\geqslant 1,$$

where $D$ is the diffusion coefficient, and $m$ is the mercury flow rate, derived from the well-known Koutecký equation[35].

The polarograms and polarisation curves of systems showing the high-coverage effect have a characteristic asymmetric shape, with an abrupt transition to the limiting diffusion current (Fig. 3). Thus, in the reduction of

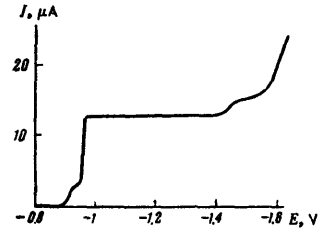



Fig. 3. Polarogram for the reduction of dipyridylethylene in aqueous solution of pH 6.7; concentration of reactant $2 \times 10^{-3}$ M; from Ref. 18.

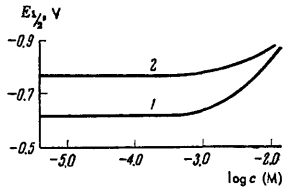



Fig. 4. Variation of the half-wave potential for the reduction of di(methoxycarbonylmethyl)mercury [$Hg(CH_2COOCH_3)_2$] with the logarithm of bulk concentration in 50% methanol.
1) 0.1 *N* $KNO_3$; 2) 0.1 *N* $NaOCOC_6H_5$; temperature 25°; from Ref. 37.

dipyridylethylene, the current increases by a factor of 4 over a range of 7 mV. If the surface concentration is decreased by making the solution more dilute with respect to the reducible substance or by adding an organic solvent, the wave reverts to the normal, symmetrical shape, and the half-wave potential shifts in the positive direction. In the reduction of di(methoxycarbonylmethyl)mercury, Butin et al.[37] observed a rather large (about 200 mV) positive displacement of the half-wave potential upon lowering the bulk concentration of the reducible compound from 0.02 to 0.001 M. At still lower bulk concentrations the half-wave potential becomes insensitive to concentration (Fig. 4).

However, we must stress that neither an asymmetric polarogram nor an increase in rate with dilution of the solution can be taken as sufficient criteria for the recognition of the high-coverage effect. According to Feoktistov, if the coverage of the electrode surface by the reactant is high at the half-wave potential, this potential for the reduction reaction suffers a negative shift even in the absence of the high-coverage effect. The maximum value of this shift is given by the formula

$$\Delta\varphi_{1/2} = \frac{RT}{\alpha nF} \ln c,$$

where $c$ is the bulk concentration of the organic substance. The reaction products can also give rise to similar effects.

Thus, Laviron† [16] suggested, from the shape of the polarogram and of the $I-t$ curves, that auto-inhibition of the electrode process by the reducible substance occurs in the reduction of dipyridylethylene, but he did not discuss the physical significance of this term. A more detailed examination of this process[17,18] showed that if the time of electrolysis on each drop exceeds 1 sec, as was the case in the work of Laviron[16], inhibition of the reduction of dipyridylethylene by the reaction product takes place (Fig. 3). Adsorption of the reaction products is responsible for the preliminary wave in the reduction of dipyridylethylene[18]. The genuine high-coverage effect is observed on the polarisation curves measured[17,18] with shorter electrolysis times (Fig. 11, see below).

The high-coverage effect is most clearly revealed by galvanostatic measurements. If the bulk concentration of reducible material is not large, but the density of polarising current is appreciable, we can ignore the diffusion of reactant from the bulk during the measurement, and the shape of the potential–time curve (ignoring the double-layer charging current) is described by Eqn. (1). For galvanostatic measurements, this equation is conveniently written in the form

$$\varphi = \psi_1 - \frac{RT}{\alpha nF} \ln i + \frac{RT}{\alpha nF} \ln nF k\Gamma = \varphi_0 + \frac{2{,}3\,RT}{\alpha nF} \log k \frac{\tau - t}{\tau_1}, \qquad (2)$$

where $t$ is the electrolysis time, $\tau$ is the transition time, $\tau_1$ is the value of the transition time when $\Gamma = \Gamma_\infty$, $i$ is the polarising current density, and $\varphi_0$ is a constant depending on $i$. If the reduction is preceded by chemical reaction, e.g. protonation of the reducible substance in the adsorbed state, the variation of potential with time becomes more complicated[17], but in any case the potential of the electrode (in the absence of the high-coverage effect) drifts monotonically towards more negative values as the surface concentration decreases during the course of electrolysis. As was stated at the beginning of this article, the high-coverage effect can be so large that the product $k\Gamma$ increases as $\Gamma$ decreases at high coverages. In the galvanostatic regime this causes a drop of potential with time at short times, thus explaining the appearance of a maximum on the potential–time curve. Curves of this type were first reported and discussed by Zolotovitskii and the present writers[17].

The phenomenon was described mathematically[17] by assuming, as a first approximation, that over a given range of surface concentrations the rate of electron transfer decreases linearly with increasing coverage. This type of variation of current density with coverage corresponds to the following empirical formula for the electron transfer rate constant[9,11]:

$$nF\Gamma_\infty k = \frac{k'}{\theta} - k''. \qquad (3)$$

Here $k'$ and $k''$ are constants. Fig. 5 shows theoretical curves of electrode potential against electrolysis time calculated on the assumption that over a range of coverages the rate constant varies as required by Eqn. (3), but at low enough coverages this quantity becomes truly constant.

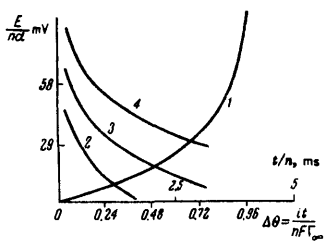



Fig. 5. Variation of electrode potential (relative to $\varphi = -\frac{0{,}058}{\alpha n} \log i$) with normalised time $\Delta\theta = \frac{it}{nF\Gamma_\infty}$ at $i = 3 \times 10^{-4}$ A cm$^{-2}$, $\alpha n = 1$, $\Gamma_\infty = 5 \times 10^{-10}$ mole cm$^{-2}$:
1) no high-coverage effect, $nF\Gamma_\infty k = 10^{-5}$ A cm$^{-2}$; [2)–4) under the conditions of the high-coverage effect the rate constant varies with coverage according to formula (3)] 2) $k' = 2.24 \times 10^{-5}$, $k'' = 2.17 \times 10^{-5}$; 3) $k' = 1 \times 10^{-5}$, $k'' = 0.97 \times 10^{-5}$; 4) $k' = 4.45 \times 10^{-6}$, $k'' = 4.31 \times 10^{-6}$ A cm$^{-2}$; from Ref. 17.

† Presumably this work is described by Tedoradze in Ref. 16, since Laviron is not mentioned in Ref. 16 (Ed. of Translation).

The disappearance of the high-coverage effect coincides with the transition from curves *2–4* to curve *1*. Irrespective of how accurately the high-coverage effect is described by the empirical formula (3), a minimum on the potential–time curve is a sufficient criterion for the existence of this effect.

In order to demonstrate the high-coverage effect with the aid of charging curves, the measurements must be made under conditions such that diffusion of the reactant to the electrode can be ignored. Otherwise, a potential minimum could arise from a trivial cause: the tangential motion of the mercury surface. We have observed this phenomenon in practically every system examined.

Charging curves with a potential minimum due to the high-coverage effect have been observed in the reduction at a mercury electrode of dipyridylethylene[17,18] (Fig. 6), ethyl bromoacetate and bromobutyrate, and di(methoxycarbonylmethyl)mercury[38].

We have found in the literature a number of charging curves showing a potential minimum, but nowhere was the cause of the phenomenon discussed[39-41].

A paper by Lorenz and Schmalz[39] describes the charging curves of eosin. Fig. 7 shows that the charging curve obtained for prepolarisation at a potential corresponding to a coverage close to the limiting value has a clear minimum, which disappears (as in the reduction of dipyridylethylene discussed above) if the electrode is previously held at a potential for which the coverage is less than unity. The transition times are so small in this case that the potential minimum cannot possibly be associated with the polarographic maximum.

Similar effects have been observed in the reduction at a mercury electrode of developers for colour photography[40] and in the reduction of hydroxylamine at a platinum electrode[41] previously activated at a potential of +0.1 V (normal calomel electrode). It should be noted that the adsorption of hydroxylamine on anodically oxidised platinum is insignificant. The potential minimum on the charging curve also disappears if the electrode is passive.

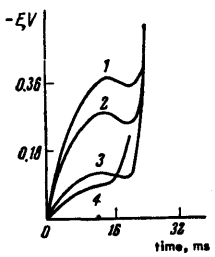



Fig. 6. Charging curves for dipyridylethylene after holding the electrode at various potentials (the zero of each curve is taken as the previous holding potential). Holding potentials: 1) -0.6; 2) -0.7; 3) -0.9; 4) -0.92 V (s.c.e.); polarising current density 10 mA cm$^{-2}$; from Ref. 18. Prior polarisation at the potential of incipient desorption of dipyridylethylene shortens the transition time and removes the fall of potential on the charging curve.

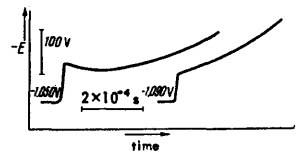



Fig. 7. Cathodic charging curve for eosin at a current density of 40 mA cm$^{-2}$; the numerals denote the prior polarisation potential; potential of incipient desorption of eosin -1.05 V; from Ref. 39.

We shall now briefly describe the electrochemical behaviour of various systems in which the high-coverage effect has been observed.

Diphenylamine[9-11]. When mercury is cathodically polarised in acid solutions of diphenylamine, the diphenylammonium cations formed by protonation of diphenylamine (B) are reduced:

$$B + H^+ \rightarrow BH^+; \quad BH^+ + e \rightarrow BH.$$

The unstable BH radicals decompose with formation of diphenylamine and molecular hydrogen:

$$2\,BH \rightarrow 2B + H_2.$$

Thus, the only product of the electrolysis of diphenylamine solutions is molecular hydrogen, which has no effect on the differential capacity of the mercury electrode[42]. The coverage of the electrode surface by diphenylamine was therefore measured from the change in differential capacity of the mercury electrode in the presence of a surface-active material. Polarisation curves for the discharge of diphenylammonium ions at various concentrations of diphenylamine are shown in Fig. 8, whence it can be seen that the overvoltage for hydrogen evolution at low current densities at first decreases and then increases with increase of catalyst concentration. The variation of current density with electrode coverage is different in 0.2 *N* and 1 *N* HCl solutions of diphenylamine. In 0.2 *N* HCl and at coverages below 0.9 (curve *b* of Fig. 9) the current density varies approximately linearly with the coverage of the electrode surface by the catalyst. At still higher coverages the rate of the reduction process falls off.

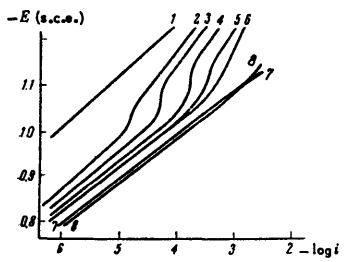



Fig. 8. Polarisation curves for the solutions 1 M HCl + $x$ M $(C_6H_5)_2NH$: 1) $x = 0$; 2) $x = 4.85 \times 10^{-5}$; 3) $x = 9.6 \times 10^{-5}$; 4) $x = 1.33 \times 10^{-4}$; 5) $x = 2.66 \times 10^{-4}$; 6) $x = 3.6 \times 10^{-4}$; 7) $x = 1.48 \times 10^{-3}$; 8) $x = 1.9 \times 10^{-3}$; from Ref. 9.

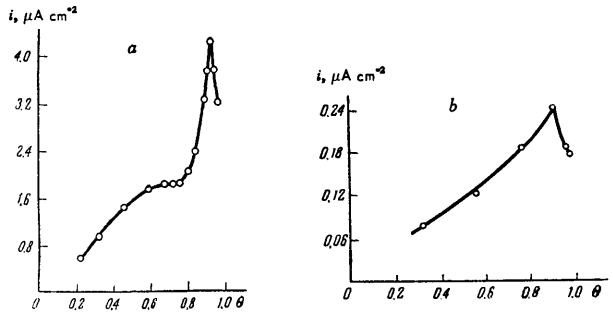



Fig. 9. Variation of the rate of electrochemical reaction with coverage of the mercury surface by an equilibrium mixture of diphenylamine and diphenylammonium ions at a potential of -0.8 V (s.c.e.); curve *a* was obtained in 1 M HCl, curve *b* in 0.2 M HCl; from Ref. 11.

In 1 *N* HCl the approximately linear variation of current density for reduction of the diphenylammonium ion with coverage of the electrode surface by catalyst holds only up to $\Theta < 0.5$. At higher coverages the current density is at first independent of coverage and then shows a steep rise. For $\Theta$ values close to 0.9 the current density (as in the case of 0.2 *N* HCl) suffers an appreciable drop with increase of surface coverage of the electrode by diphenylamine. The complicated shape of this plot has been qualitatively explained by invoking blocking of the electrode surface by electrochemically inactive diphenylamine molecules. However, it is impossible to explain the fall in current at high coverages, whether in 0.2 *N* or in 1 *N* HCl, in terms of blocking. The reasons are as follows.

Measurements of the differential capacity of the electrical double layer give only the degree of coverage of the electrode by the equilibrium mixture of diphenylamine and diphenylammonium. In 0.2 *N* HCl the adsorption layer consists almost entirely of molecules of diphenylamine. In 1 *N* HCl the proportion of diphenylammonium in the adsorption layer becomes much greater. Therefore, inhibition of the process through surface blocking by diphenylamine molecules should be less pronounced in the latter case, or else it should set in at higher coverages, but neither of these effects is found in practice (see Fig. 9).

Dipyridylethylene in water–alcohol mixtures is reduced reversibly, according to Volke and Holubek's polarographic data[43], by addition of two electrons and two protons:

$$\text{Py—CH=CH—Py} + 2e + 2H^+ \longrightarrow \text{Py—CH}_2\text{—CH}_2\text{—Py},$$

where Py is a pyridine ring.

Measurements of Faradaic impedance[18] show that in aqueous solution at pH ≤ 2 the reduction is likewise reversible. Essentially, at pH ≤ 2 dipyridylethylene exists in solution and is reduced in a weakly adsorbed protonated form, whereas at pH > 9 it exists in solution and on the surface exclusively as readily adsorbed, unprotonated molecules, and protonation is not one of the potential-determining stages. Between pH 4 and pH 9 both the protonated and the unprotonated forms exist in solution, but the mercury surface is covered only with unprotonated molecules, owing to the large difference in adsorbability between the two forms. However, despite the fact that under these conditions the dipyridylethylene is adsorbed mostly in the unprotonated form, it is the protonated species which undergo reduction (the half-wave potential is a function of pH). This is the region of pH in which the high-coverage effect can be observed on the polarograms, on the current–time curves, and on the charging curves (Figs. 3 and 6) if the surface concentration of reducible material exceeds $3 \times 10^{-10}$ mole cm$^{-2}$. On decreasing the surface concentration by diluting the solution or by adding ethanol (up to 50 wt.%), the high-coverage effect was removed (Fig. 10).

It should be noted that a similar phenomenon is observed also in the reduction of diphenylammonium ions in 0.2 *N* HCl: a negative shift of the potential causes partial desorption of diphenylamine molecules and makes the relation between $\log i$ and the potential deviate from linearity in the sense of accelerating the process[44].

Ethyl bromoacetate and α-bromobutyrate are reduced irreversibly without prior protonation by addition of two electrons and one proton and splitting off a molecule of bromine. The high-coverage effect was detected in both compounds by the charging-curve method at $\Gamma > 2 \times 10^{-10}$ mole × × cm$^{-2}$; for the second compound the effect disappears at $\Gamma < 1 \times 10^{-10}$ mole cm$^{-2}$. However, studies of the variation of current (at constant potential and electrolysis time) with bulk concentration have made it clear, in both cases, that, when the charging curve indicates a surface concentration of reactant close to the limiting value, and the high-coverage effect operates, the current density remains proportional to the bulk concentration of reactant. Further increase in bulk concentration causes some deviation from linearity in the relation between current density and bulk concentration, but no maximum has been observed on this curve. We have concluded[38] that under conditions of constant-potential electrolysis (before plotting the charging curve) there is an accumulation of an intermediate (or side-product) of the reduction of bromoalkanoic acids at the electrode, this product being highly surface-active. Therefore the shape of the charging curve is determined by the adsorption of this intermediate. Since these products could be the corresponding organomercury compounds, we examined the charging curve of di(methoxycarbonylmethyl)mercury and methoxycarbonylmethylmercury bromide under conditions similar to those used for the esters of the bromoalkanoic acids. Clearly defined minima, indicative of the high-coverage effect, were observed on the charging curves of the symmetrical organomercury compound at $\Gamma = 2.5 \times 10^{-10}$ mole cm$^{-2}$.

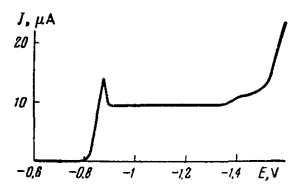



Fig. 10. Polarogram for the reduction of dipyridylethylene in 50 wt.% ethanol; pH 6.7; concentration of dipyridylethylene $2 \times 10^{-3}$ M; from Ref. 18.

Zhdanov and Pozdeeva[45] found a high-coverage effect in the reduction of the 1,2-diphenyl-3-hydroxycyclopropenyl cation, which undergoes one-electron reduction in the first wave. The radicals formed by the electrode reaction disappear from the solution by two competing reactions: dimerisation, or decomposition to diphenylcyclopropenone and hydrogen. The half-wave potential of this wave moves towards more negative potentials upon increasing the concentration of diphenylcyclopropenone in solution. The shift can amount to 400 mV in 5 : 30 ethanol for concentrations between $10^{-5}$ and $10^{-4}$ M. Solutions which are dilute in ethanol show a sudden increase in current before the limiting current is reached. On the current–time curves corresponding to the first wave we find a falling off of the current before a quantity of electricity sufficient to give rise to surface blocking has passed through the electrode: therefore, the fall of current can only be ascribed to the high-coverage effect[45].

Phenomena interpreted as high-coverage effects have been observed also in the study of anodic reactions on platinum by Bagotskii and Vasil'ev[30], Hira Lal et al.[46], Podlovchenko and Iofa[47], Petrii et al.[48], Podlovchenko et al.[49], and Khazova et al.[50] (see Fig. 11). Some other results[29,51] also justify the conclusion that the high-coverage effect was operative.

Lastly, it may not be out of place to mention the results of a study[52] of the electrochemical behaviour of cobalt complexes on platinum. Anson found[52] that the oxidation process is accelerated when chloride, bromide, and iodide ions, and also pentanol (which is readily adsorbed on platinum[53]), are added to an aqueous solution of a divalent cobalt complex ($CoY^{2-}$, where Y is ethylenediamine tetraacetic acid). Special experiments having shown that chemical reaction between the reactant and the additives could not account for this effect, the author[53] suggested that the cause lay in adsorption of the additive, and consequent desorption of the reactant from the electrode.

In fact, if we plot the product $i\tau$ against $1/i$ from Anson's experimental results[52] (Fig. 12), we find that, when iodide ions are present in a solution of $CoY^-$, the graph goes through the origin, which shows that the cobalt complex is not adsorbed. If iodide ions are not added to the solution of $CoY^-$, the graph yields an intercept on the ordinate axis corresponding to the quantity of electricity needed to remove the adsorbed chelate. However, the surface concentration of the complex cannot be calculated in this way because the true surface area of the electrode is not quoted in the original paper[52]. The plots of $i\tau$ against $1/i$ for

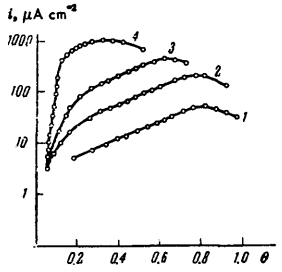



Fig. 11. Variation of the rate of oxidation of methanol on platinum with degree of coverage; from Ref. 50.

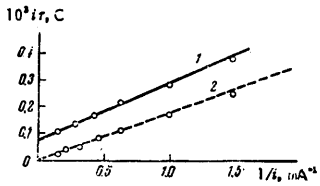



Fig. 12. Variation of the product $i\tau$ (where $\tau$ is the transition time) with $1/i$ for the reduction of cobalt(III) ethylenediaminetetraacetate on platinum:
1) in the absence of iodide ions; 2) in the presence of $10^{-4}$ M KI; concentration of complex $13.3 \times 10^{-3}$ M; phosphate buffer (pH 7); from Ref. 52.

the oxidation of $CoY^{2-}$ in the presence and in the absence of surface-active additives are similar to those for $CoY^-$.

Although this paper does not give the short-time charging curves for cobalt chelates, it would appear that high-coverage effects are present, and are neutralised by surface-active additives.

We may conclude that the study of the high-coverage effect is still in its early stages. In some cases, a choice between the various possible causes of the effect can be made on the basis of the structure of the reacting molecule. The most important requirements now are additional experimental information on the high-coverage effect and new criteria on which to base an unambiguous choice between possible alternative mechanisms. Studies of the influence of temperature and of the nature of the metal are a promising long-term approach.

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# ANIONHALOGENATES OF THE ALKALI METALS AND AMMONIUM

B. D. Stepin, V. E. Plyushchev, and A. A. Fakeev

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## I. INTRODUCTION

Anionhalogenates is the name given to complexes of the type $M[X'_nX''_mX'''_k]$, where $M^+$ is the cation of an alkali metal, ammonium, or thallium(I) or the singly-charged cation of an organic base, and $X_j^i$ represents various halogens constituting a complex singly-charged anion†. Usually $n + m + k = 3$, 5, 7, or 9. Anionhalogenates containing four different halogens are unknown.

† In some instances doubly- and triply-charged metal ions can be the cations.

These complexes are often called polyhalide compounds (polyhalogenides), which is not completely accurate, as the latter could also include some polynuclear compounds, for example $K_2[Mo_3Cl_4Br_4].2H_2O$, $Ta_6Br_{14}.7H_2O$, etc. Cationhalogenates (not considered in the present review) are also known; they include a small number of complexes with the general formula $[X'_nX''_m]MX'''_k$, where M = Sb, Bi, Nb, Ta, Ti, and a few other elements, $X'''_k$ is fluorine or chlorine, and $X'_n$ and $X''_m$ are different halogens.

The terminology we have suggested is not completely new. Zintl and Kaiser[1] recommended that compounds of the alkali metals with the elements occupying the four nearest places before each of the noble gases in the Long Periods should be called "polyanion salts". Fialkov[2] also classified polyhalides into cationic and anionic complexes, emphasising that the latter "have much in common with the halogeno-salts which are formed by other non-metallic and multivalent elements", but Grinberg[3] considers it more correct to term, for example, compounds of the type $M[ICl_4]$ tetrachloroiodates.

It is characteristic of anionhalogenates that their complex anion is entirely constructed from halogens with iodine or bromine most often as the central atom. In ions containing different halogens, the more electronegative (the lightest) halogens always are coordinated around the less electronegative (heavier) halogen, which is located at the centre of the complex anion.

It is thought[2] that the formation by any substance of complexes of anionic or cationic type depends considerably on the ability of this substance to show either donor or acceptor properties with respect to the halogens. Thus in reacting with antimony pentafluoride, bromine trifluoride is a donor of fluorine and therefore gives a cationic complex $[BrF_2]^+$ in the compound $[BrF_2][SbF_6]$; however, in reacting with potassium fluoride bromide trifluoride behaves as an acceptor of fluorine, by forming the anionic complex $[BrF_4]^-$ in potassium tetrafluorobromate $K[BrF_4]$.

As Wells and Wheeler[4,5] have already proposed, anionhalogenates are classified according to the number of atoms

of halogens in the molecule of the compound, into trihalogenides, pentahalogenides, etc. Such a formal classification is scarcely justified, since it does not reflect the physicochemical and structural features of the anionhalogenates. We consider it more correct, in conformity with Werner's views[6], to divide the anionhalogenates into two large groups: the isopolyhalogenates (in Werner's terminology, "pure polyhalogenides") and heteropolyhalogenates (in Werner's terminology, "mixed polyhalogenides"). In the last group, taking into account stereochemical data, it is desirable to distinguish between heteropolyhalogenates with a linear anion and heteropolyhalogenates with a square planar anion.

Anionhalogenates are not just of purely scientific interest; they are beginning to find ever-increasing use, both in the technology of the separation of alkali metals with very similar properties, and also in the preparation of extremely pure rubidium and caesium salts[7-14].

## II. GENERAL CHARACTERISTICS OF ANIONHALOGENATES

The anionhalogenates are a class of complexes whose stability in the solid state and in solution is greatly determined by the polarisation interaction of the ions and molecules, and consequently by the dimensions and charge of both the outer-sphere cation and the central atom. It is known, for example, that small cations (lithium and sodium), which are surrounded by an electric field of rather considerable potential, coordinate the most electronegative ligands of the complex anion, thus destroying the latter. Therefore all the attempts to isolate from solution anhydrous anionhalogenates of lithium and sodium were unsuccessful and yielded only the simple halides of these metals. For the same reason, anionhalogenates with doubly-charged‡ (and especially triply-charged) cations are almost unknown. Multicharged ions can here only enter into the composition of anionhalogenate molecules when they are capable of forming large complex cations, for example, $[Be(H_2O)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$, etc., which exhibit low polarising power and therefore have little effect on the coordination of the ligands in the complex anion. Thus Ephraim and Mosimann[17] prepared $[Co(NH_3)_6][I(I)_2]_3$ and salts of tetrachloroiodic acid with beryllium(II), zinc(II), manganese(II), cobalt(II), nickel(II) and the alkaline earth metals with the general formula $[M(H_2O)_6][ICl_4]_2$.[18,19] For this reason when lithium and sodium form anionhalogenates it is always with molecules of solvent, which stabilise the complex owing to the decrease in the energy of interaction of the cation with one of the ligands.

The thermal stability (see Table 1) of the anionhalogenates of a single alkali metal is determined by the nature of the complex anions. The alkali metal diiodoiodates and dibromoiodates have the greatest thermal stability. The thermal stability of the anionhalogenates is also determined by the size of the outer-sphere cation (see Table 1): it increases with the radius of the cation and therefore the caesium salts are the most stable of the alkali metal anionhalogenates. From the standpoint of the electrostatic theory the thermal stability of the anionhalogenates is the greater, the weaker the electric field of the cation, that is, the less its ability towards counterpolarisation, which weakens the chemical bond between the halogen atoms[3].

‡ With the exception[15,16] of $Ba[IF_4]_2$ and $Ba[BrF_4]_2$.

TABLE 1. Dissociation pressures of anionhalogenates, mmHg.

| Compound | Temperature, °C | | | | | Reference |
|---|---|---|---|---|---|---|
| | 25 | 50 | 100 | 150 | 200 | |
| $K[I(I_2)]$ | — | — | 115 | 450 | — | 20 |
| $(NH_4)[I(I_2)]$ | $1.6\cdot10^{-3}$ | — | — | 760(146°) | — | 21,22 |
| $Rb[I(I_2)]$ | — | — | 2.97 | 38.9(160°) | 172.4 | 20,23 |
| $Cs[I(I_2)]$ | $7.4\cdot10^{-3}$ | — | — | 12 | 126 | 20,24 |
| $K[ICl_4]$ | 1.3 | 6.0 | 186.6 | — | — | 25,26 |
| $(NH_4)[ICl_4]$ | — | 9.8 | 35.2 | 51.2 | 60.3 | 26 |
| $Rb[ICl_4]$ | — | 5.3 | 22.6 | 43.4 | 54.8 | 26 |
| $K[IBr_2]$ | 2.5 | 5.5 | 19(80°) | — | — | 27,28 |
| $[K(H_2O)][IBr_2]$ | 11 | 31 | 232 | — | — | 28,29 |
| $(NH_4)[IBr_2]$ | — | 6 | 45 | 387 | — | 20 |
| $Rb[IBr_2]$ | — | — | 33 | 248 | 760(186°) | 20 |
| $Cs[IBr_2]$ | — | — | — | 39 | 203 | 20 |
| $[K(H_2O)][ICl_2]$ | 12 | 48 | 276 | 704(136°) | — | 20,27 |
| $Rb[ICl_2]$ | — | — | 96.5 | 507 | — | 20 |
| $Cs[ICl_2]$ | — | — | 24(112°) | 114 | 563<br>760(209°) | 20 |
| $K[I(BrCl)]$ | 13.5 | 48 | 166(79°) | — | — | 27 |
| $Cs[I(IBr_2)]$ | $4.8\cdot10^{-3}$ (6°) | — | — | 290(172°) | 655 | 20,30 |
| $(NH_4)[Br(Br_3)]$ | 7 | 32 | — | — | — | 20,31 |
| $Rb[Br(Br_3)]$ | 7(35°) | 18 | 565 | — | — | 20,32 |
| $Cs[Br(Br_3)]$ | — | — | 132 | 760(148°) | — | 20 |
| $(NH_4)[BrCl_2]$ | 105 | 484 | — | — | — | 20 |
| $Rb[BrCl_2]$ | 27 | 60 | 760(93°) | — | — | 20 |
| $Cs[BrCl_2]$ | — | — | 132 | 760(138°) | — | 20 |
| $Rb[Br(BrCl)]$ | 39 | 80 | 760(81°) | — | — | 20 |
| $Cs[Br(BrCl)]$ | — | 15(54°) | 270 | 760(124°) | — | 20 |

This partly explains why complicated complex anions such as $[I(I_2)_4]^-$, $[Br(Br_2)_2]^-$, $[I(I_3Cl)]^-$, $[I(I_5Br)]^-$, etc. are unstable in aqueous solutions of caesium halides but comparatively readily form stable, well-crystallising compounds with large singly-charged organic cations, for example, tetramethylammonium and trimethylphenylammonium. Symmetrically constructed anionhalogenate complex ions with iodine as the central atom are always the most stable (see Table 1). We must note in passing that Ephraim's results[20] on the thermal stability of many anionhalogenates are rather too high owing to the imperfections of the method used. All the alkali metal anionhalogenates decompose on heating close to the melting point but when heated in a sealed capillary they melt at quite definite temperatures.

In aqueous solutions the anionhalogenates undergo complex transformations[33-35]. At first the compound dissociates:

$$Rb[IBr_2] \rightleftharpoons Rb^+ + [IBr_2]^-.$$

Then the complex anion decomposes into its original components:

$$[IBr_2]^- \rightleftharpoons IBr + Br^-.$$

After this, the interhalogen compound formed undergoes hydrolysis:

$$IBr + H_2O \rightleftharpoons IOH + H^+ + Br^-;$$
$$5IOH \rightleftharpoons 2I_2 + IO_3^- + H^+ + 2H_2O.$$

From the increase in the degree of hydrolysis at 25° in 0.05 M aqueous solutions, the complex anions can be arranged in the following series:

$$[ICl_4]^- < [IBr_2]^- < [I(BrCl)]^- < [ICl_2]^-.$$

Moderately concentrated aqueous solutions of anionhalogenates which contain iodine show a strong acid reaction, although it is impossible to detect the liberation of elemental iodine even by spectrophotometry. Evidently here the hydrolysis of the interhalogen compound stops at

the stage of formation of hypoiodous acid, which is stabilised under certain conditions by the addition of a neutral molecule of an interhalogen compound, for example, IOH.IBr.

The hydrolysis is accelerated when the pH is increased and in alkaline solutions it goes to completion, with formation of the corresponding halide, iodate, and iodine (or iodide)[2]. The hydrolysis is suppressed by the introduction into the solution of acids, halogens, iodates, or halides of the alkali metals.

A point worth remembering is that in aqueous solutions some anionhalogenates also undergo partial disproportionation:

$$2Cs[I(BrCl)] \rightleftharpoons Cs[IBr_2] + Cs[ICl_2].$$

The solvolytic reactions of anionhalogenates have been little studied and the above facts really exhaust all our present knowledge in this field.

The theory of the absorption spectra of the anionhalogenates which is now being developed allows for the use of the $p$-orbitals of iodine and bromine central atoms in forming bonds[28,36-38]. The position of the absorption bands of the anionhalogenates is almost independent of the outer-sphere cation and solvent and depends mainly on the corresponding energy transitions characteristic of the type of chemical bond involved. Spectrophotometric investigations[39-48] of various solutions of diiodoiodates indicate that the chromophoric group $I^+-I^-$ corresponds to two absorption bands, at 290 and 360 m$\mu$. The chromophoric group $Br^+-Br^-$ in dibromobromates characterises the absorption bands at 265 and 395 m$\mu$,[40,42,49] and the $I^+-Br^-$ chromophoric group in dibromoiodates corresponds to absorption bands[40,42] at 256 and 380 m$\mu$. Analogously, the $I^+-Cl^-$ bonds in dichloroiodates have absorption bands at 227 and 340 m$\mu$,[40,42,50-52] and the $Br^+-Cl^-$ bonds in dichlorobromates absorption bands at 254 and 385 m$\mu$.[42] In its energy transitions the $Br^+-Cl^-$ bond appears to be close to the $I^+-Br^-$ bond. The successive replacement of the ligands (iodine atoms) in diiodoiodates by bromine and chlorine leads to a displacement of the absorption band at 290 m$\mu$ to shorter wavelengths.

The absorption spectra of anionhalogenates with two different ligands usually show absorption bands corresponding to a few chromophoric groups. For example, water-alcohol solutions of bromochloroiodates have absorption bands at 220, 255, and 455 m$\mu$;[53] in other solvents, the absorption band characteristic of the $I^+-Cl^-$ chromophoric group can be displaced to 237 m$\mu$,[40] and sometimes there is superposition of the absorption bands of the $I^+-Cl^-$ and $I^+-Br^-$ chromophoric groups and the formation of an inflection at 230-250 m$\mu$.[42] In trifluoroacetic acid the absorption band of tetramethylammonium bromochloroiodate, for example, is at 486 m$\mu$.[54] The absorption spectra of the iodochloroiodates show all the frequencies characteristic of both the $I^+-I^-$ and the $I^+-Cl^-$ bonds[40,42,51]. A somewhat different absorption spectrum is observed for bromochlorobromates and iodobromoiodates, where perturbations in the $Br^+-Br^-$ and $I^+-I^-$ chromophoric groups dominate and therefore in the spectra of these compounds there are only absorption bands at 265 and 400 m$\mu$ [42,55] and 280 and 360 m$\mu$ respectively[40,42].

The dependence of the molar extinction coefficient on the nature of the solvent shows that the latter play an important part in the corresponding energy transitions of the excited complex anion. Thus, in alkali metal diiodoiodates and dibromoiodates, as the dielectric constant of the solvent is reduced the molar extinction coefficient for the absorption bands at 290 and 256 m$\mu$ increases linearly. Almost the same thing is observed for the absorption bands at 360 and 380 m$\mu$. Such a linear dependence is not observed for dichloroiodates and bromochloroiodates; here there is another relation: the molar extinction coefficient of the complexes increases (although also not proportionately) with the dipole moment of the solvent.

A study of the infrared and Raman spectra[56,57] allowed the force constants of the bonds of the ions $[Br(Br_2)]^-$, $[ICl_2]^-$, $[ICl_4]^-$, and $[BrCl_2]^-$ to be calculated. It was found that the force constants for the interaction between bonds at an angle of 180° in these ions, equal to $0.26 \times 10^{-5}$-$0.36 \times 10^{-5}$ dyn cm$^{-1}$, can be arranged in a sequence which corresponds qualitatively with the thermal stability sequence: the less stable anionhalogenates correspond with the smaller force constants.

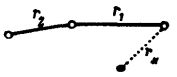
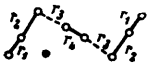
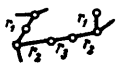
The nature of the chemical bonds in anionhalogenates is discussed mainly in terms of localised covalent bonds (the localised electron pairs method) and molecular orbitals (delocalisation of the $p$-electrons of the halogen atoms)[4,58,59]. Electrostatic theory, which is more graphic, is also sometimes used[3,60-65]. For example, the formation of a bond between the $I^-$ ion and an iodine molecule can be explained by the polarisation of the latter by the $I^-$ ion, the creation of a dipole, and subsequent ion-dipole interaction. This leads to an increase in the interatomic distance in the iodine molecule, from 2.67 Å to 2.82-2.90 Å (see Table 2). The decrease in the electrostatic interaction between the cation and an $[I(I_2)]^-$ anion, associated with the increase in the dimensions of the cation (replacement of ionic bonds by covalent), leads to a decrease in $r_1$ and an increase in $r_2$. In tetraphenylarsonium diiodoiodate, for example, the complex anion is already becoming strictly symmetrical ($r_1 = r_2 = 2.90$ Å) with the greatest value of $r_k$ (see Table 2). The electrostatic interaction of small cations with the $I^-$ ion is so strong that a complex anion is not formed. For that very reason, as we have already mentioned, potassium diiodoiodate exists only as a crystalline hydrate in which the water forms part of an aquocation[66].

From the standpoint of the molecular orbital method[36,37,66,73,77,82-84], the bonding in anionhalogenates is explained by the large value of the overlap integral of the $p$-orbitals, which are extended in the direction of the bonds. The molecular orbitals here are represented by linear combinations of the most distant $p$-orbitals of the halogen atoms. The delocalisation energy calculated for different configurations of the number of halogen atoms involved, was least for the structures of the anionhalogenates which were actually observed. The large value of the integral of the interaction perpendicular to the position of the various $p$-orbitals of one halogen atom in relation to the $p$-orbital of another atom naturally explains the fact that all the valence angles in the anionhalogenates are close to 90°, or to 180° (see Tables 2 and 3).

Some remarks must be made about several anionhalogenate structures. The complex $Cs_2I_8$§ or $2CsI_3.I_2$ [76] consists of two asymmetric $[I(I_2)]^-$ ions which are weakly interacting with one molecule of iodine[4,70,76]. The complex anion $[I(I_2)_2]^-$ or $[I_5]^-$ has a planar, V-shaped form (Table 2)

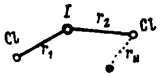
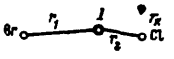
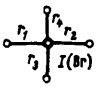
§ The diamagnetism of $CsI_4$ [85] necessitated doubling the formula, since otherwise this compound would contain an odd number of electrons and be paramagnetic.

TABLE 2. Interatomic distances in isopolyhalogenates.

| Compound | Form of structural species | Interatomic distances $r_1$ | $r_2$ | $r_3$ | $r_k$ | Angle between bonds, deg | Reference |
|---|---|---|---|---|---|---|---|
| $NH_4[I(I_2)]$ |  | 3.10 | 2.82 | — | 3.6 | 177 | 66,69 |
| $Cs[I(I_2)]$ | | 3.03 | 2.83 | — | 3.70 | 176 | 21,28,70—72 |
| $[As(C_6H_5)_4]\,[I(I_2)]$ | | 2.90 | 2.90 | — | — | 176 | 73,74 |
| $(Br^-)\,[(CH_3)_3NH]_2[Br(Br_2)]$ | | 2.54 | 2.53 | — | — | 171 | 4,75 |
| $Cs_2I_8$ |  | 2.85 | 3.00 | 3.42 | 3.85 | ∢ $r_1r_2$ 177<br>∢ $r_2r_3$ 81<br>∢ $r_3r_4$ 175 | 76 |
| | | | $r_4$=2.80 | | | | |
| $[(CH_3)_4N]\,[I(I_2)_2]$ |  | 2.82 | 3.17 | — | — | ∢ $r_1r_2$ 175<br>∢ $r_2r_2$ 95 | 77,78 |
| $[(C_2H_5)_4N]\,[I(I_2)_3]$ |  | 2.904 | 3.435 | 2.735 | — | ∢ $r_1r_1$ 180<br>∢ $r_1r_2$ 80.5<br>∢ $r_2r_3$ 176 | 4,79,80 |
| $[(CH_3)_4N]\,[I(I_2)_4]$ |  | 2.67 | 3.43 | 3.24 | — | ∢ $r_1r_2$ 168<br>∢ $r_2r_3$ 156<br>∢ $r_3r_4$ 178<br>∢ $r_2r_4$ 85<br>∢ $r_3r_4$ 89<br>∢ $r_4r_5$ 175<br>∢ $r_5r_3$ 87<br>∢ $r_3r_5$ 169 | 4,81 |
| | | $r_4$=3.18 | | $r_5$=2.90 | | | |

Symbols: o atom of iodine (or bromine); ● cation; $r_k$ distance from cation to nearest halogen.

TABLE 3. Interatomic distances in heteropolyhalogenates

| Compound | Form of structural species | Interatomic distances $r_1$ | $r_2$ | $r_k$ | Angle between bonds, deg | Reference |
|---|---|---|---|---|---|---|
| $[(CH_3)_4N]\,[ICl_2]$ | | | | | | 4, 69, 86 |
| $[(C_4H_{10}N_2)HClH^+]\,[ICl_2]$ |  | 2.34 | 2.34 | — | | 87 |
| $Cs[ICl_2]$ | | 2.47 | 2.69 | 3.23 | 180 | 28, 86, 88 |
| $[PCl_4]\cdot[ICl_2]$ | | — | — | — | | 89 |
| | | 2.36 | 2.36 | — | | |
| $(NH_4)\,[I(BrCl)]$ |  | 2.50 | 2.38 | 3.35 | 178 | 90, 91 |
| $K[ICl_4]\cdot H_2O$ |  | 2.53 | 2.47 | 3.27 | 89—90 | 65, 92, 93 |
| | | $r_3$=2.60 | | $r_4$=2.42 | | |
| $K[BrF_4]$ | | 1.81—1.88 | — | 2.84 | | 4,94—96 |

Symbols: see Table 2.

in which the interaction between the iodine central atom and the iodine molecules is much stronger[77] than in the $[I_3]^{2-}$ ion. In the crystal lattice of the complex compound $M[I(I_2)_3]$ each $[I(I_2)]^-$ ion is surrounded by four iodine molecules and each iodine molecule by two $[I(I_2)]^-$ ions (unit cell)[4,79].

In ammonium bromochloroiodate the cation is coordinated with four chlorine atoms and four bromine atoms, which are arranged alternately at the corners of a greatly distorted cube (see Table 3). Hence the structure of this complex is reminiscent of the structure of caesium chloride[90]. Calculation of the structure of the $[I(BrCl)]^-$ ion by the molecular orbital method showed that a linear configuration of this complex anion with a centrally situated iodine atom is the most favourable energetically[97].

The $[ICl_4]^-$ ion has a slightly pyramidal configuration with an iodine atom at the apex of the pyramid (see Table 3). The chlorine atoms lie in a plane 0.02–0.05 Å from the iodine atom and occupying the corners of a somewhat distorted square[82,92,93]. The potassium ions are situated between the planes of such squares and are coordinated with six chlorine atoms at a mean distance of 3.32 Å. Apparently the size of the potassium cation is limiting for the formation of a sufficiently stable crystal lattice of potassium tetrachloroiodate. Hence in all the anionhalogenates which have been considered the angles between the bonds are approximately 90° and 180° and the interatomic distances are always greater than the sum of the covalent radii; this is expressed especially sharply in the isopolyiodates (see Tables 2 and 3).

The results of X-ray structural analysis and studies of isotopic exchange reactions of the halogens[98], which show the equality of all the bonds in the complex anion, provide a basis for assuming that in the latter the central atom is

a positively charged bromine atom or an iodine atom with a valency electron orbital displaced towards the ligands [2,37,38,99]. This is also suggested by the formal charges of the halogens which are constituents of the complex anion. Thus the charges of the iodine, bromine, and chlorine atoms in the $[I(BrCl)]^-$ ion are respectively [97] +0.07, -0.045, and -0.62. The formal charge in the $[I(I_2)]^-$ ion for the two extreme iodine atoms is -0.5 whereas for the central atom it is almost zero. In the $[ICl_2]^-$ ion the formal charge of each chlorine atom [4,37] is -0.55, and that of the iodine is +0.11. In the $[ICl_4]^-$ ion the chlorine atom has a formal charge of -0.52 and the iodine atom +1.07.

In several chemical properties there is great similarity between the halogens and cyanogen $(CN)_2$ and thiocyanogen $(NCS)_2$, which may be able to form both independent complexes with the alkali metals analogous to the anionhalogenates, for example $Rb(NCS)_3$, and also mixed complexes in which the halogens participate.

## III. ISOPOLYHALOGENATES

### Difluorofluorates

The alkali metal difluorofluorates, which contain the anion $[F(F_2)]^-$, have not been prepared. Repeated attempts to make them [100-107] by the action of fluorine free of hydrogen fluoride on the alkali metal chlorides, bromides, and iodides at 15–250° usually led either to the production of compounds with a variable fluorine concentration, for example, $RbF_{1.96-1.98}$, or to the isolation of compounds of the type $M[ClF_4]$ and $M[IF_6]$.

### Dichlorochlorates

The alkali metal dichlorochlorates have also not yet been obtained. Various attempts to isolate them from aqueous solutions were unsuccessful [32,108-115] evidently on account of the low degree of conversion (0.74%) of $Cl^-$ ions into $[Cl(Cl_2)]^-$ ions in aqueous hydrochloric acid solutions by the reaction:

$$Cl_2(gas) + Cl^- \rightleftharpoons [Cl(Cl_2)]^-.$$

Zimmerman and Strong [113] found the instability constant of the $[Cl(Cl_2)]^-$ ion to be 5.23. The formation of the complex anion is possible also during the dissociation of iodine trichloride by the equation $ICl_3 \rightleftharpoons I^+ + [Cl(Cl_2)]^-$. On dilution of the solution the $[Cl(Cl_2)]^-$ ion decomposes with evolution of chlorine [115].

Solid dichlorochlorates have been obtained only with large cations, such as tetramethylammonium, tetraethylammonium, etc. [116]

### Dibromobromates

These are a more stable class of compounds than the dichlorochlorates. Thus, Ray [117] isolated hydrogen dibromobromate $H[Br(Br_2)]$ from a concentrated solution of bromine in 1.5 *N* hydrobromic acid below 0°, as yellow, extremely unstable crystals. As long ago as 1903, Rikhter-Rzhevskaya [118] suggested the formation of a compound in the $HBr-Br_2-H_2O$ system. The heat of formation of the complex acid at 25° is 1.29–2.03 kcal $mole^{-1}$. [49,117,119-121]. Therefore the absence [122] of compounds of the type $HBr_n$ in the $HBr-Br_2$ system below -50° is improbable.

Many investigators [109,123-133] have studied the equilibrium:

$$Br^-.aq + Br_2(liquid) \rightleftharpoons [Br(Br_2)]^-.aq.$$

It was found that the equilibrium constant determined either by the distribution of bromine between carbon tetrachloride and aqueous solutions (0.1–0.5 moles per 1000 g $H_2O$) [109,123,124,130,131] or from the solubility of bromine in aqueous 0.01–1.0 *N* solutions of sodium and potassium bromides [125-130,132,134,135] is 16–20.7 $mole^{-1}$ litre at 25–33°; the most accurate results [125] give 16.0 $mole^{-1}$ litre at 25°.

Ammonium, rubidium, and caesium dibromobromates have been isolated as solids but the existence of potassium and sodium dibromobromates has been established only in aqueous solutions. The instability constants obtained by various investigators [49,120,127,134,136,137] for aqueous solutions of sodium and potassium dibromobromates at 0–25° range from $4.4 \times 10^{-2}$ to $6.2 \times 10^{-2}$.

In studying the $KBr-Br_2-H_2O$ system at 0°, 25°, and 85°, Harris [138] and Zernike and coworkers [139] found only the crystalline hydrate $KBr_6.1.5H_2O$¶, which separates from solutions rich in bromine as long, red needles, m.p. 25.85°. An analogous sodium compound was not obtained. These reliable investigations [138,139] raise doubt about the earlier reports [20,114,130,131,140-142] of the possibility of obtaining at 0–85° potassium dibromobromate and tetrabromobromate as individual chemical compounds. The existence of a series of potassium polybromobromates in aqueous solution is postulated, particularly the tetrabromobromate [135], with an instability constant of $2.46 \times 10^{-2}$. Evidently, during the separation of the polybromobromates from aqueous solutions destruction of the aquocation occurs, with simultaneous breakdown of the molecule; this is shown indirectly by the fact that dry potassium bromide does not react with bromine [143].

Ammonium, rubidium, and caesium dibromobromates are usually obtained by the addition of bromine, in slight excess (2–3%) of the stoichiometric quantity, to hot, concentrated, aqueous solutions of the bromides. On cooling the solution to 0°, very hygroscopic, orange-red crystals separate [5,21,108,143-145]. These complexes can also be obtained by a dry method – either by heating stoichiometric proportions of the alkali metal bromide and bromine until a melt is formed [31,32,143,145], or by the action of bromine vapour on the bromides [143].

Caesium dibromobromate was the only compound observed in a study [147] of the $CsBr-Br_2-H_2O$ system at 0° and 25°. The compounds taken earlier [31,146] to be $Cs[Br_4]$ and $Cs[Br(Br_2)_2]$ do not exist and the solid phase which was then isolated must be considered to be a mixture of bromine-10-water and caesium dibromobromate; Rae [145] and Cremer and Duncan [148] have also noted that it is impossible to obtain $Cs[Br_4]$.

Ether and absolute ethanol decompose ammonium, rubidium, and caesium dibromobromates [33,149] with precipitation of the corresponding bromide. Complex anions containing more than three bromine atoms can exist in solution, from which they can be isolated as compounds with large organic cations. For example, tetramethylammonium octabromobromate is known [150]; it melts congruently at 56.7°.

¶ Because of the diamagnetism of $KBr_6.1.5H_2O$, the formula $2KBr.5Br_2.3H_2O$ was proposed for it.

Diiodoiodates

These are the most studied of all the alkali metal anion-halogenates. Hydrogen diiodoiodate was first obtained as a solid film[46] and then as red crystals on cooling a concentrated solution of iodine in 1.5 *N* aqueous hydriodic acid to -4°.[117] The compound $H[I(I_2)].4C_6H_5CN$ is also known[151].

The equilibrium $I^- + I_2(solid) \rightleftharpoons [I(I_2)]^-$ has been studied frequently[39,152-162] in aqueous and non-aqueous solutions. The instability constant of the $[I(I_2)]^-$ ion, determined at 25° from the distribution of iodine between the aqueous phase and organic solvents (carbon disulphide, carbon tetrachloride, nitrobenzene, etc.) was found to be $1.3\times10^{-3}$–$1.43\times10^{-3}$ for 0.03–1.0 *N* KI solution[59,124,152,153,157,158,163-165]. The heat of the reaction $I_2(solid) + I^-.aq \rightleftharpoons [I(I_2)]^-.aq$ at 25° is 0.893 kcal mole$^{-1}$.[166-169] The heats of formation of the alkali metal and ammonium diiodoiodates in aqueous solutions at 10–20° increase with the atomic weight of the cation[153].

In addition to the diiodoiodate anion, the presence of the ions $[I_{14}]^{3-}$, $[I_4]^{2-}$, and $[I_6]^{2-}$ in aqueous solutions has also been established[155]; their instability constants at 20–25° are 4.5, $1.2\times10^{-2}$, and $1.6\times10^{-6}$ respectively. However, complexes with the first two anions could not be isolated from the solutions; the third anion is evidently a dimer of the $[I(I_2)]^-$ ion, as Job suggested[49,170].

Study of the electrical conductivity of solutions of the alkali metal iodides and iodine in nitrobenzene have indicated the possible existence of di-, tetra-, hexa-, and octa-iodoiodates[160,161,171].

Lithium diiodoiodate was obtained only as the double salt [sic] with benzonitrile, $Li[I(I_2)].4C_6H_5CN$, which forms[151] dark green acicular crystals unstable in moist air and melting at 92.5°. The analogous lithium diiodoiodate–*o*-toluonitrile compound is known[151]. According to Dawson[161,171] the formation of lithium tetra-, hexa-, and octa-iodoiodates is possible in nitrobenzene saturated with iodine.

Free sodium diiodoiodate has not been isolated. Only sodium iodide dihydrate, with iodine as impurity, crystallises from solutions containing sodium iodide and iodine at 25°.[172-175] On lowering the crystallisation temperature to 10–12°, a product separates which Grace[176] thought to be sodium diiodoiodate tetrahydrate. A study[177] of solubility in the sodium iodide–iodine–water system at 0° showed the absence of solid phases corresponding to sodium diodoiodate; the compounds obtained were the double salts $NaI.Na[I(I_2)].6H_2O$ and $Na[I(I_2)].Na[I(I_2)_2].4H_2O$. The later results of Briggs and coworkers[178], who studied the same system at 0° and -15° support the existence of rather complex solid phases, of low stability and greatly hydrated, of the type $Na_4I_{14}.(13-15)H_2O$, $Na_5I_{11}.(17-19)H_2O$, and $Na_2I_8.(10-11)H_2O$, m.p. 16.4°, 2°, and -7° respectively. The first of these phases approximates in composition to sodium diiodoiodate tetrahydrate.

With strongly polar organic solvents, such as nitriles and nitro-compounds of the aromatic series, sodium diiodoiodate forms rather stable addition products which crystallise well and contain two molecules of solvent[151].

Potassium diiodoiodate separates as extremely hygroscopic azure-black (or dark brown) crystals of cubic or prismatic form when a concentrated KI solution containing the stoichiometric amount of iodine is cooled to 0°.[179-183]

Careful study of the potassium iodide–iodine–water system at 0° and 25° by several investigators[155,184-189] has shown that potassium iodide and iodine can react in aqueous solution, forming only two incongruently melting complexes $K[I(I_2)].H_2O$ and $K[I(I_2)_3].H_2O$. Potassium diiodoiodate monohydrate has two modifications[189], m.p. 12.3° and 30°; potassium hexaiodoiodate monohydrate melts at 38°. It has been shown[190] that small quantities of a complex close in composition to potassium octaiodoiodate can form in 5.4 *N* aqueous KI saturated with iodine.

Potassium diiodoiodate was not observed[191,192] in the solid phases which separate in the potassium iodide–iodine–40–60% ethanol (or methanol) systems at 25°.

Potassium diiodoiodate readily forms various addition products with organic solvents. It was found[171,172,176,193,194] that $K[I(I_2)].C_6H_6$, $K[I(I_2)_2].2C_6H_6$, and $K[I(I_2)_4].3C_6H_6$ separate in the solid phase in the potassium iodide–iodine–benzene system at 6–25°.

The formation of stable solvated potassium polyiodoiodates in non-polar benzene is very interesting when it is considered that such solvation is characteristic only for organic solvents with a high dipole moment. Incongruently melting brown-green crystals of $K[I(I_2)].2C_6H_5CN$ separate from benzonitrile containing potassium iodide and iodine[151]. When nitrobenzene, nitromethane, and some other nitro-compounds are saturated with iodine and potassium iodide, a viscous, dark brown liquid is formed, with a constant ratio of these components, corresponding to potassium octaiodoiodate, which could not be isolated[161,195-198].

The ease of formation of potassium diiodoiodate in aqueous and non-aqueous solutions and the difficulty of obtaining it in the absence of a solvent† are linked with the solvation of the cation, which results in an increase in its volume and a decrease in its polarising action on the complex anion[199-201]. With large cations, stable isopolyiodates are formed in the absence of a solvent[173,198,202]. Thus in the $(CH_3)_4NI$–$I_2$ system the formation of tetramethylammonium octaiodoiodate, m.p. 106.4°, has been shown[173]; it crystallises from benzene as a finely crystalline green-brown powder, which is stable in the air and is not decomposed by water[200,203].

The formation of potassium diiodoiodate in the potassium iodide–iodine system between 75° and 160° and at iodine concentrations of 47–100 mole % has not been established[204-206].

Ammonium diiodoiodate crystallises[181] from aqueous solutions as dark blue crystals, density 3.749 g cm$^{-3}$, which slowly deliquesce in the air. Studies[208,209] of the ammonium iodide–iodine–water system at 0° and -15° showed the existence of incongruently melting diiodoiodates (anhydrous and trihydrate) and tetraiodoiodate monohydrate, with decomposition temperatures 175.7° and 9.8° respectively. The existence of the octaiodoiodate in nitrobenzene saturated with ammonium iodide and iodine has been demonstrated[171], whereas in benzene, toluene, and benzonitrile at 6–25° complexes other than the unsolvated ammonium diiodoiodate were not observed[151,210].

Rubidium diiodoiodate separates as red-brown rhombs, readily soluble in water, absolute alcohol, and ether[5,146,211-214]. Its solubility[23] in water is 77.5 wt. % at 25° and 84.1 wt. % at 40°.

† The existence of anhydrous and non-solvated potassium diiodoiodate is doubted[199,206,207].

Investigation[173,185,213] of the rubidium iodide–iodine–water system showed the existence of only one anhydrous rubidium diodoiodate, congruently soluble in water at temperatures between 7.8° and 132°.

Hexa- and octa-diodoiodates including four molecules of the solvent have been isolated at 6° from benzene containing rubidium iodide and iodine, but only rubidium diiodoiodate from toluene[24,172,173,176]. In the absence of water or an organic solvent reaction of iodine and RbI was not observed at 60–238°.[205,214]

Caesium diiodoiodate is deposited from aqueous solutions as rhombs or acicular blue-black crystals which become tabular after recrystallisation from absolute alcohol[108,185,211]. Caesium diiodoiodate is stable at room temperature[211]: decomposition with formation of free iodine starts at 115°. $Cs[I(I_2)]$ dissolves incongruently at 25°.[108]

Studies[215,216] of the caesium iodide–iodine–water system at 25° showed that only two[217,218] isopolyiodates can be isolated from aqueous solutions: the diiodoiodate and the polynuclear compound $Cs_2[I_8]$. The individuality of the latter was established not just by chemical and X-ray analyses[76,215] but also by measurement of the rate of loss of iodine from mixtures of caesium iodide and iodine over sodium hydroxide[219].

In studying[176,220] the caesium iodide–iodine–benzene (toluene) systems at 6° and 25°, $Cs[I(I_2)]$ and $Cs_2[I_8]$ were obtained, with heats of dissociation of -17.50 and -15.8° kcal mole$^{-1}$ respectively. Furthermore, a solvate of composition $Cs[I_{9-10}].(1.5–2.0)C_6H_6$, very unstable in air, was isolated from benzene[176,220]; its existence had been mentioned earlier[171,172].

Interesting results have been given[221] about the formation of the compounds $Cs[I(I_2)]$ and $Cs_2[I_8]$ in the caesium iodide–iodine system, which was studied between 60° and 303°.

Yamatera[222] recently suggested the existence of double diiodoiodates of rubidium and caesium: $2Cs[I(I_2)].Rb[I(I_2)]$, $3Cs[I(I_2)].2Rb[I(I_2)]$, and $Cs[I(I_2)].Rb[I(I_2)]$, but they could not be isolated.

Thallium diiodoiodate, isomorphous with $Rb[I(I_2)]$ and $Cs[I(I_2)]$, and tetraiodoiodate are known[30,223,224]. Thallium diiodoiodate separates as black-violet crystals during slow evaporation of a methanol solution of TlI and iodine in a molar ratio between 1 : 1.18 and 1 : 1.30. Its aqueous solutions exhibit the tautomeric equilibrium $Tl[I(I_2)] \rightleftharpoons TlI_3$, which is sharply displaced to the right, owing to the partial oxidation of thallium by iodine and the formation of the stable $[TlI_4]^-$ complex ions in the presence of a large excess of iodine and alkali metal halides: the stability of the alkali metal tetraiodothallates rises from caesium to lithium.

The thallium(I) tetraiodoiodate isolated by Mironov[223] forms light, glistening plates, the colour of iodine, which decompose to TlI and $I_2$ when heated to 60–100°.

## IV. HETEROPOLYHALOGENATES WITH A LINEAR ANION

The common main feature of these compounds is their stereochemical similarity, based on linearity of the complex anion, which consists of three halogen atoms. In the crystals these elongated complex anions are, in the presence of potassium, rubidium, or caesium cations, situated parallel to some plane but at right angles to one another. Therefore the crystals of the heteropolyhalogenates with a linear anion are characterised by high negative double refraction. From the standpoint of the localised electron pair theory[225], the mutual orientation of the chemical bonds in the three-halogen linear anion can be represented on the basis of $dsp^3$ hybridisation in the form of a trigonal bipyramid with two halogen-ligands at its vertices and with three lone pairs of electrons in the plane of the central section.

### Dichloroiodates

The dissolution of iodine monochloride in concentrated hydrochloric acid gave[35,45,143,226–231] a dark brown liquid with 80% $H[ICl_2]$. The instability constant of hydrogen dichloroiodate[230] in perchloric acid at 25° is $6 \times 10^{-3}$.

According to recent work[232] solutions of iodine monochloride in hydrochloric acid of various concentrations contain only the complex acid hydrogen hexachloroiodate(V).

Of the alkali metal dichloroiodates, the lithium compound has not yet been obtained and the possibility of obtaining sodium dichloroiodate is doubted[35,143,148,223].

Potassium dichloroiodate[5,37,38,183,234] crystallises as a monohydrate of low stability[234], and the anhydrous compound can be obtained by drying this over magnesium perchlorate[37]. Potassium dichloroiodate was also found to be formed in the KCl–ICl system in nitrobenzene[235,236] and in studying electrical conductivity in the KCl–ICl system[235,237,238]. A thermogravimetric study of this compound showed that it decomposes at 108–110°: the iodine monochloride formed boils off[2]. It has been suggested that a compound of the type KCl.2ICl exists[239].

Crystals of ammonium dichloroiodate are extremely hygroscopic, gradually lose iodine monochloride in air, and are readily soluble in water. There is 87% hydrolysis of ammonium dichloroiodate in its 0.05 *N* aqueous solution at 25°.[35]

Rubidium dichloroiodate crystallises[5,20,37,143,240] as bright yellow anisotropic hexagonal crystals, whose solubility[241] in water is 54.93 wt.% at 25°.

A study[241] of the rubidium chloride–iodine chloride–water system at 25° showed that the solubility isotherm consists of an RbCl crystallisation branch, of insignificant extent, and the much longer crystallisation branch of the congruently soluble anhydrous rubidium dichloroiodate which is formed in the system.

On heating, rubidium dichloroiodate has been found[241] to be stable up to 136°, above which it decomposes with formation of RbCl and liberation of ICl. The endothermic effect associated with the thermal decomposition of $Rb[ICl_2]$ is at 210°.

Caesium dichloroiodate, according to Wells and Penfield[108], is dimorphous. Crystals of the hexagonal modification separate as hexagons when $Cs[ICl_2]$ is recrystallised from aqueous solutions. The same structure is also observed with caesium dichloroiodate crystals, obtained on passing chlorine into 20% caesium chloride solution containing iodine which has been heated almost to boiling[183,240].

A study[37,88] of the crystal structure of caesium dichloroiodate obtained from aqueous solutions containing various amounts of caesium chloride did not confirm the polymorphism of this compound.

Thorough investigations[242] of the solubility of caesium and rubidium dichloroiodates in hydrochloric acid of various concentrations showed that the solubility curves have minima, at 12.5 M HCl, with concentrations of 2.59 and 10.83 g per 100 ml solution respectively at 0°. In studying the solubility of alkali metal chlorides in iodine monochloride it was found[243] that the golden yellow residues from the evaporation of the filtrate were the dichloroiodates of the corresponding metals. However, the stabilities given[243] for the compounds differ considerably from the results of other authors.

The formation of alkali metal dichloroastatates $M[AtCl_2]$ in solution has been established[244].

## Dibromoiodates

The alkali metal dibromoiodates correspond with the acid $H[IBr_2]$, aqueous solutions of which were obtained by Cremer and Duncan[35,143] on dissolving iodine bromide in concentrated hydrobromic acid, as a dark red viscous liquid containing 6% water. The instability constant of hydrogen dibromoiodate(I)[245,246] at 25° is $2.7 \times 10^{-3}$–$3.3 \times 10^{-3}$. Of all the alkali metal dibromoiodates, only the lithium salt has not been obtained, although the possibility of preparing sodium dibromoiodate is doubted[35,148,218].

Potassium dibromoiodate crystallises[5,20,27,29] as the monohydrate, which forms red rhombs, decomposing in air[143,148,183,218,247].

The formation of potassium dibromoiodate was established in physicochemical investigation of the various systems. $KI-Br_2-I_2$ (by electrical conductivity[248]), $KBr-IBr-C_6H_5NO_2$ (by cryoscopy and electrical conductivity[249]), and KBr–IBr.[250]

Thermographic investigation of potassium dibromoiodate showed[2] that partial decomposition of this complex starts at 120°, with a small endothermic effect; complete decomposition takes place at 160°, the iodine bromide formed boiling off.

Potassium dibromoiodate is readily soluble in water (1200 g dissolve in 100 ml water at 18°[27]), decomposes in alcohol and ether, with precipitation of potassium bromide and reacts both with ammonia[251] and with amines, to form addition products of the type $K[IBr_2].2NH_3$, and with ozone and chlorine[148] by the reactions:

$$K[IBr_2] + O_3 \rightarrow KIO_3 + Br_2;$$

and

$$K[IBr_2] + Cl_2 \rightarrow K[ICl_2] + Br_2.$$

These reactions confirm the results of other investigators (see Section II) concerning the coordinating ability of the postively charged iodine central atom.

Ammonium dibromoiodate was obtained as dark red prisms[20,148,218,247]. This compound, unlike the analogous potassium compound, is stable in absolute ethanol, ether, and carbon tetrachloride. Therefore these solvents are sometimes used[143,252] as media for its preparation.

Rubidium and caesium dibromoiodates have been isolated from solutions as red rhombs and prisms[5,21,148,151,218,253,254], which exhibit very low birefringence (the refractive index of $Rb[IBr_2]$ is[255] 1.418). There is a complete analogy between caesium, rubidium, ammonium, and potassium dibromoiodates as regards conditions of preparation and chemical properties[256].

A study of solubility[255] in the rubidium bromide–iodine bromide–water system at 25° showed that iodine and rubidium bromides react to form only one rubidium dibromoiodate, which is anhydrous and congruently soluble. Thermographic and thermogravimetric investigations[255] showed that decomposition, with liberation of iodine bromide, starts at 60° and ends at 238°. The endothermic effect due to this decomposition is at 233°.

The stability of the alkali metal dichloro- and dibromo--iodates in carbon tetrachloride does not correspond with their thermal stability: in carbon tetrachloride at 25° dichloroiodates are more stable[27]. The equilibrium concentration of iodine monochloride in carbon tetrachloride for potassium, ammonium, rubidium, and caesium dichloroiodates is: $2.9 \times 10^{-3}$, $5.7 \times 10^{-2}$, $3.5 \times 10^{-4}$, and $6.0 \times \times 10^{-5}$ M respectively; those of iodine monobromide under the same conditions for potassium, ammonium, rubidium, and caesium dibromoiodates are $4.7 \times 10^{-2}$, $8.4 \times 10^{-3}$, $1.0 \times 10^{-3}$, and $1.4 \times 10^{-4}$ respectively[27].

## Dichlorobromates

Ammonium, rubidium, and caesium dichlorobromates crystallise as bright yellow prisms. They can be made by passing chlorine into hot (50–60°) concentrated aqueous solutions of ammonium, rubidium, and caesium chlorides containing the equivalent amount of bromine[5,20,108,240]. Caesium dichlorobromate can also be made by a "dry method"[143]. Rubidium dichlorobromate decomposes, without melting, at 110°, with evolution of bromine chloride. Caesium dichlorobromate can be recrystallised from aqueous alcoholic solutions, but it breaks down completely in absolute ethanol and ether.

It is suggested[257] that in the dissolution of bromine monochloride in hydrochloric acid the complex acid $H[BrCl_2]$ is formed, with instability constant[117] 0.058 at -1.5°.

## Iodochloroiodates

These compounds of the alkali metals and ammonium are derivatives of the acid hydrogen iodochloroiodate, $H[I(ICl)]$, which has not been isolated in the free state. Its instability constant in 0.06–6.5 M HCl is[44,51,117,258,259] 0.6–0.81 at 25° and 0.543 at 3.8°. The instability constants of lithium, sodium, and potassium iodochloroiodates in 0.05–6.0 M aqueous solutions of the chlorides of these metals are[49,51,142,260-263] respectively 0.79, 0.44–0.77, and 0.43–0.67 at 25°.

It is worth mentioning that the values of the instability constants[258,264,265] determined by different authors differ considerably; it is clear that the constant depends not only on the concentration of hydrochloric acid or metal chloride but also on the nature of the extractant used to determine the distribution of iodine between the two phases. Some investigators[240] assume that under these conditions the ions $[I(I_2)_2]^-$ and $[ClI_4]^-$ are formed as well as $[I(ICl)]^-$.

The alkali metal and ammonium iodochloriodates exist only in solutions; attempts to obtain them in the free state have been unsuccessful[5,41,108,260,265-267]. Study of the equilibrium in the potassium chloride–bromine–water system at ordinary temperatures showed that only potassium chloride separates in the solid phase[264,265].

Obviously the polarising action of even a cation as large as caesium is completely sufficient to destroy the coordination of the chlorine and iodine atoms around the iodine central atom. Only tetraethylammonium iodochloroiodate has yet been isolated[116].

### Iodobromoiodates

The alkali metal iodobromoiodates can also be considered as derivatives of a complex acid, H[I(IBr)], which Ray[117] succeeded in obtaining at -4° as orange-red crystals (mixed with ice) from concentrated solutions of iodine in 1.5 *N* aqueous hydrobromic acid. At ordinary temperatures this acid is unstable[41,265]; its instability constant at 25° is[258,268] 0.083. It is thought[259,269] that the anion $[I(IBr)]^-$ may be the product of the dissociation of dibromoiodates, by the reaction:

$$2[IBr_2]^- \rightleftharpoons [I(IBr)]^- + [Br(Br_2)]^-.$$

Lithium, sodium, potassium, ammonium, and rubidium iodobromoiodates are unknown in the solid state and the existence of lithium iodobromoiodate even in solution has not been established. The instability constant of sodium iodobromoiodate in 0.9–8.3 *N* aqueous KI at 25° is[126,260,264] 0.069–0.081. In the sodium bromide–iodine–benzene system at 6° the formation of sodium iodobromoiodate was not established[24].

The instability constant[49] of potassium iodobromoiodate in 0.02–8.3 *N* aqueous potassium bromide at 25° is[124,260,262–264] 0.065–0.078.

The formation of complexes was not observed in the potassium (or rubidium) bromide–iodine–benzene systems[24] at 6° or in the potassium bromide–iodine–carbon tetrachloride system[27] at 25°.

Caesium iodobromoiodate is the only alkali metal compound of this type to have been isolated in the free state; it was obtained as reddish-brown rhombs undergoing marked hydrolysis in water and solvolysis in ether[10,108,270].

The study[24,30] of equilibria in the caesium bromide–iodine–benzene (toluene) system at 6° has shown the existence of only one unsolvated caesium iodobromoiodate with a dissociation pressure of 0.00486 mmHg at 6°. According to some results[265] the formation of a compound of the type $CsBr.12I_2$ is possible in a solution containing caesium bromide and iodine.

### Bromochlorobromates

It has been shown[55,117,134,271] that the complex acid H[Br(BrCl)] is formed in hydrochloric acid solutions containing bromine; its instability constant[258] is 0.708 at 30°.

Study of the equilibria at -1° in the sodium (potassium) chloride–bromine–water systems has shown that sodium and potassium bromochlorobromates may exist in aqueous solutions, with instability constants of 0.18–0.77 and 0.17–0.91 respectively at 25–30°.[124,134,263] Only the rubidium and caesium bromochlorobromates have been obtained in the free state[42,108].

### Bromochloroiodates

This group of anionhalogenates is the most interesting since the complex anion consists of three different halogens. An acid corresponding to these compounds is known, H[I(BrCl)], formed to the extent of 83% acid and 17% water during the dissolution of iodine monobromide in concentrated hydrochloric acid[143]. The instability constant[53,230] of the complex anion at 25° in 0.05–0.09 *N* HCl and in aqueous alcoholic media is 0.022.

Only the ammonium, rubidium, and caesium bromochloroiodates have been obtained from aqueous solutions as individual chemical compounds and described.

A spectrophotometric investigation[53] of the reaction of KCl with iodine monobromide in aqueous alcoholic solutions showed that within the range of component concentrations 0.005–0.5 M potassium bromochloroiodate is not formed, but the complexes 7KCl.3IBr, 3KCl.2IBr, and 2KCl.3IBr.

Ammonium, rubidium, and caesium bromochloroiodates have been isolated as long garnet-red or reddish-orange prisms[5,90,123,272], incongruently soluble in water. They are rather stable when stored in sealed vessels, but in air they gradually lose iodine monobromide and are converted into the chlorides. Rubidium bromochloroiodate decomposes at 231.5° into rubidium chloride and iodine monobromide[9,272]. In aqueous alcoholic solutions containing rubidium chloride and iodine monobromide at concentrations of 0.001–0.01 M, the formation of compounds of the type RbCl.2IBr is possible[53]. The conventional solubility of rubidium and caesium bromochloroiodates in water is 34.7 and 3.7% at 0°, and 56.8 and 6.3% at 20° respectively[272].

When rubidium and caesium bromochloroiodates are recrystallised from aqueous solutions, their molecular compositions change, approaching that of dibromoiodates[13,108]. This behaviour of bromochloroiodates is due to their partial disproportionation by the reaction:

$$2[I(BrCl)]^- \rightleftharpoons [IBr_2]^- + [ICl_2]^-$$

and the lower solubility of the dibromoiodates.

### Hexafluoroiodates

The hexafluoroiodates can be considered as derivatives of the hexaiodoiodates $M[I(I_2)_3]$, in which fluorine atoms replace iodine atoms. They evidently have a Γ-shaped anion, with a structure similar to that of the $[I(I_2)_3]^-$ ion (see Table 2).

Lithium hexafluoroiodate is unknown and sodium hexafluoroiodate could not be obtained by fluorination of sodium iodide[104,273]. Potassium hexafluoroiodate[14,16,273–266] separates as white crystals in a very low yield on cooling a saturated (97–98°) solution of potassium hydrogen fluoride, fluoride, or nitrate in iodine pentafluoride. Carbon tetrachloride does not affect potassium hexafluoroiodate, but dioxan brings about slight decomposition of it[16]. The compound is stable up to 150–200° above which it gives iodine pentafluoride and potassium fluoride.

The preparation of rubidium and caesium hexafluoroiodates is identical with that of the potassium salt, but here it is possible to isolate other complexes as well[273]: $2RbF.IF_5$ and $Cs[IF_4].IF_5$. The last of these decomposes at 60° into $IF_5$ and $Cs[IF_4]$. Rubidium hexafluoroiodate can also be obtained by fluorination of rubidium iodide at 100–300° in the absence of hydrogen fluoride[104].

### Other Heteropolyhalogenates

Bode and Klesper[104] obtained rubidium hexafluorobromate by fluorinating rubidium bromide with elemental fluorine

above 200°. They did not establish the existence of potassium and sodium hexafluorobromates. Hexafluorochlorates have not been obtained. In the fluorination of rubidium chloride a compound $Rb_3[ClF_6]$ was isolated[104], which later investigators[105] found to be a double salt $2RbF.Rb[ClF_4]$. Alkali metal hexaiodobromates have not been obtained in the free state. From solutions of tetramethylammonium tetraiodobromate in boiling alcohol saturated with iodine, dark green crystals of $[(CH_3)_4N][BrI_6]$, melting at 109°, could be isolated[116,120].

## V. HETEROPOLYHALOGENATES WITH A SQUARE PLANAR ANION

The principal common feature of the anionhalogenates described below is the structure of their five-halogen anion (see Section II). Mooney[92] considered that the bonds in this anion must be formed by the combination of the $sp^3d^2$ orbitals and belong to the octahedral type. Two positions in the octahedron around the atom of iodine (or bromine) are apparently occupied not by atoms but by two lone pairs of electrons of the iodine (or bromine) atom: one above the plane of, for example, the $[ICl_4]^-$ ion and the other below this plane[225]. Hence the structures of the anionhalogenates of this group are reminiscent of the structures of the octahedral complex anions $[TeBr_6]^{2-}$, $[SnCl_6]^{2-}$, $[PbCl_6]^{2-}$, etc. Actually, the I–Cl interatomic distance of 2.34 Å falls within the limits of the Te (or Sn, Pb, Se, Pt)–Cl interatomic distances, which vary between 2.32 and 2.54 Å.

### Tetrafluoroiodates

Potassium, rubidium, and caesium tetrafluoroiodates are obtained as white powders which decompose in moist air. The stability of these complexes depends greatly on the size of the cation[105,273]. It has been found that potassium tetrafluoroiodate can be isolated from its solution in $IF_5$ only at temperatures below 70°, and rubidium tetrafluoroiodate at 70°. Caesium tetrafluoroiodate forms a compound with $IF_5$ of the type $Cs[IF_4].IF_5$, separating below 60°. When $Cs[IF_4].IF_5$ is heated to 100° in a vacuum, it decomposes with the formation of caesium tetrafluoroiodate. Caesium tetrafluoroiodate separates immediately from its solution in iodine pentafluoride above 120°.

Potassium tetrafluoroiodate slowly decomposes even at room temperature, with loss of iodine; therefore the chemical analysis of this compound gives a low (2–3%) figure for iodine and a high one for fluorine. Rubidium and caesium tetrafluoroiodates are more stable.

### Tetrachloroiodates

The alkali metal and ammonium tetrachloroiodates are salts[19,31,143,146,278,279] of the acid hydrogen tetrachloroiodate(III), $H[ICl_4].4H_2O$. This compound, which Caglioti[280] first isolated in the free state, crystallises as orange-yellow hygroscopic plates, not very stable in air. There is 13% hydrolysis of $H[ICl_4].4H_2O$ in its 0.05 *N* aqueous solutions at 25°.[35] In 4–6 *N* hydrochloric acid, ~4.5% of the iodine trichloride present in the form of hydrogen tetrachloroiodate dissociates into iodine chloride and chlorine[281,282].

Hydrogen tetrachloroiodate(III) is the only anionhalogenate acid for which all the alkali metal salts are known.

Lithium tetrachloroiodate is isolated as the tetrahydrate, which forms yellow hygroscopic acicular crystals when chlorine is passed into a suspension of iodine in a concentrated aqueous solution of lithium chloride[146,247,283]. In air, lithium tetrachloroiodate rapidly deliquesces give a yellow liquid.

Sodium tetrachloroiodate[247,283] crystallises as the dihydrate, which is not very stable in air, and forms pale orange rhombs.

Potassium tetrachloroiodate was first obtained as the monohydrate by Filhol[278,279]. It forms golden-yellow crystals[27,143,146,283] which are monoclinic, with lattice parameters[93]: $a = 13.282$, $b = 14.351$, $c = 4.284$ Å, $\beta = 95.72°$, isomorphous with $K[AuCl_4]$.[25] To obtain the anhydrous product the monohydrate was held in a desiccator over phosphorus pentoxide at 4°, or was dried at 40–50° in a stream of chlorine to constant weight[37,38].

The heat of dissociation of the anhydrous potassium tetrachloroiodate in the range 67.5–85° is 29.5 kcal mole$^{-1}$. The dissociation proceeds in two stages[26,218,247]:

$$K[ICl_4] = K[ICl_2] + Cl_2,$$
$$K[ICl_2] = KCl + ICl,$$

but at 15° iodine trichloride can be isolated[25].

A redox equilibrium is characteristic for solutions of alkali metal tetrachloroiodates:

$$[ICl_4]^- \rightleftharpoons [ICl_2]^- + Cl_2,$$

by virtue of which their concentrated aqueous solutions attack all metals, including gold and platinum, and also react with iodides, with liberation of iodine[35,284]:

$$[ICl_4]^- + 3I^- \rightarrow 2I_2 + 4Cl^-.$$

Ammonium tetrachloroiodate, which crystallises with three molecules of water, has similar properties[25,143,247,278,279].

Spacu and Popea[285] found that the reaction of ammonium tetrachloroiodate trihydrate with ammine complexes leads to the formation of very stable dichloroiodates with a complex cation.

Rubidium and caesium tetrachloroiodates crystallise as anhydrous orange-yellow monoclinic crystals[26,38,143,146,148,247,286,287].

The solubility of rubidium tetrachloroiodate in water at 0° is 7.2%.[283] At room temperature rubidium tetrachloroiodate gradually decomposes with liberation of iodine trichloride. It is noteworthy that Mooney[92] think that rubidium and potassium tetrachloroiodates cannot be isomorphous. A study of the kinetics of the thermal decomposition of caesium tetrachloroiodate showed that the first stage of this process, at 28–116°, is the formation of caesium dichloroiodate, which decomposes at 116–118° into caesium chloride and iodine monochloride (the rate of the first reaction is considerably greater than that of the second). Caesium tetrachloroiodate dissolves slightly in water[146,218].

### Tetrabromoiodates

The alkali metal tetrabromoiodates have not yet been obtained in the free state, and are obviously not stable under ordinary conditions[218]. The complex anion $[IBr_4]^-$ exists in hydrobromic acid solutions and has an instability constant of $5.0 \times 10^{-2}$.

### Trichlorofluoroiodates

Booth and coworkers[274,288] obtained the alkali metal and ammonium trichlorofluoroiodates with the general formula $M[I(Cl_3F)]$ as orange-yellow needles. However, the methods of analysis used by these authors and the fact that they did not determine fluorine directly means that the existence of these compounds at room temperature in the free state has not been substantiated.

### Iodotrichloroiodates

Potassium iodotrichloroiodate was obtained as ruby-red crystals below 45° by Cornog and Bauer[239] in studying the KCl–ICl system. The formation of such a complex was confirmed by the same investigators by studying the solubility of potassium chloride in iodine monochloride. However, Fialkov expressed doubt about the possibility of forming the anion $[I(ICl_3)]^-$ in this system[2,238]. It is worth mentioning that solid tetramethylammonium iodotrichloroiodate was obtained over 100 years ago[289].

### Tetrafluorobromates

In studying the reaction of isotopic exchange of $^{18}F$ between HF and $BrF_3$, Rogers and Katz[290] observed rapid and complete exchange in the liquid phase at 27°. The exchange of fluorine can be explained by the presence in the system of the equilibrium

$$HF + BrF_3 = H^+ + [BrF_4]^-.$$

The formation of the complex anion $[BrF_4]^-$ is also possible as a result of the dissociation of bromine trifluoride[291]:

$$2BrF_3 \rightleftharpoons [BrF_2]^+ + [BrF_4]^-.$$

The solubility of the alkali metal fluorides in bromine trifluoride at 25° increases from lithium fluoride (0.125%) to caesium fluoride (18.8%).[292] The sodium, potassium, rubidium, and caesium fluorides, which are readily soluble in bromine trifluoride, form complexes with it, but the rubidium and caesium tetrafluorobromates were obtained in this way only as solutions in bromine trifluoride[15]. Lithium fluoride does not react with $BrF_3$ but the chloride reacts with release of elemental chloride and bromine:

$$6LiCl + 2BrF_3 = 6LiF + 3Cl_2 + Br_2.$$

Ammonium fluoride and chloride react with bromine trifluoride explosively. Of all the alkali metal tetrafluorobromates, only the potassium salt has been isolated in a sufficiently pure form; the others usually contain fluorides as impurities, and a sufficiently effective method to remove these has not yet been found. The stability of the tetrafluorobromates corresponds to the sequence[105]: $K[BrF_4] > Na[BrF_4] > Rb[BrF_4] > Cs[BrF_4]$.

Sodium tetrafluorobromate was obtained by reaction of sodium carbonate or fluoride with bromine trifluoride[293]. Heating sodium chloride, bromine, or iodide with bromine trifluoride to 120° and then cooling the solution with liquid air and sucking off the excess of bromine trifluoride leads to the formation of solid phases of variable composition[15] but the fluorination of sodium bromide gives only sodium fluoride in the residue[104,273].

Sodium tetrafluorobromate decomposes rapidly at 80° and does not react (unlike bromine trifluoride) with organic solvents.

Potassium tetrafluorobromate was obtained as a white crystalline powder by recrystallising from bromine trifluoride the product of the reaction of bromine trifluoride with potassium fluoride, chloride, nitrate, chlorate, iodate, or other potassium compounds[15,96,293-296].

When heated, potassium tetrafluorobromate attacks platinum, to give the fluoride and potassium hexafluoroplatinate, and it reacts with potassium bromide and iodide with the violent evolution of bromine and iodine.

Rubidium and caesium tetrafluorobromates are stable only in the presence of an excess of rubidium and caesium fluorides[15,200]. It is possible to obtain these complexes by fluorinating[104,105] rubidium or caesium bromides at 200–250°.

### Tetrafluorochlorates.

Study of the infrared spectra of mixtures of hydrogen fluoride and chlorine trifluoride showed that in the $HF–ClF_3$ system the complex $H[ClF_4]$ is formed at low concentrations of the components. The heat of the reaction $HF + ClF_3 = H[ClF_4]$ is 3.92 kcal mole$^{-1}$.[297] Potassium, rubidium, and caesium tetrafluorochlorates are made[104,105] by the fluorination of the chlorides of these metals at 160–210°. The tetrafluorochlorates are white substances with low melting points (100–200°), and react vigorously with water and alkali metal iodides.

Other tetraheterohalogenates have not been obtained. Only the tetramethylammonium tetraiodochlorate is known[116]; it separates as azure-green crystals from an alcoholic solution when tetramethylammonium chloride and iodine react. Tetramethylammonium tetraiodobromate $[(CH_3)_4N].[BrI_4]$ is also known; it was made by the reaction of tetramethylammonium bromide and iodine in boiling alcohol. On cooling the solution, dark green crystals separated[116], m.p. 124.5°. Caesium and rubidium tetraiodobromates can exist in aqueous solutions[258].

Of the other anionhalogenates which do not belong to any of the classes considered above, we must remember potassium heptafluorochlorate $K_2[ClF_7]$, which was obtained[298] by the action of concentrated hydrofluoric acid on potassium chlorate. However, recent work[16] rejects the possibility of making this compound.

## VI. USE OF ANIONHALOGENATES

The chemical properties peculiar to anionhalogenates (ease of thermal decomposition, comparatively low solubility, etc.) were appreciated by even the first investigators of this interesting class of compounds. Thus, first Wells[299] and then Archibald[300] proposed to use the fractional crystallisation of rubidium and caesium dichloroiodates for obtained the pure chlorides. To obtain $Cs[ICl_2]$ Wells dissolved the stoichiometric amounts of caesium nitrate and iodine in hydrochloric acid (1 : 1) at a temperature close to the boiling point of the solution. On cooling, crystals separated; they were recrystallised once or twice from hot acid (1 : 1), then heated to yield pure caesium chloride. Later, Archibald[7] developed the technological production of pure rubidium and caesium compounds free from Li, K, Na, Si, Fe, and Al, based on the use of fractional crystallisation of rubidium and caesium dichloroiodates and dibromobromates. Subsequently Archibald's method was perfected by Ishibashi and coworkers[8], who

found that fourfold recrystallisation of rubidium dichloroiodate gives a spectrographically pure preparation (as regards potassium) even when the initial solution is saturated with potassium. To use this method, rubidium sulphate or any other rubidium salt is dissolved in the minimal quantity of concentrated hydrochloric acid, the stoichiometric quantity of iodine monochloride is added and the mixture cooled to 0°. The precipitate of rubidium dichloroiodate is filtered off, washed with a little cold concentrated hydrochloric acid, dissolved in a little more of this acid containing iodine monochloride, and recrystallised, by adding each time a little iodine monochloride in hydrochloric acid[7,8]. Fractional crystallisation of caesium dichloroiodate was used to obtain pure caesium chloride. After seven recrystallisations a 99.9% product was obtained from 71% caesium chloride[7,8]; this product did not give the spectrographic lines of rubidium. The separation factor of rubidium and caesium[8] when fractional crystallisation is used was 29.1.

Some chemical and physical properties of diiodoiodates were used for the separation of some alkali metals in the presence of others[222]. The possibility of using diiodoiodates for the extractive separation of the alkali metals has also been mentioned[301]. Study[213] of the $RbI-I_2-H_2O$ system showed that the crystallisation of rubidium diiodoiodate is most favourable between 0° and 5° and at a concentration of the components in the solution determined by the section of the isotherm of the crystallisation of this complex, which is adjacent to the $RbI + Rb[I(I_2)]$ eutonic point. On this basis a method of freeing rubidium diiodoiodate from caesium impurity was developed[212,302,303]. After four successive precipitations of rubidium diiodoiodate with the separation of 40% of the rubidium iodide present in the solution, rubidium iodide with 0.02% caesium was obtained from the filtrate — the initial rubidium iodide contained 1.5% caesium. The crystallisation coefficient for this process (Khlopin constant) was 23.4 at 25°.[212,302]

The precipitation of rubidium bromochloroiodate from aqueous solutions was proposed for the preparation of especially pure rubidium chloride, free from potassium impurity[9,11,12,270,271]. It appeared that the coprecipitation of potassium with rubidium bromochloroiodate is very slight; after a single precipitation the concentration of potassium had fallen from 0.5–1.0% to 0.02% or less, and in the precipitation from acetic acid medium the purification factor reaches 300 (from 0.06 to 0.0002%); the factor for purification from lithium is here 15–55 and that for sodium 30–37.[9,272] The precipitate is enriched in caesium when this is present, owing to the lower solubility and greater stability of caesium bromochloroiodate, compared with the rubidium salt.

The precipitation of caesium iodobromoiodate from aqueous alcoholic solutions was recently suggested[10,270] for the preparation of especially pure caesium bromide containing ~0.002% lithium and sodium and 0.005% potassium, and 0.02% rubidium as impurities.

Alkali metal bromides can be separated (with isolation of caesium bromide) by making use of their differing abilities to form stable and readily soluble polybromates[14]. The ease of passing from some anionhalogenates to others without the introduction into technological processes of expensive reagents and the simplicity of thermal decomposition has enabled a complex technological scheme[13] to be worked out for the purification of commercial rubidium chloride with the simultaneous preparation of especially pure caesium salts.

The possibilities of the alkali metal anionhalogenates are, of course, not yet finally exhausted, since the appearance of new representatives of them in the course of the search for new methods of preparation and new interesting properties of the compounds already known cannot be ruled out.


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# AROYLENEIMIDAZOLE DYES

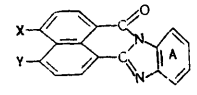
J. Arient

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## I. INTRODUCTION

Aroyleneimidazole dyes are usually regarded as forming a separate group of synthetic dyes. They are characterised by the structure




The ring A may be substituted with various groups or fused rings, and positions X and Y may contain hydrogen atoms, various substituents, or another benzimidazole group[1-3].

For obvious reasons this group is also taken to include imides of *ortho*- or *peri*-dicarboxylic and tetracarboxylic acids, as well as compounds, obtained by the interaction of these acids with aromatic *peri*-diamines, which, although they contain no imidazole ring, are very similar to the parent compounds in method of preparation and dyeing properties.

The early aroyleneimidazole dyes were vat dyes. Their brilliance and beauty of shade, great fastness, and comparatively simple manufacture gave the impression that such dyes would displace thioindigoid dyes from the market.

The most important representative of the group of aroyleneimidazole dyes is Indanthren Scarlet GG (Vat

Scarlet 2J), which consists of a mixture of *cis*- and *trans*--naphthoylenebisimidazole — Indanthren Bordeaux RR (Vat Bordeaux) and Indanthren Brilliant Orange GR (Vat Brilliant Orange) — which are formed by the reaction of naphthalene-1,4,5,8-tetracarboxylic acid with *o*-phenylenediamine.

Development of the aroylenebenzimidazole dyes was halted for a long time, but during the past four or five years great interest has been renewed in dyes of this group, mainly based on naphthalene-1,8-dicarboxylic acid, which have found application as disperse dyes for the coloration of synthetic materials and fibres.

Besides the two main intermediates — naphthalene--1,4,5,8-tetracarboxylic and -1,8-dicarboxylic acids — other aromatic dicarboxylic acids have been used for the production of aroyleneimidazole dyes, e.g. naphthoylenebenzimidazole-*peri*-dicarboxylic acid, perylenetetracarboxylic acid, anthraquinone-2,3-dicarboxylic acid, pyrenic acid, etc.

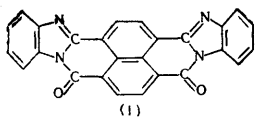
## II. DYES BASED ON NAPHTHALENE-1,4,5,8-TETRACARBOXYLIC ACID

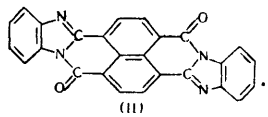
The practical use of *ortho*- and *peri*-diamines in the synthetic dye industry began during 1925–1930, when several patents appeared describing the interaction of *ortho*- and *peri*-diamines with naphthalene-1,4,5,8-tetracarboxylic acid. The insertion of a naphthalene ring system between two benzimidazole ring systems gave the necessary affinity of the dye for the fibre; the conjugated carbonyl groups facilitate the formation of leuco-compounds and their reoxidation.

The excellent dyeing properties of the dyes and the straightforward manufacturing process made possible the rapid development of the initial discoveries in this field.

### 1. Industrial Production of Indanthren Scarlet GG (Vat Scarlet 2J)

Indanthren Scarlet GG was the first and is still the most important of these dyes. It is formed by heating *o*-phenylenediamine with naphthalene-1,4,5,8-tetracarboxylic acid in glacial acetic acid[4-9]. The dye is not a pure substance: the reaction involves the formation of equal proportions of the *cis* (I) and *trans* (II) isomers.


(I)


(II)

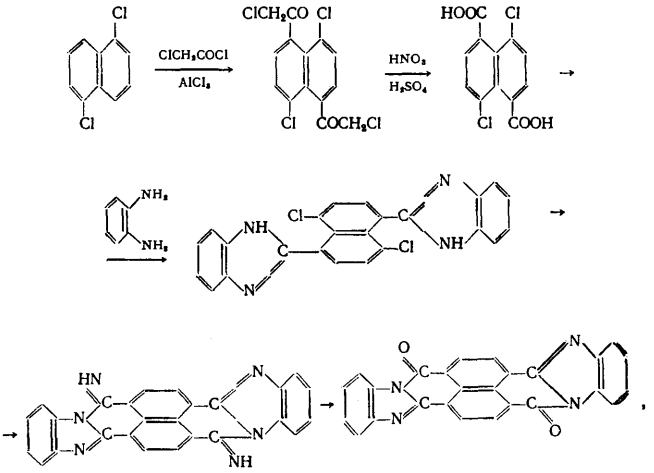
Both isomers can be isolated from the dye. Like all *trans* isomers of aroylenebenzimidazole dyes, (II) shows a hypsochromic shift in its absorption spectrum compared with the *cis* isomer.

The *trans* isomer appears on the market under the name Indanthren Brilliant Orange GR, and the *cis* isomer as Indanthren Bordeaux RR. Both are used as vat dyes for the dyeing of cotton. Whereas there is a great demand for the *trans* isomer because of its interesting shade, the Bordeaux finds limited use, and new applications are still being sought for it. The latter was placed on the market in a very finely divided form under the name Permanent Red TG Extra[10] as a colorant for lacquers, cellulose nitrate varnishes, and air-drying and stoving artificial--resin varnishes, and for the mass coloration of polymethacrylate, polystyrene, and polyethylene. It is distinguished by good fastness to solvents and to heat-treatment, and unusually high light fastness (grade 8 in cellulose nitrate varnish!). The orange dye is also suitable for similar application, and has been placed on the market as a pigment under the name PV Fast Orange GRL.[11]

The technical manufacture of Indanthren Scarlet GG itself is relatively straightforward. The process was originally conducted in boiling acetic acid[9]. The dye formed is accompanied by ~10% of naphthoylenebenzimidazole-*peri*-dicarboxylic acid, which must be removed by subsequent treatment. It is more convenient to conduct the reaction in water containing 1–2% of sulphuric acid at a moderate pressure. Kinetic study of the process shows that the optimum temperature for the reaction is 120–130°. Decomposition products are formed at higher temperatures[12,13].

The dye is obtained in almost quantitative yield, without the formation of naphthoylenebenzimidazole-*peri*-dicarboxylic acid, by working without a solvent at 140°, when both components are molten. The dye thus obtained contains rather more of the *trans* isomer, and hence has a more interesting shade than the dye synthesised as described above; its other dyeing properties are similar[14].

As already mentioned, the presence of both isomers in the final product is inconvenient for application. Methods were therefore sought for obtaining the pure *trans* isomer, or at least mixtures in which the content of the orange dye had been increased. A process was therefore worked out for preparing the pure orange dye by the scheme[15]



but this proposed synthesis cannot compete with the original method.

### 2. Effect of Solvent and Substituents on the Formation of Isomers of Indanthren Scarlet GG

The ratio of *cis* and *trans* isomers remains practically unchanged when a different solvent is used for the reaction, e.g. chlorobenzene, nitrobenzene, 2-ethoxyethanol,

glycerol, dimethylaniline. On the other hand, the relative proportions are changed fundamentally when halogen atoms are introduced into the positions 2,6 or 2,7 of the naphthalene-1,4,5,8-tetracarboxylic acid[16].

The above *trans* derivative is almost the sole product of the reaction of 2,6-dichloronaphthalene-1,4,5,8-tetracarboxylic acid with *o*-phenylenediamine, whereas the corresponding 2,7-dichloro-acid yields a monoaroylenebenzimidazole derivative. Measurement of the relative reaction velocities of 2,6- and 2,7-dichloronaphthalene-1,4,5,8--tetracarboxylic acids in comparison with the unsubstituted acid has established that at the same time the chlorine atoms slow down the reaction.

Analysis of the kinetic data and of the effect of steric, mesomeric, and inductive factors on the course of individual stages in the reaction indicates that the two consequences of the introduction of chlorine atoms into the molecule differ in origin. The general slowing down in the reaction is due to the fact that the chlorine atom impedes addition of the nitrogen atom of *o*-phenylenediamine by sterically blocking the neighbouring carbonyl carbon atom, while the effect on the relative proportions of *cis* and *trans* dye isomers is due to the fact that the chlorine atom, by mesomeric and inductive interaction, lowers the activity of the *ortho*-carbonyl group during final closing of the imidazole ring.

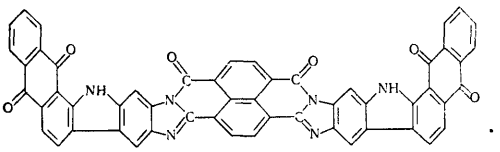
### 3. Oxidation of Naphthoylenebisbenzimidazole

According to the patent literature, oxidation of Indanthren Scarlet GG with sexivalent chromium in acid medium should yield Indanthren Brilliant Orange[17]. The product will be more or less yellowish or reddish depending on the quantity of oxidant employed; it is stated that oxidation of a mixture of the two isomers yields new dyes of quinoid character, whose shade moves towards the desired orange. However, oxidation of the pure *cis* isomer (Bordeaux) yields a dye similar in shade to the original dye[18]. The orange *trans* isomer also gives a dye similar in shade to the original dye. Oxidation of the individual isomers or of a mixture in 80% sulphuric acid, in which the dye dissolves completely (whereas in 60% sulphuric acid it is partly in suspension), yields dyes similar in shade to the original dyes.

Oscillographic polarography has proved that the structures of the *cis* and *trans* isomers remain unchanged on oxidation. These facts suggest that, during oxidation of a mixture of the isomers, neither undergoes chemical conversion to a dye of different shade; rather, the change in shade occurring during oxidation of the dye in suspension is due to the greater rate of reaction of the more soluble *cis* isomer compared with the less soluble *trans* isomer, with the formation of almost colourless products which are insoluble in alkalis.

### 4. Derivatives of Naphthoylenebenzimidazole

Chlorination of Indanthren Scarlet GG with chlorine in nitrobenzene[19] gives an orange vat dye, and chlorination with sulphuryl chloride gives a brown vat dye[20]. Bromination of Indanthren Bordeaux RR yields a dibromo-derivative, which on interaction with 1-aminoanthraquinone yields an anthrimide, cyclisation of which forms reddish--brown carbazole dyes[21].



When Indanthren Scarlet GG (or the individual isomers) is nitrated, orange and red pigments are obtained[22], which however, when applied as vat dyes, give greys and blacks on cotton[19] owing to reduction of the nitro-groups during vatting.

By using the corresponding substituted *ortho*-diamines, we can obtain various substituted aroylbenzimidazole dyes of various shades. Of the large number of dyes obtained in this way, Indanthren Printing Brown B, synthesised by the interaction of 4-ethoxyphenylene-1,2-diamine and naphthalene-1,4,5,8-tetracarboxylic acid, and Indanthren Printing Brown 5R, obtained by reaction of 4-chlorophenylene-1,2-diamine with the same acid, have found industrial application[4,7].

Dyes prepared by the use of *ortho*-diamines of the naphthalene[19], phenanthrene[23], and fluorene[24] series have not found application because of solubility difficulties during vatting.

On the other hand, dyes for which 1,2- and 2,3-diaminoanthraquinones are used as the amine component appear to be very interesting. When such diamines react with naphthalene-1,4,5,8-tetracarboxylic acid in high-boiling solvents, vat dyes are formed which produce on cotton olive shades of high fastness properties[25].

Some of the *ortho*-diamines which are not very readily available can be replaced in the reaction by the corresponding *ortho*-nitroamino-[26] or *ortho*-aminoazo-compounds[27]. The intermediates formed when they react with naphthalene-1,4,5,8-tetracarboxylic acid are further reduced in alkaline medium with sodium sulphide or dithionite, or else with iron in acid medium with simultaneous formation of the naphthoylenebenzimidazole skeleton.

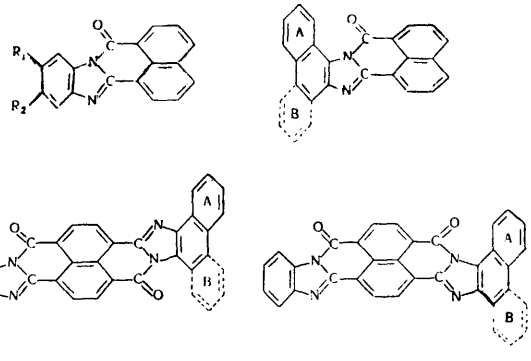
## III. SEPARATION OF ISOMERIC AROYLENEBENZIMIDAZOLES

As already mentioned in the previous Section, reaction of *ortho*- or *peri*-dicarboxylic or tetracarboxylic acids with aromatic *ortho*- or *peri*-diamines involves the formation of mixtures of isomers of the corresponding aroylenebenzimidazoles. Various technical processes are available for the separation of these isomers, and can in principle be divided into four groups. (*a*) The mixture of isomers is dissolved at an elevated temperature in an alkali-metal alkoxide or amide; on cooling, the insoluble *trans* derivative separates, while the soluble *cis* derivative is obtained by acidifying the filtrates[28]. (*b*) A solution of the dye in concentrated sulphuric acid (or chlorosulphuric acid) is cautiously diluted with water; at first the less soluble sulphate of the *trans* isomer separates, and after its removal the *cis* isomer is obtained by further dilution[29]. (*c*) The technical dye is stirred into mixtures of organic sulphonic acids and organic solvents, and separation is effected by use of the differing solubilities of salts of the individual isomers[30]. (*d*) The mixture is stirred into chlorosulphuric acid in the presence of hydrochloric, hydrobromic, or sulphuric acid, and the insoluble *trans* form is filtered off[31].

All these processes are directed primarily towards obtaining the pure, coloristically more valuable *trans* isomer from the dye produced by the interaction of naphthalene-1,4,5,8-tetracarboxylic acid and *o*-phenylenediamine. The *cis* isomer contains almost all the impurities formed in this reaction, which comprise firstly those soluble in alkalis and organic solvents (mainly naphthoylenebenzimidazole-*peri*-dicarboxylic acid) and secondly impurities which are soluble solely in organic solvents.

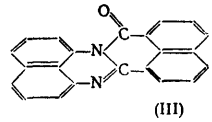
The steadily increasing demand for Indanthren Bordeaux RR as a pigment is responsible for the more exacting purity requirements. The very pure *cis* and *trans* isomers are obtained by a somewhat modified process[32], in which the sparingly soluble adduct of the *trans* isomer with potassium ethoxide is separated in a medium containing excess alcohol, while the *cis* isomer is isolated from the filtrate by alkaline hydrolysis after salting-out in water[32].

Only two isomers are formed in the reaction of naphthalene-1,4,5,8-tetracarboxylic acid with *o*-phenylenediamine. The number of isomers increases when substituted *ortho*-diamines are used. It has not proved possible to separate these isomers by a technical process. Only partial separation, i.e. into *cis* and *trans* isomers, is achieved. Several aroyleneimidazole dyes can be separated into their isomers by chromatography[33]. Dyes (I)–(VI) have been separated chromatographically on aluminium oxide, and the fluorescence spectra of the resulting isomers determined.

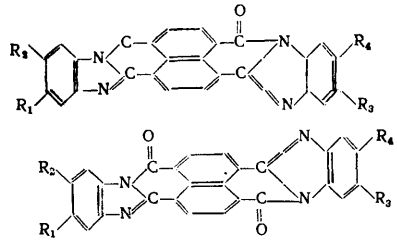


(Ia) $R_1 = OC_2H_5$; $R_2 = H$,
(Ib) $R_1 = H$; $R_2 = OC_2H_5$,

(IIa) Benzene ring in position A,
(IIb) Benzene ring in position B,

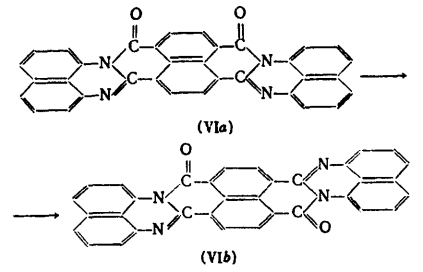


(III)



(IVa) $R_1, R_2 = OC_2H_5$; $R_3, R_4 = H$,
(IVb) $R_1, R_4 = OC_2H_5$; $R_2, R_3 = H$,
(IVc) $R_3, R_4 = OC_2H_5$; $R_1, R_2 = H$,
(Va) Benzene rings in positions A and C,
(Vb) Benzene rings in positions B and C,
(Vc) Benzene rings in positions B and D,

(IVd) $R_1, R_2 = OC_2H_5$; $R_3, R_4 = H$,
(IVe) $R_1, R_4 = OC_2H_5$; $R_2, R_3 = H$,
(Vd) Benzene ring in position A,
(Ve) Benzene ring in position B.



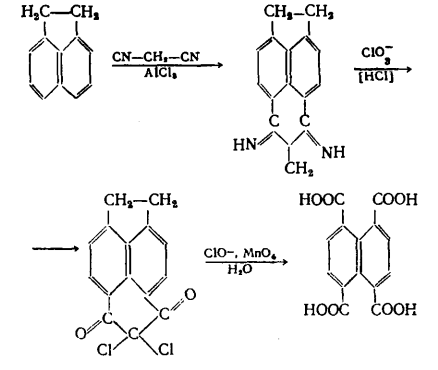
(VIa)

(VIb)

## IV. PRODUCTION OF NAPHTHALENE-1,4,5,8-TETRACARBOXYLIC ACID

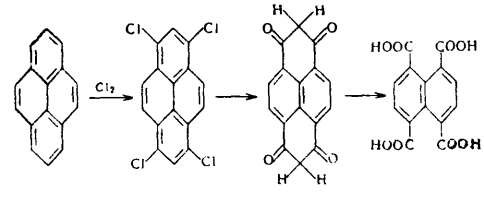
The principal intermediate in the manufacture of aroyleneimidazole dyes, naphthalene-1,4,5,8-tetracarboxylic acid, is obtained mainly in two ways.

The first process[34-36] starts from acenaphthene and is conducted according to the scheme



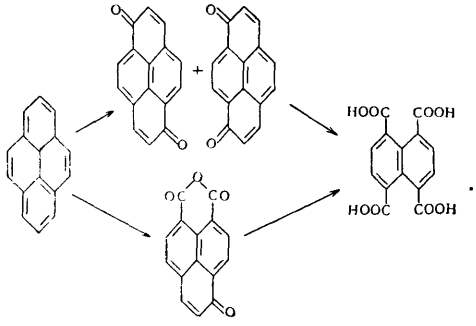
The second process starts from pyrene, from which naphthalene-1,4,5,8-tetracarboxylic acid can be obtained by chlorination or oxidation.

When chlorination is used, the chlorination or bromination of pyrene is followed by oxidation of the tetrahalogenopyrene:



According to the literature[37-40] high yields are obtained by this method, but technologically it makes increased demands on the equipment. A simpler process is oxidation, which, furthermore, does not require complicated

apparatus. The course of the process can be clearly represented by the following scheme




The oxidation of pyrene to a mixture of pyrene-3,8- and -3,10-quinones and pyrenic acid has been known since 1870.[41] The structure and properties of these substances have been investigated by several workers[42-51]. Pyrenequinones and pyrenic acid are obtained by oxidising pyrene with chromic mixture in aqueous suspension or with chromium trioxide in acetic-acid solution. Subsequently pyrenequinones were also obtained by the oxidation of pyrene with hydrogen peroxide in glacial acetic acid[52]. This last method is unsuitable for the manufacture of pyrenequinones, since it requires the use of a large excess of a comparatively expensive oxidant, and the oxidation product is insufficiently pure.

The oxidation of pyrene with chromium trioxide in acetic acid was mentioned in the very early literature, but a more detailed method has been given only in a patent[53] of the Rütgerswerke AG. In this method double the theoretical quantity of chromium trioxide is used, and the reaction mixture is boiled; a quantitative yield of almost 100% quinone is formed. However, the industrial application of this method is impeded by the high cost of acetic acid.

The oxidation of pyrene in suspension with chromic mixture has been examined in greatest detail by Bamberger and Philip[44-46] and in the patent mentioned above[53]. According to Bamberger, finely ground pyrene is oxidised by the theoretical quantity of dichromate in sulphuric acid diluted with five volumes of water. The paper gives neither the precise temperature conditions nor the yield and purity of the product, only that the latter contains pyrenic acid. Bamberger's results were checked by Vollmann[39], who does not give the procedure but describes in greater detail the reaction product, allegedly obtained in 90% yield; it contained hardly any unchanged pyrene and only a few per cent of pyrenic acid. The Rütgerswerke patent contains quite contradictory data on the substance obtained by Bamberger and Philip's method, and states that the reaction product consists of 36% of pyrenequinones, 14% of chromic salts, 50% of unchanged pyrene, and traces of pyrenic acid. The patent gives a recipe according to which 98–99% quinones can be obtained in almost quantitative yield. This recipe differs from Bamberger and Philip's procedure in the quantity of dichromate used (178% of theoretical) and a smaller quantity of sulphuric acid. Here, too, the temperature conditions of the reaction are given in insufficient detail.

It follows from the contradictions in the literature quoted that insufficient study has been made of the conditions for the oxidation of pyrene to pyrenequinones, and that the oxidation process is very sensitive to variation in the conditions.

The oxidation of pyrene to pyrenequinones with hydrogen peroxide in acetic acid and with oxygen or air in the presence of a catalyst has been described. Owing to the unsatisfactory course of the oxidation, neither method is applicable to manufacture.

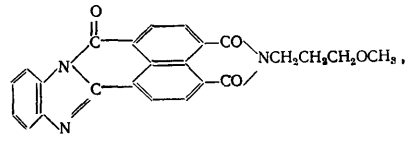
Naphthalene-1,4,5,8-tetracarboxylic acid can be obtained from the pyrenequinones (or pyrenic acid) by oxidation in either acid or alkaline medium. In acid medium excess of oxidant (dichromate in dilute sulphuric acid) is used. Pyrenic acid, which itself was obtained in low yield, is supposedly converted into naphthalenetetracarboxylic acid in quantitative yield. The yield of the latter acid from pyrenequinones is insignificant. This method of oxidation forms the subject of a 1932 patent of the IG. Farbenindustrie AG.[54], according to which pyrene is dissolved in concentrated sulphuric acid and, after dilution with water, oxidised with excess of dichromate. The intermediate oxidation products, pyrenequinones, are not isolated. The yield of naphthalenetetracarboxylic acid is not high.

Considerably better results are achieved by oxidising pyrenequinones in alkaline medium. Information on this method is given only in two patents dating from 1933. According to the first patent[55] pyrenequinones or pyrenic acid are oxidised in alkaline medium by heating with excess of permanganate solution; the excess of permanganate remaining should accelerate crystallisation of the naphthalenetetracarboxylic acid from solution after acidification, and is removed in the purification of the acid. According to published data, the yield of naphthalenetetracarboxylic acid by this method is 70–75% based on the pyrene taken for the reaction. The second patent[56] describes the use of an alkaline solution of sodium hypochlorite or of a mixture of bleaching powder and calcium hydroxide for the oxidation. The operating technique is very simple: a suspension of pyrenequinones is stirred up with an alkaline solution of sodium hypochlorite, and the mixture allowed to stand for a few hours at room temperature and then for a few hours at 50–80°. The quinones are converted into naphthalenetetracarboxylic acid, which is isolated. According to the patent the yield is 70–80% based on the pyrenequinones.

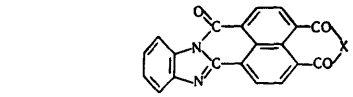
## V. DYES BASED ON NAPHTHOYLENEBENZIMIDAZOLE-*peri*-DICARBOXYLIC ACID

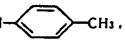
Besides the symmetrical dyes obtained by reaction of naphthalenetetracarboxylic acid with two moles of an *ortho*-diamine, unsymmetrical dyes can also be synthesised. When the acid reacts with *o*-phenylenediamine in aqueous medium in the presence of sodium acetate, equimolar cyclisation yields the so-called naphthoylenebenzimidazole-*peri*-dicarboxylic acid[57-59], which can react further with other variously substituted aromatic *ortho*- or *peri*-diamines or else with aliphatic or aromatic amines. In the former case, vat dyes of various shades are formed[62], and in the latter case disperse dyes[63].

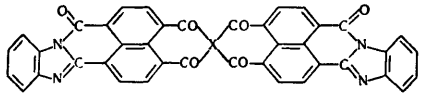
Among disperse dyes of this type, Samaron Brilliant Yellow HRL[60] having the structure[61]

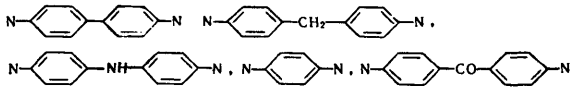


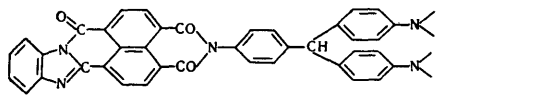
has appeared on the market. This group includes also dyes of types (I)–(V)



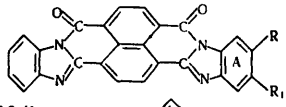
I: X = O, NH, $NCH_3$,  , $NCH_2CH_2OH$,  , $NCH_2CH_2CN$, $N(CH_2)_7CH_3$, $N(CH_3)_{17}CH_3$



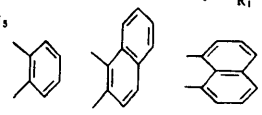
II: X = 

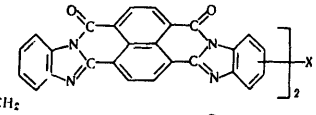


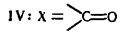


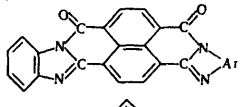


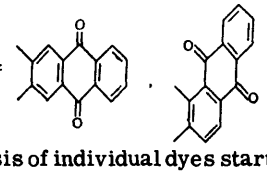
III: R, $R_1$ = $CH_3$, Cl, $OC_2H_5$

A = 

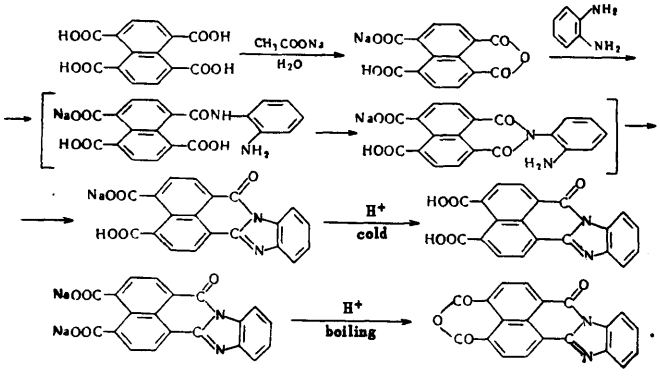


IV: X = 

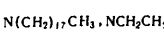


V: Ar = 

The synthesis of individual dyes starts from naphthoylenebenzimidazole-*peri*-dicarboxylic acid (X), which is made to react with various aliphatic or aromatic amines. This acid is obtained, according to patent information[59], by the reaction of naphthalene-1,4,5,8-tetracarboxylic acid with one molecule of *o*-phenylenediamine in aqueous sodium acetate solution. The disagreement on the mechanism of this reaction encountered in the literature has been cleared up by Arient and Dvořák, who suggest the following scheme to explain the course of the reaction[64]



These workers have established the relation between the structure and the spectra of dyes of types (I)–(V).[64] The effect of substituents in dyes of this type on the bathochromic shift in the absorption band increases in the sequence

O, $NCH_3$, $N(CH_2)_{17}CH_3$, $NCH_2CH_2OH$,  ,  , $NH$, $NCH_2CH_2CN$.

These dyes can be employed as either vat or disperse dyes. With lengthening of the aliphatic chain, dyeing power is lost owing to the insolubility of the vat; dyeing power also decreases as the chain becomes longer when the compounds are used as disperse dyes.

The doubling of the naphthoylenebenzimidazole-*peri*-dicarboxylic acid moiety in dyes of type (II) results in a bathochromic shift in colour compared with dyes of type (I). The element uniting the two moieties of the dye molecule has hardly any perceptible effect. The dyes can be applied as vat dyes with good fastness properties.

The absorption spectrum of dyes of type (III) is considerably affected by substituents — methyl, chlorine, and ethoxyl — in the molecules of symmetrical and unsymmetrical aroylenebenzimidazoles. In contrast to the previous types (I) and (II), these dyes exhibit a considerable bathochromic shift, and they yield reds, violets, and browns. The influence of substituents is strongly marked within this group; their bathochromic effect increases in the sequence H, $CH_3$, Cl, $2CH_3$, $OC_2H_5$. Dyes formed from naphthoyleneimidazole-*peri*-dicarboxylic acid with naphthylene-1,2- and -1,8-diamines exhibit a further shift in the absorption band towards longer wavelengths. Analogous results have been obtained for naphthalene-1,4,5,8-tetracarboxylic acid.

All dyes were separated into *cis* and *trans* isomers, which showed an analogous variation in colour to that observed with their mixtures. Most of the dyes, mainly derivatives of naphthoylenebenzimidazole-*peri*-dicarboxylic acid, are distinguished by their brilliance and excellent fastness, and can be used as vat dyes. Dyes derived from naphthalenetetracarboxylic acid are sparingly soluble (with the exception of naphthoylenebisbenzimidazole), so that they cannot be used as vat dyes. Dyes containing the naphthalene ring system have inadequate fastness.

The influence of naphthoylenebenzimidazole-*peri*-dicarboxylic acid on the relative proportions of *cis* and *trans* isomers formed in the synthesis of such dyes was checked, its reaction with *o*-phenylenediamine being taken as example. The ratio of these isomers obtained with such a consecutive synthesis was practically 1 : 1, equal to the ratio obtained by the direct interaction of naphthalene-1,4,5,8-tetracarboxylic acid with *o*-phenylenediamine. This indicates that naphthoylenebenzimidazole-*peri*-dicarboxylic acid exerts no influence on the formation of one isomer or the other.

Dyes of type (IV), i.e. dyes having two naphthoylenebisbenzimidazole moieties, have been obtained by the reaction of naphthoylenebenzimidazole-*peri*-dicarboxylic acid with 3,3′,4,4′-tetraaminobenzophenone and with diphenylmethane-3,3′,4,4′-tetraamine. In the former case the dye contains one double conjugated system, but in the latter case it contains two conjugated systems isolated from one another by the methylene bridge. A dye resulting from the diphenylmethanetetra-amine has a red colour with a moderate hypsochromic shift in comparison with naphthoylenebisbenzimidazole; a dye from the tetraaminobenzophenone shows practically the same absorption.

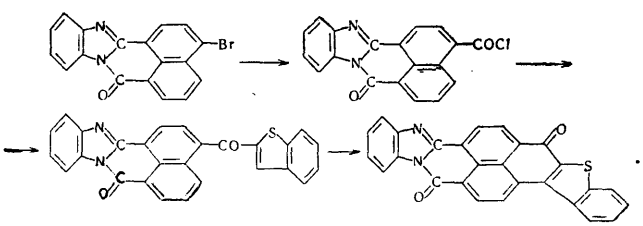
Dyes of type (V), which result from the reaction of naphthoylenebenzimidazole-*peri*-dicarboxylic acid with 1,2- and 2,3-diaminoanthraquinone, exhibit a large bathochromic shift towards reddish browns and browns.

## VI. DYES BASED ON NAPHTHALIC (NAPHTHALENE--1,8-DICARBOXYLIC) ACID

Interest in this group of dyes has arisen during the past four or five years. They are suitable for use as disperse dyes for the coloration of polyester, polyamide, polyvinyl, and polyethylene fibres. They are distinguished by brilliance, thermal stability, and excellent fastness to light, organic solvents, gas fumes, and sublimation.

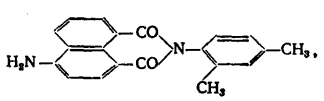
### 1. Preparation of Dyes

These dyes are obtained by the reaction of naphthalic acid with various substituted aromatic diamines (yellows and oranges with intense fluorescence) or *peri*-diamines (reds and violets) in an organic solvent. Derivatives of 1,2-*peri*-naphthoylenebenzimidazole are the most interesting. Many of its derivatives, with chlorine, bromine, alkyl, alkoxyl, hydroxyl, nitro, acylamino, etc. substituents, have been described in the patent literature[65-69]. Derivatives of this intermediate are also used, according to the patent literature, as intermediates for the synthesis of brown vat dyes[70].

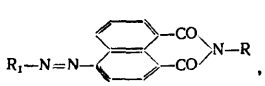


The process for obtaining naphthaloperinone dyes, which are formed by the reaction of naphthalic acid with naphthylene-1,8-diamine, is analogous to the preparation of naphthoylenebenzimidazole dyes[71-75]. A whole range of derivatives having various substituents has been patented[76-78]. Orange and red lakes for the mass coloration of polyamides and polyesters can be obtained by the sulphonation of some substituted naphthaloperinones, the resulting sulphonic acids being precipitated as their barium salts[79].

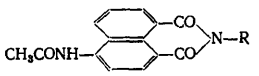
Naphthalimides are employed to a less extent as disperse dyes. They are obtained by the action of ammonia or primary amines on naphthalic anhydride. Among such dyes are Celliton Brilliant Yellow FF2



for cellulose acetate rayon, red and brown disperse dyes of the type[80]



and fluorescent brightening agents of the type[81,82]

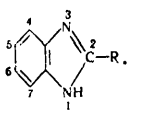


where R = H, Alk, Ar and $R_1$ = Ar.

The introduction of substituents into the dye produces a change in their shade. Nitration occurs especially readily; the resulting mono- or di-nitro-derivatives can be used firstly as individual dyes and secondly as intermediates for the synthesis of new compounds.

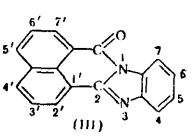
### 2. Substituted 1,2-*peri*-Naphthoylenebenzimidazoles

The work of Efros on the nitration of simple 2-alkyl and 2-aryl derivatives of benzimidazole showed that the presence of the imidazole ring in the benzimidazole molecule disturbs the distribution of electrons in the benzene ring, in the sense that the 5–6 bond approaches a single bond in character, while the 4–5 and 6–7 bonds become more nearly double bonds. This explains the unusual course of several substitutions, for example the dinitration of 2-methylbenzimidazole, when 2-methyl-5,6-dinitrobenzimidazole is formed[84].



Arient and Marhan[85] subjected 1,2-*peri*-naphthoylenebenzimidazole (III) and its 3'-, 4-, 4'-, 5-, 6-, and 7-nitro-derivatives to nitration. Each isomer was nitrated under identical conditions, by the action of the nitrating mixture on a solution of the original compound in concentrated sulphuric acid at 20°. The products were isolated by salting-out the solution into water. The course of the nitration was investigated chromatographically. The mono- and di-nitro-compounds formed were identified by comparing their electronic spectra with those of known specimens.

The nitration of 1,2-*peri*-naphthoylenebenzimidazole yields a single compound, which was identified as the 6-nitro-derivative. In the nitration of 4'-nitro-1,2-naphthoylenebenzimidazole, too, a nitro-group enters position 6, with the formation of 4',6-dinitro-1,2-*peri*-naphthoylenebenzimidazole, and the nitration of 3'(and 6')-nitro-1,2--*peri*-naphthoylenebenzimidazole yields 6,3'(and 6')--dinitro-1,2-*peri*-naphthoylenebenzimidazole



(III)

The high reactivity of position 6 is due to the activating effect of the non-acylated nitrogen in position 3, reaction at the *ortho* position in the benzene ring (position 4) evidently being sterically hindered. The activating influence of the lone electron pair on the other, acylated nitrogen in position 1 is distributed between the acylating part of the molecule and the benzene ring (in lesser degree). This result is fully consistent with mathematical calculation of

the electron distribution at individual carbon atoms in the naphthoylenebenzimidazole structure[86], according to which the reactivity of the carbon atoms diminishes in the sequence 6, 5, 6′, 3′.

Further nitration of derivatives of 1,2-*peri*-naphthoylenebenzimidazole in which the nitro-group is located in positions 4–7 in the benzene ring involves entry of the second nitro-group in position 6′. A nitro-group in position 5 or 7 prevents entry of the next nitro-group in position 6, which is the most active. A nitro-group in position 4 deactivates the benzene ring, and interferes with the activating influence of the lone electron pair of the non-acylated nitrogen.

In the synthesis of known derivatives of 1,2-*peri*-naphthoylenebenzimidazole, these workers have also investigated, apart from methods of preparation, the influence of substituents in *o*-phenylenediamine or in naphthalic acid on the course of the reaction[87].

Reaction of naphthalic anhydride with 4-nitrophenylene-1,2-diamine may yield 5- and 6-nitro-1,2-*peri*-naphthoylenebenzimidazole (IX) and (IV). The effect of the nitro-group on the basic character of the two amino-groups in nitro-*o*-phenylenediamine has not yet been accurately established, but the influence of the nitro-group in nitroanilines on the variation in pH is well known. The course of the reaction can be approximately predicted on the basis of these results. The weakening of electron density on the amino-nitrogen *para* to the nitro-group induces great reactivity in the second amino-group, and consequently preferential formation of *N*-(2-amino-5-nitrophenyl) naphthalimide (II: R = $NO_2$), which is converted with ring-closure into 6-nitro-1,2-*peri*-naphthoylenebenzimidazole (IV). In fact, the reaction of naphthalic anhydride with 4-nitrophenylene-1,2-diamine has been used to synthesise the 6-nitro-derivative (IV) as the main product, whereas the 5-nitro-isomer (IX) was formed in far smaller quantity; the latter was identical with a substance obtained from 2,4-dinitroaniline and naphthaloyl dichloride (XVI). Their interaction gave *N*-(2,4-dinitrophenyl)naphthalimide (XIV: R = $NO_2$), which was partly reduced, the resulting *N*-(2-amino-4-nitrophenyl)naphthalimide (VIII: R = $NO_2$) then being converted into the pure 5-nitro-isomer (IX). The yield of 6-nitro-1,2-*peri*-naphthoylenebenzimidazole from 2,5-dinitroaniline and naphthaloyl dichloride is not very high. The *N*-(2,5-dinitrophenyl)naphthalimide (XV: R = $NO_2$) formed in this reaction is hydrolysed to a considerable extent on reduction. The reactivity of 2,4-dinitroaniline is so low that it reacts only with the dichloride (XVI). A similar conclusion was reached by Krasovitskii and Matskevich, who obtained negative results for the reaction of naphthalic anhydride with nitroanilines[83].

The 4- and 7-nitro-1,2-*peri*-naphthoylenebenzimidazoles were obtained in an analogous manner. Reaction of 3-nitrophenylene-1,2-diamine with naphthalic anhydride gives only one of the two possible isomers, to which Arient and Marhan ascribe the structure 4-nitro-1,2-*peri*-naphthoylenebenzimidazole (XIX). The isomeric 7-nitro-derivative (XVIII) is formed by reaction of the dichloride (XVI) with 2,6-dinitroaniline. Owing to considerable steric hindrance, reaction takes place with great difficulty and gives a low yield.

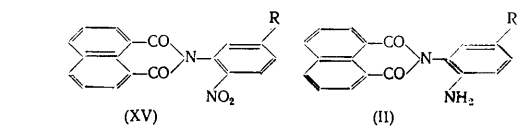
Naphthoylenebenzimidazole derivatives containing substituents in the naphthalene ring or in both the naphthalene and the benzene rings have been obtained by methods similar to that employed to obtain the benzene-substituted derivatives[85]. Reaction of 3-nitrophthalic acid with *o*-phenylenediamine and its mononitro-derivatives gave 3′(and 6′)-nitro- and 4,3′(and 6′)- and 6,3′(and 6′)-dinitro--1,2-*peri*-naphthoylenebenzimidazoles; 4-nitrophthalic acid similarly gave the 4′(and 5′)-nitro- and the 4,4′(and 5′)- and 6,4′(and 5′)-dinitro-derivatives.

An *ortho*-diamine containing a chlorine atom behaves in a more specific fashion than a nitro-derivative. Reaction of 4-chlorophenylene-1,2-diamine with naphthalic anhydride (I) begins at the amino-group *para* to the chlorine atom, the final product being 5-chloro-1,2-*peri*-naphthoylenebenzimidazole (X), which is identical with the compound prepared from 4-chloro-2-nitroaniline and naphthaloyl dichloride (XVI) by a method analogous to the synthesis of 5-nitro-1,2-*peri*-naphthoylenebenzimidazole. For comparison, 6-chloro-1,2-*peri*-naphthoylenebenzimidazole (V) was obtained also by Sandmeyer's reaction from the amine resulting from the reduction of the 6-nitro-derivative (IV).

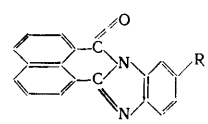
Naphthalic anhydride (I) was then made to react with 4-methylphenylene-1,2-diamine and 3,4-diaminobenzoic acid. In both cases reaction occurred with that amino--group which had become the more reactive under the influence of the remaining substituent. As was to be expected, 4-methylphenylene-1,2-diamine yielded mainly 5-methyl-1,2-*peri*-naphthoylenebenzimidazole (XI), together with a smaller quantity of the 6-methyl isomer. The isomers could not be separated chromatographically, but the acids obtained by their oxidation were separated chromatographically and identified. 1,2-*peri*-Naphthoylenebenzimidazole-5-carboxylic acid was obtained by oxidising pure 5-methyl-1,2-*peri*-naphthoylenebenzimidazole, prepared by fusing 4-methyl-2-nitroaniline with the anhydride (I). With permanganate or dichromate in sulphuric acid hardly any oxidation occurs (only traces of the corresponding acids were obtained).

Almost quantitative oxidation was accomplished by the action of oxygen in glacial acetic acid in the presence of a cobalt compound as catalyst.

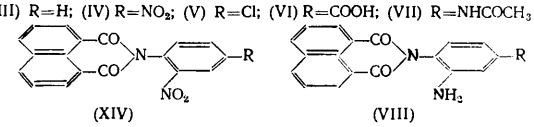
The final product of reaction of the anhydride (I) with 3,4-diaminobenzoic acid was 1,2-*peri*-naphthoylenebenzimidazole-6-carboxylic acid (VI).



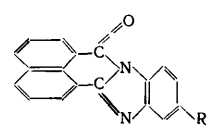
(XV) (II)



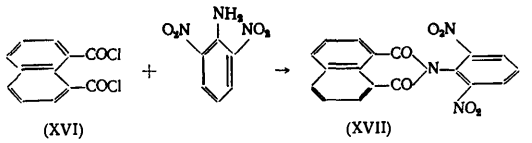
(III) R=H; (IV) R=$NO_2$; (V) R=Cl; (VI) R=COOH; (VII) R=$NHCOCH_3$



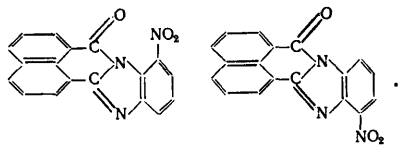
(XIV) (VIII)



(X) R=$NO_2$; (X) R=Cl; (XI) R=$CH_3$; (XII) R=COOH; (XIII) R=$NHCOCH_3$



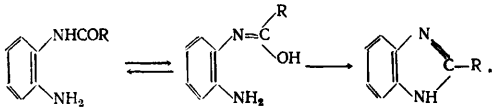
(XVI) (XVII)



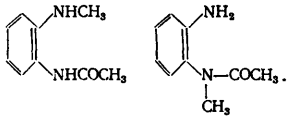
(XVIII) (XIX)

### 3. Interaction of Benzene-1,2,4,5-tetraamine with Dicarboxylic Acids

Many workers have investigated the reaction of aromatic *ortho*-diamines with carboxylic acids. Benzimidazoles were first obtained by this method by Phillips[88], by interaction of the components in boiling dilute hydrochloric acid. High yields were obtained with aliphatic acids, whereas aromatic acids reacted very feebly. Roeder and Day[89] explained the formation of benzimidazole compounds by a mechanism involving an intermediate monoacyl derivative



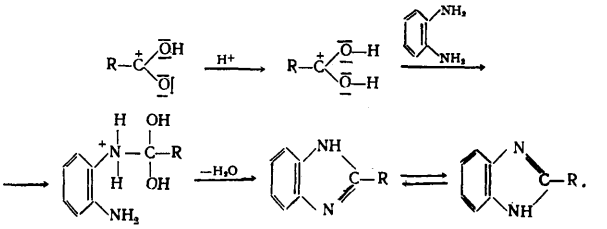
At the same time it was established that the postulated intermediate compound should be capable of enolisation, since the compound (II), unlike (I), is incapable of forming an imidazole ring.



(I) (II)

The synthesis of imidazole derivatives by Phillips' method has been widely investigated and developed by Soviet workers, who have established[90] that the concentration of hydrochloric acid used greatly affects the yield. The reaction was conducted by heating equimolecular quantities of the *ortho*-diamine with the carboxylic acid in dilute hydrochloric acid medium in sealed tubes at 150–180°. By this method 2-aryl derivatives were also obtained in high yields. With increase in the hydrochloric acid concentration the yield of the benzimidazoles first increased to a definite level, after which the yield fell again.

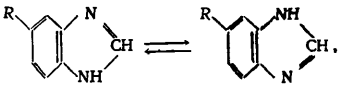
The optimum hydrochloric acid concentration differs for different carboxylic acids and also diamines. Hydrochloric acid forms salts with the amine, and this retards the reaction, since the amine reacts as the free base. The main factors determining the yield obtained are the concentration of the hydrochloric acid and the basic strength of the amine: it was concluded from the results[91,92] that hydrochloric acid of lower concentration must be used with amines which are stronger bases. However, the highest yield was achieved with *o*-phenylenediamine: other *ortho*-diamines, which were stronger or weaker bases, gave lower yields. The effect of the hydrochloric acid on the carboxylic acid is to diminish the ionisation of the latter, and the addition of a proton to the polarised oxygen atom of the carboxyl results in a positive charge on its carbon atom. From measurements of the dissociation constants of the acids, Porai-Koshits and Kharkharova drew the significant conclusion that reactivity decreases in the sequence — aralkane-, alkane-, and arene-carboxylic acid — and that the optimum concentration of hydrochloric acid should be higher the higher the degree of dissociation of the carboxylic acid. On the basis of these results a new mechanism was then proposed for the formation of benzimidazole derivatives



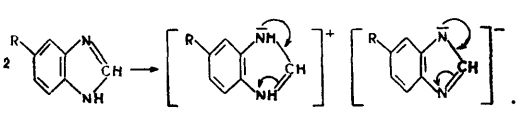
It has recently been established[93] that polyphosphoric acid could be used to obtain high yields of alkyl and aryl derivatives of benzimidazole.

Efros investigated substitution reactions in benzimidazole and its derivatives[94-97], and found that no clear substitution rules exist for the benzene ring in benzimidazole, although positions 5 and 6 are more active than the others. The nitration of benzimidazole, for example, yields only the 5,6-dinitro-derivative. His results demonstrated that, under the influence of the imidazole ring, the benzene ring loses its aromatic character, in the sense that the bond between the rings and the 4–5 and 6–7 carbon–carbon bonds approach double bonds in character.

The unsuccessful earlier attempts to isolate the two hypothetical isomers



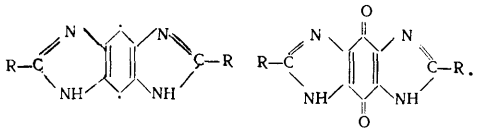
are explained by the ease of their tautomeric interconversion[98]. Study of the amphoteric character of benzimidazole proved significant for an understanding of some of its properties[99]. In acid medium it exists as a cation, whereas in alkaline medium its acid properties are developed, and the corresponding anion is formed. Among salts of benzimidazole, the greatest interest attaches to those which can be used for the gravimetric determination of certain metals. In neutral medium benzimidazole can exist in a state of equilibrium between the hypothetical cationic and anionic forms



Efros prepared[94] several derivatives of linear diimidazobenzene (III) by reducing 5,6-dinitrobenzimidazole, and

then treating the resulting *ortho*-diamine with a carboxylic acid. Whereas the first imidazole ring is formed readily under mild conditions, it was necessary to work under pressure to close the second ring. Both symmetrical and unsymmetrical derivatives can be obtained in this way. Earlier Kym and Ratner[100] had synthesised 2,6-dimethyldiimidazobenzene (V) by fusing 5,6-diaminobenzimidazole with anhydrous sodium acetate and acetic anhydride. This derivative was described also by Ruggli and Fischer[101], who synthesised it by the action of acetic anhydride on the substance obtained by reducing supposedly pure 4,6-diphenylazophenylene-1,3-diamine. The properties of substances described by different workers differ somewhat.

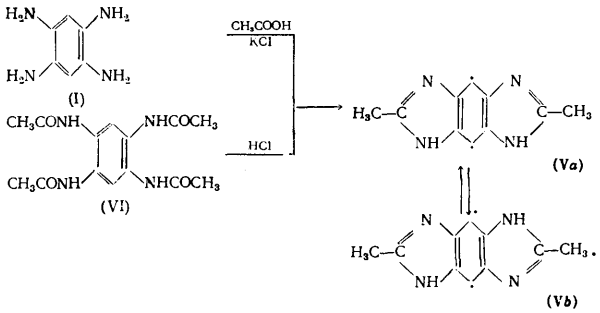
The above effect of the imidazole ring on the benzene ring in benzimidazole stabilises the double bond between the rings. This entails an increase in electronic charge at the free *meso* positions in the linear diimidazobenzene (III), which appears in their considerable radical unsaturation[102,103]. In their properties these compounds show a notable resemblance to anthracene, especially in their ease of oxidation to the quinones (IV).



(III) (IV)

Arient and Marhan have established[104] that the direction of the reaction depends on the medium in which it occurs. Prolonged boiling of the tetraamine with 90% acetic acid gives the linear 2,6-dimethyldiimidazobenzene (V). Heating the tetraamine (I) with acetic anhydride yields 1,2,4,5-tetraacetamidobenzene (VI) in addition to (V). In the presence of an equivalent quantity of anhydrous sodium acetate to neutralise the hydrogen chloride present in the tetrahydrochloride of the tetraamine, only (VI) is formed. Substitution in the imidazole ring obviously requires the presence of dissociated hydrochloric acid, which catalyses the reaction. In dilute acetic acid, where hydrochloric acid is liberated on hydrolysis of the benzene-1,2,4,5-tetraamine hydrochloride, only the diimidazo-derivative is formed.

In anhydrous medium, formation of the latter, which occurs to a considerably smaller extent, is accompanied by acetylation of the amino-groups of the tetraamine. In the presence of a substance which will combine with hydrogen chloride, ring-closure is completely suppressed, the sole process being acetylation of all the amino-groups. The resulting 1,2,4,5-tetraacetamidobenzene (VI) is stable in aqueous medium, and is not hydrolysed on being heated; boiling in hydrochloric acid readily converts it into the diimidazo-derivative with the elimination of two acetyl groups:



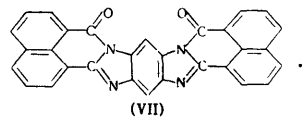
The two workers obtained the highest yield of (V) by treating the tetraamine with acetic acid in dilute hydrochloric acid medium under pressure at 180°. Their results agree well with those obtained by Porai-Koshits and his coworkers[90,91] in the synthesis of 2-alkylbenzimidazoles. In this case, too, the yield of benzimidazole first increased with increase in the concentration of hydrochloric acid, reached a definite maximum, and fell again.

Reaction in water and 5–20% hydrochloric acid gives the diimidazobenzene (V) as the main product. In more concentrated hydrochloric acid the hydrolysis of the benzenetetraamine hydrochloride, which itself cannot react, is in considerable measure suppressed, and a large part of it remains unchanged at the end of the reaction. Use of excess of acetic acid slightly increases the yield. The fine white crystalline needles of the compound (V) obtained are completely homogeneous, and their properties do not indicate the existence of two isomers (V*a*) and (V*b*). By analogy with benzimidazole it can be assumed that these represent two tautomeric forms of the same substance. The compound (V) is also amphoteric in character, dissolving in dilute acids and forming salts (mostly insoluble in the cold) with several metals.

The tetraamine reacts with formic, phenylacetic, and cinnamic acids under the same conditions as with acetic acid. With formic acid, the linear diimidazobenzene (III: R = H), similar in properties to the dimethyl derivative (V), is formed. Similarly, phenylacetic acid yields the 2,6-dibenzyldiimidazobenzene (III: R = $C_6H_5CH_2$), and 5-amino-2-benzyl-6-hydroxybenzimidazole as by a product. When cinnamic acid is used, the 2,6-distyryldiimidazobenzene (III: R = $C_6H_5CH:CH$), which possesses an intense fluorescence, is formed.

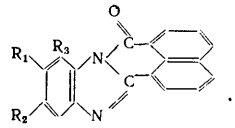
Benzoic acid and benzoyl chloride do not react with benzenetetraamine; nor does the more reactive *p*-nitrobenzoic acid give the expected compound, but decomposes under the reaction conditions. The behaviour of these acids had been investigated earlier[105].

On the basis of a study of the simpler linear diimidazobenzenes, Arient and Marhan attempted to obtain the bisaroyleneimidazo-derivative (VII) by reaction of the tetraamine with naphthalic acid[106].



(VII)

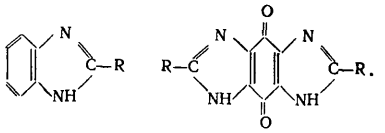
Instead of the suggested compound (VII), however, the principal reaction product was 5,6-diacetamido-1,2-*peri*-naphthoylenebenzimidazole (VIII). Doubt is cast on data given in a French patent[107], describing the preparation of a diimidazo-derivative, since a monoimidazole is also formed when the reaction is carried out under severe conditions — in boiling tetrahydronaphthalene — as indicated in the patent.



(VIII) $R_1 = R_3 = CH_3CONH$; $R_2 = H$; (IX) $R_1 = CH_3CONH$; $R = R_3 = H$; (X) $R_1 = CH_3COO$; $R_2 = R_3 = H$; (XI) $R_1 = R_2 = CH_3CONH$; $R_3 = CH_3$.

The main product contains, besides unchanged naphthalic acid, also 5-acetamido-1,2-*peri*-naphthoylenebenzimid-azole (IX) and 5-acetoxy-1,2-*peri*-napthoylenebenzimid-azole(X).

The formation of only one ring can be explained by distortion of the electron cloud of the benzene ring in the tetraamine resulting from the action of the aroyleneimidazole ring. A series of detailed investigations was made[108-111] on the effect of the imidazole ring on the electron distribution of the benzene ring in benzimidazole derivatives (XII). The results show that the benzene ring loses its aromatic character, and the bond between the rings approaches closely to a double bond in character. The simplest compounds of the diimidazo-type resemble anthracene in their chemical properties, mainly in their ease of oxidation to quinones (XIII).



(XII)



(XIII)

In conformity with this work, it may be supposed that the loss of symmetry and hence of aromatic character in the benzene ring of compound (VIII), resulting from the effect of the aroyleneimidazole structure, is so great that the 4–5 and 6–7 carbon–carbon bonds approach double bonds in character, while the 5–6 bond becomes more nearly a single bond. Consequently the carbon atoms at positions 5 and 6 appear as the two ends of the conjugated system of benzimidazole, which are subject to the action of the heterocyclic nitrogen atoms. This breakdown in the uniform distribution of the electron cloud of the benzene ring has an unfavourable effect on the formation of the diimidazo-compound.

The benzenetetraamine can be replaced in the synthesis of 5,6-diacetamido-1,2-*peri*-naphthoylenebenzimidazole (VIII) by 4,6-dinitrophenylene-1,3-diamine. This reacts in an analogous manner with naphthalic acid in glacial acetic acid medium on simultaneous reduction of the nitro-groups with iron. Application of the same method to 3,5-diphenylazotoluene-2,6-diamine gave the dye (XI), whose properties were analogous to those of the benzene derivative.

## 4. Mechanism of Interaction of Phthalic Anhydride with *o*-Phenylenediamine

Products of the condensation of *o*-phenylenediamine with phthalic anhydride were described in the earlier papers, the results being well known[112,113]. Depending on the stoichiometric proportions of the components and the reaction conditions, *o*-phthalimidoaniline (II), *o*-benzimidazol-2′-ylbenzoic acid (III), 1,2-*o*-benzoylenebenzimidazole (IV), *o*-bisbenzimidazol-2′-ylbenzene (V), and *o*-diphthalimidobenzene (VI) were obtained. By the reaction of phthaloyl dichloride with *o*-phenylenediamine, Stetter prepared[114] a compound having an eight-membered ring (VII). Porai-Koshits and Antoshul'skaya[115] investigated the production of compounds (III)–(VI) by fusing the components in various proportions, and found that the diphthaloyl derivative (VI) is formed with the greatest difficulty, whereas compounds (III) and (V), which contain imidazole rings, are more readily formed. The compound (IV), unlike other aroyleneimidazole compounds, exhibits properties characteristic of lactam rings, and can be cleaved to give *o*-benzimidazol-2′-ylbenzoic acid and its derivatives.

In order to explain the interrelationship of the individual stages in the conversion, Arient and Marhan examined the reaction of *o*-phenylenediamine with phthalic anhydride under mild conditions[116]. They found that two amino-compounds are formed initially, one existing for a very short time and being present in very small amount. This is probably the addition product (I). When the boiling point is reached, only the amino-compound (II) is present in the mixture, and the imidazole derivative (III) is formed. The composition of the mixture remains almost unchanged on further heating, the reaction product containing the two compounds in roughly equal proportions.

The reaction in methanol is considerably affected by the presence of hydrochloric acid. As its concentration increases, the quantity of the imidazole derivative (III) first increases at the expense of the amino-compound (II), and at the same time *o*-bisbenzimidazol-2′-ylbenzene (V) is also formed; when 0.5 equivalent of hydrochloric acid is used per mole of *o*-phenylenediamine, (V) becomes the main reaction product.

Further increase in the concentration of hydrochloric acid leads again to the formation of the amino-compound (II) as the final reaction product. The highest yield is obtained in the presence of one equivalent of hydrogen chloride; the amine hydrochloride which is formed crystallises out, and reaction ceases. The hydrochloric acid concentration is so decisive that variation in the relative proportions of the starting materials has no effect on the course of the reaction.

Reaction of *o*-phenylenediamine with phthalic anhydride at higher temperatures yields mainly *o*-benzimidazol-2′-ylbenzoic acid (III). In the presence of one equivalent of hydrochloric acid in water, the amino-compound (II) and traces of the imidazole derivative (III) are at once formed on heating, whereas in methanol the sole reaction product is the amino-compound (II). On further heating, the amount of the compound (III) increases, the proportions of the two compounds being 1 : 1 after 1 h and only compound (III) remaining after 2–3 h.

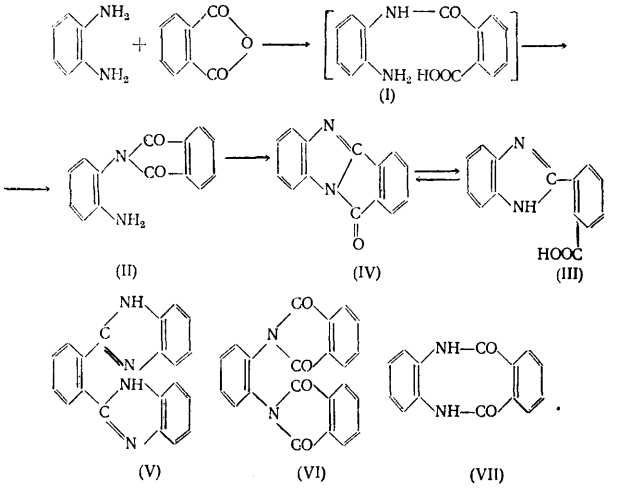
In the presence of hydrochloric acid under pressure at 180°, the reaction gives no typical maximum yield[90,91] at an optimum hydrochloric acid concentration, in contrast to the preparation of benzimidazole derivatives from *o*-phenylenediamine and monocarboxylic acids. The reaction in water is anomalous, with the formation of *o*-diphthalimidobenzene (VI).

In acetic acid reaction follows the same course as in water. As soon as the boiling point is reached, the initially formed amino-derivative (II) passes quantitatively into the imidazole (III) together with a small amount of 1,2-*o*-benzoylenebenzimidazole (IV) and the bisimidazole derivative (V). Reaction products of the same composition are formed in pyridine. The use of nitrobenzene accelerates the reaction and increases the quantity of 1,2-*o*-benzoylenebenzimidazole (IV) in the final product.

1,2-*o*-Benzoylenebenzimidazole (IV) is obtained from (II) and (III) by fusion at 250–290° or boiling in acetic anhydride. In contrast to 1,2-*peri*-naphthoylenebenzimidazole, which is readily formed when *o*-phenylenediamine and naphthalic acid are heated in acetic acid, the reaction of *o*-phenylenediamine with phthalic anhydride terminates under these conditions with the formation of the imidazole (III), the compound (IV) being present in the mixture in very small amount. Closure of the second five-membered ring requires great deformation of the molecule, which can be achieved under severe conditions.

Examination of the rearrangement of *o*-phthalimidoaniline (II) to *o*-benzimidazol-2'-ylbenzoic acid (III) revealed that the hydrochloride of the amino-compound remains unchanged even after heating in methanol for several hours, and the same result is obtained after adding various quantities of either hydrochloric acid or sodium carbonate. In water rearrangement occurs quantitatively after 2–3 h, and hydrochloric acid has no effect on the course of the reaction. High-boiling organic solvents (pyridine, acetic acid, nitrobenzene) accelerate the rearrangement, but the reaction product also contains 1,2-*o*-benzoylenebenzimidazole. Rearrangement leading to the formation of the imidazole derivative is, of course, facilitated by raising the temperature, and probably involves an intermediate stage of formation of 1,2-*o*-benzoylenebenzimidazole (IV), which in aqueous medium, however, is almost immediately hydrolysed to *o*-benzimidazol-2'--ylbenzoic acid (III).

If the process takes place in anhydrous medium (in acetic anhydride or on fusion), reaction stops at the first stage. In high-boiling solvents, partial hydrolysis by water formed in the reaction occurs. On the basis of the above results, the following mechanism has been suggested for the reaction.



5. Mechanism of Interaction of Naphthalic Acid with *o*-Phenylenediamine

Products of the interaction of naphthalic acid with *o*-phenylenediamine do not possess properties analogous to those of the benzene derivatives. These compounds have been described in less detail, and probably not always entirely correctly. Bistrzycki and Risi[118] obtained from *o*-phenylenediamine and naphthalic anhydride the amide (I), which on being heated to 230–240° was converted into 1,2-*peri*-naphthoylenebenzimidazole (m.p. 189°). Both compounds were later obtained by the same method by Chakravarti[119], who also described 8-benzimidazol-2'--ylnaphthoic acid (V). The 1,2-*peri*-naphthoylenebenzimidazole prepared in a similar manner[120,121] melted at 206°. Krasovitskii and Matskevich[122] obtained negative results for the reaction of naphthalic acid with *o*-nitroaniline, but by simultaneous reduction they isolated[123] *N*-*o*-aminophenylnaphthalimide (II) together with 1,2-*peri*--naphthoylenebenzimidazole (m.p. 189°). It is interesting that papers on the hydrolytic cleavage of benzimidazole derivatives make no mention of the possibility of the cleavage of naphthoylenebenzimidazole, although the analogous benzoylenebenzimidazoles are extremely labile to hydrolysis.

In a study of the interaction of *o*-phenylenediamine with naphthalic acid, Arient and Marhan established that the temperature of the medium has a decisive influence on the direction of the reaction[124]. At temperatures up to 60° in various solvents, the amide (I) is gradually formed, and from it *N*-*o*-aminophenylnaphthalimide (II). In all cases the final reaction product is the imide (II), containing a minute amount of 1,2-*peri*-naphthoylenebenzimidazole (IV).

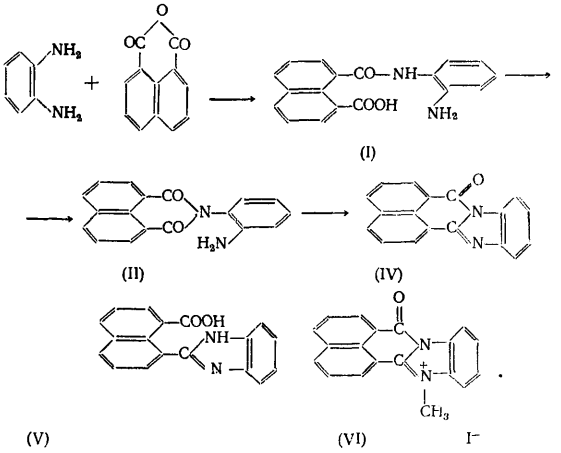
The undoubted formation of the amino-compound (II) is not consistent with results obtained for the reaction of *o*-phenylenediamine with phthalic anhydride. In the latter case not only amino-compounds of types (I) and (II) but also *o*-benzimidazol-2'-ylbenzoic acid and *o*-bisbenzimidazol-2'-ylbenzene are formed under analogous conditions. The proportions of these products are decisively affected by the content of hydrochloric acid in the reaction mixture.

When naphthalic acid is used, analogous benzimidazole derivatives are not formed with the most varied changes in reaction medium.

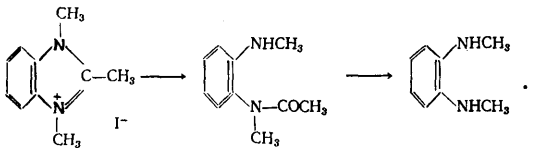
Interaction at higher temperatures leads to the formation of 1,2-*peri*-naphthoylenebenzimidazole. Reaction occurs very readily, especially in boiling acetic acid, and with a quantitative yield, as well as when *N*-*o*-aminophenylnaphthalimide or the starting materials are heated. The course of the reaction is not affected by additions of various quantities of hydrochloric acid, which is the effective agent in the synthesis of benzimidazole derivatives.

The 1,2-*peri*-naphthoylenebenzimidazole obtained is very stable, and does not undergo cleavage on prolonged boiling or heating at higher temperatures under pressure, either in acid or in alkaline medium. This distinguishes it significantly from the analogous 1,2-*o*-benzoylenebenzimidazole, which is so readily hydrolysed that the final reaction product from *o*-phenylenediamine and phthalic anhydride is *o*-benzimidazol-2'-ylbenzoic acid. An absolutely anhydrous medium is required for the preparation of 1,2-*o*-benzoylenebenzimidazole. The great stability of 1,2-*peri*-naphthoylene-1',2'-benzimidazole means that the reaction of *o*-phenylenediamine with naphthalic acid does not proceed beyond the stage at which it is formed, and the postulated imidazole derivative (V) cannot be obtained.

The following reaction mechanism has been suggested on the basis of the above results



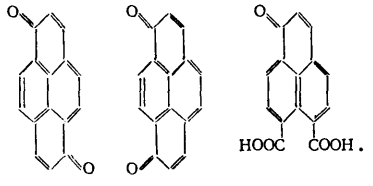
Several methods have been developed for cleaving the imidazole ring in benzimidazole derivatives, among which the most convenient is in most cases alkaline hydrolysis of the 1,2,3-trialkyl derivatives[125-127]



1,2-*peri*-Naphthoylenebenzimidazole forms with methyl iodide a methiodide (VI). Even in this case, however, the naphthoylenebenzimidazole derivative behaves differently from simple benzimidazoles. This compound (VI) is as stable as the original 1,2-*peri*-naphthoylenebenzimidazole, and is not cleaved by any of the usual methods.

## VII. DYES BASED ON PYRENIC ACID

The oxidation of pyrene yields naphthalene-1,4,5,8--tetracarboxylic acid, a necessary intermediate for the synthesis of several vat dyes. A mixture of pyrene-1,6- and -1,8-quinones (I) and (II) can be isolated as intermediate oxidation products, together with 1-oxophenalene--6,7-dicarboxylic acid (III), which is termed pyrenic acid in the literature.



(I) (II) (III)

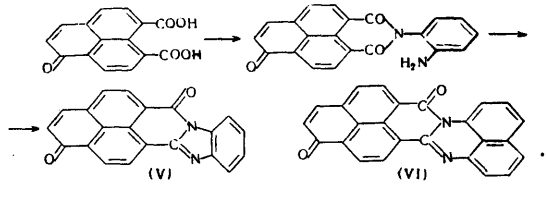
Pyrenic acid was first obtained by Hintz[128], and isolated in pure form by Goldschmiedt[129], its structure later being determined by Bamberger and Philip[46]. More recently its preparation has been mentioned in a paper by Vollmann et al.[130] The only method available for preparing pyrenic acid is that given by Bamberger and Philip, who oxidised pyrene in aqueous suspension with a slight excess of chromic mixture (6 instead of 5.3 moles calculated as chromium trioxide). Oxidation is not complete. Pyrenic acid was isolated from the reaction products by extraction with dilute sodium carbonate solution at 50°. The residue remaining after extraction was again subjected to further oxidation. Complete oxidation of the pyrene was achieved after six repetitions of the oxidation process. The yield of the unpurified acid is 20.6%. Our results indicate that, apart from resinous impurities, this acid still contains ~20% of naphthalene-1,4,5,8-tetracarboxylic acid. The pyrenic acid is purified by several recrystallisations from acetic acid. The yield of the pure acid was not indicated in the early work[46]. Its anhydride, obtained by prolonged heating above 100°, does not melt, but chars at 260°. Vollmann gives for it m.p. 174°. In a more detailed study of the oxidation of pyrene to pyrenic acid in aqueous suspension, Arient and Dvořák established that the low yield of the acid is due to the fact that a large proportion of the pyrene is oxidised to compounds which dissolve readily in water, or to carbon dioxide.

A method was developed for the identification of naphthalene-1,4,5,8-tetracarboxylic acid which consisted in treating it with *o*-phenylenediamine to form a scarlet aroyleneimidazole dye. Pyrenic acid, which gives a yellow spot on a chromatogram, is converted into a brownish-orange dye by reaction with *o*-phenylenediamine.

Bromination of pyrenic acid in acetic acid yields a monobromo-derivative. Neither increasing the excess of bromine nor prolonging the duration of reaction produces further bromination. The bromine is probably present in position 2 in pyrenic acid, by analogy with the bromination of pyrenequinone, in which the bromine enters positions 2 and 7, and also from the fact that oxidation of the brominated pyrenic acid with alkaline hypochlorite solution yields naphthalene-1,4,5,8-tetracarboxylic acid containing no bromine.

Reaction of pyrenic acid or its bromo-derivative with *ortho*- or *peri*-diamines of the benzene or naphthalene series in glacial acetic acid gives an almost theoretical yield of aroyleneimidazole (V) or naphthaloperinone (VI) dyes[117].

A mixture of *cis* and *trans* isomers can theoretically be formed by the reaction. However, the compounds obtained could not be separated into two isomers either by the usual methods or chromatographically. The dyeing properties also indicate that the dyes are single compounds. It may be suggested that, under the influence of the keto--group in the nucleus of pyrenic acid, the electron density will decrease on the carbonyl carbon nearer to the keto--group, which after initial formation of the corresponding imide will take part preferentially in formation of the imidazole ring:



Unlike the products obtained from naphthalic acid, these substances are vatted with *ortho*- or *peri*-diamines. Some of the dyes of this type and their characteristic properties are listed in the accompanying Table.

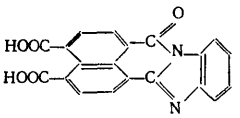
Bromination of the dye obtained from pyrenic acid and *o*-phenylenediamine yields monobromo- and dibromo--derivatives. The first bromine atom enters the ring containing the keto-group, probably at position 4. The monobromo-derivative is identical with the product of the interaction of 4-bromopyrenic acid and *o*-phenylenediamine. Oxidation of the monobromo-derivative with hypochlorite or with alkaline potassium permanganate solution gives naphthoylenebenzimidazole-*peri*-dicarboxylic acid, which contains no halogen.

The second bromine atom enters the benzene ring of the imidazole. Oxidation with hypochlorite yields naphthoylenebenzimidazole-*peri*-dicarboxylic acid (VII) containing one bromine atom in the molecule. More severe oxidation with chromium trioxide in acetic acid forms a tetracarboxylic acid containing no bromine, to which the structure (VIII) has been assigned on the basis of the work of Bamberger and Berlé[131] and of Efros and his coworkers,

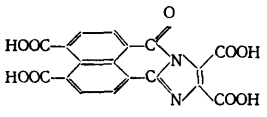
TABLE.

| Acid | Diamine | Colour of dye | Colour of vat | Shade |
|---|---|---|---|---|
| Pyrenic | *o*-phenylene-diamine | yellowish brown | orange with green fluorescence | brownish orange |
| » | 4-chlorophenyl-ene-1,2--diamine | ditto | ditto | reddish brown |
| » | 4-ethoxyphenyl-ene-1,2--diamine | reddish brown | » | pure brown |
| » | naphthylene--1,2-diamine | dark brown | orange | violet-brown |
| » | naphthylene--1,8-diamine | blue-black | red | khaki |
| Monobromo-pyrenic | *o*-phenylene-diamine | brownish orange | orange with green fluorescence | orange-brown |

and which forms with *o*-phenylenediamine orange-coloured reaction products.



(VII)



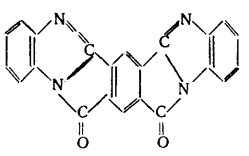
(VIII)

The aroylenebenzimidazole or aroyleneperinone dyes obtained give interesting and brilliant shades on cotton from a vat, but these are less fast to washing than shades obtained with available vat dyes.

## VIII. DYES BASED ON BENZENE-1,2,4,5-TETRACARBOXYLIC ACID

Benzene-1,2,4,5-tetracarboxylic acid has attracted the attention of chemists because of the possibility of obtaining dyes analogous to those of the aroyleneimidazole series from naphthalene-1,4,5,8-tetracarboxylic acid. Little work has been done on the reactions of pyromellitic acid, apart from the formation of functional derivatives. The preparation of complex compounds with thiourea has been described[132], and also the use of pyromellitic anhydride with 2-methylquinoline for the synthesis of benzoindanones[133].

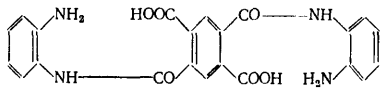
The only mention of the reaction of this acid with aromatic diamines is contained in a Swiss paper of 1941, which describes also 1,2,4,5-benzoylene-1′1′,1″,2″-dibenzimidazole[134]. The paper describes the preparation of the *trans* isomer of terephthaloylenebisbenzimidazole (I) by fusing pyromellitic anhydride with the appropriate quantity of *o*-phenylenediamine. The structure of this compound was postulated without further explanation, and was supported by elementary analysis.



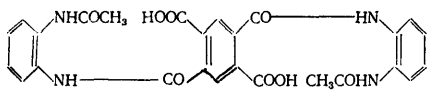
(I)

Formation of the *trans* isomer would be of great interest for the dye industry, since by using various substituted *o*-phenylenediamines it would be possible to obtain a range of dyes which could be vatted and would be of interest as disperse dyes.

Arient and Havlíčková have obtained the compounds (II) and (III) together with a mixture of other products by the reaction of *o*-phenylenediamine with pyromellitic acid in acetic acid[135].

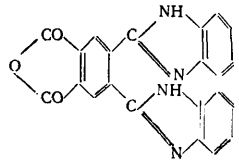


(II)



(III)

Reaction of *o*-phenylenediamine with pyromellitoyl tetrachloride in chlorobenzene gave a mixture of two compounds, which were separated by means of their solubility difference. One of them could be vatted in ammoniacal medium, from which it colours cotton an orange shade; this is the *trans* isomer of terephthaloylenebisbenzimidazole (I). The second substance could not be vatted, melts above 400°, and has the structure (IV).



(IV)

## IX. DYES BASED ON PHTHALIC ACID

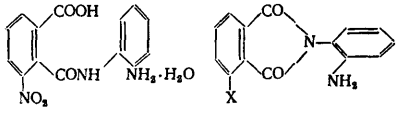
The mechanism of the interaction of *o*-phenylenediamine with monocarboxylic and *ortho*- or *peri*-dicarboxylic acids presupposes the initial addition of the lone pair of electrons on the amino-nitrogen to the carbonium ion formed by protonation of the carboxy-group. According to this mechanism a carboxy-group having a diminished electron density on the carbon atom will react preferentially. The magnitude of the electron density on the carboxy-carbon will depend on the nature and position of substituents in the aromatic ring of the carboxylic acid. Krasovitskii et al.[136] point to the formation of a single isomer of naphthoylenebenzimidazole when 4-nitronaphthalic acid reacts with *o*-phenylenediamine. On the above considerations this isomer was assumed to be 1,2-(4-nitronaphth-1,8-oylene)benzimidazole. A similar conclusion was drawn by Arient and Marhan when discussing the results of the reaction of various nitronaphthoic acids with *o*-phenylenediamine and of nitro-*o*-phenylenediamine with naphthalenedicarboxylic acid[87,116].

Nitro- and acetamido-groups present in phthalic anhydride should exert different effects on the formation of nitro- and acetamido-benzoylenebenzimidazoles respectively: 3-nitrophthalic anhydride should yield 1,2-(6′-nitrobenz-1′,2′-oylene)benzimidazole (VII), and 4-nitrophthalic

anhydride the corresponding 4'-nitro-derivative (XIII) or the corresponding intermediate products. The acetamido--group should have the opposite effect: 3-acetamidophthalic anhydride should give 1,2-(3'-acetamidobenz--1',2'-oylene)benzimidazole (XXIII), and 4-acetamidophthalic anhydride the corresponding 5'-acetamido--derivative (XXV).[152]

Paper chromatography indicates that four compounds are formed by the reaction of 3-nitrophthalic anhydride with *o*-phenylenediamine. Among them have been identified 2-benzimidazol-2'-yl-3-nitrobenzoic acid (V), 1,2-bisbenzimidazol-2'-yl-3-nitrobenzene (IX), and the hydrate of 2-*o*-aminophenylcarbamoyl-3-nitrobenzoic acid (I). The fourth compound could be neither isolated nor identified. The corresponding 1,2-(6'-nitrobenz-1',2'--oylene)benzimidazole (VII) was obtained by subliming the benzimidazolylbenzoic acid (V) or boiling it in acetic anhydride.

Reduction of (V) and (IX) followed by acetylation of the resulting amino-derivatives effected the synthesis of 3-acetamido-2-benzimidazol-2'-ylbenzoic acid (VI) — together with 1,2-(6'-acetamidobenz-1',2'-oylene)benzimidazole (VIII) — and 3-acetamido-1,2-bisbenzimidazol--2'-ylbenzene (X).

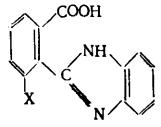


(I)

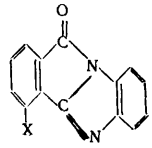


(II)

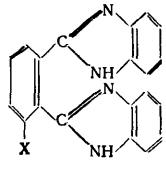
(II) X=$NO_2$;
(III) X=$NH_2$;
(IV) X=$NHCOCH_3$



(V) X=$NO_2$;
(VI) X=$NHCOCH_3$;

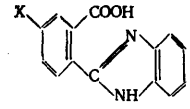


(VII) X=$NO_2$;
(VIII) X=$NHCOCH_3$.

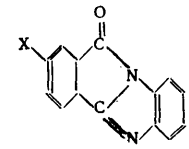


(IX) X=$NO_2$;
(X) X=$NHCOCH_3$.

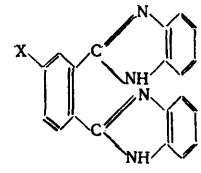
All three compounds formed by the reaction of 4-nitrophthalic anhydride with *o*-phenylenediamine — 2-benzimidazol-2'-yl-5-nitrobenzoic acid (XI), 1,2-bisbenzimidazol-2'-yl-4-nitrobenzene (XVI), and 2-*o*-aminophenylcarbamoyl-5-nitrobenzoic acid (XIX) — have been identified. 1,2-(4'-Nitrobenz-1',2'-oylene)benzimidazole (XIII) is formed only when the benzimidazole (XI) is sublimed or is boiled in acetic anhydride; it was not detected among the initial reaction products. Reduction of the diimidazole (XVI) followed by acetylation gave 4-acetamido-1,2-bisbenzimidazol-2'-ylbenzene (XVIII); reduction of the benzimidazole (XI) gave the amino-derivative (XII), which on being boiled in acetic acid was converted into 1,2-(4'-acetamidobenz-1',2'-oylene)benzimidazole (XV). The same substance was obtained also by the acetylation of (XIV), synthesised from the amino-acid (XII) by sublimation.



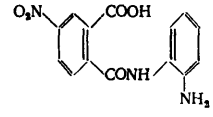
(XI) X=$NO_2$;
(XII) X=$NH_2$;



(XIII) X=$NO_2$;
(XIV) X=$NH_2$;
(XV) X=$NHCOCH_3$.



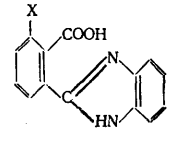
(XVI) X=$NO_2$;
(XVII) X=$NH_2$;
(XVIII) X=$NHCOCH_3$.



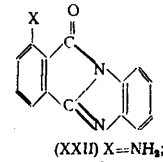
(XIX)

Reaction of 3-acetamidophthalic anhydride with *o*-phenylenediamine yields seven compounds — 1,2-(3'-aminobenz--1',2'-oylene)benzimidazole (XXII) and its *N*-acetyl derivative (XXIII), 2-amino-6-benzimidazol-2'-ylbenzoic acid (XX) and its *N*-acetyl derivative (XXI), 3-acetamido--1,2-bisbenzimidazol-2'-ylbenzene (X), 3-amino-*N*-*o*--aminophenylphthalimide (III), and 3-acetamido-*N*-*o*--aminophenylphthalimide (IV).

Hydrolysis of the acetyl group is observed not only on reaction in dilute hydrochloric acid under pressure but also under milder conditions, even in methanol.

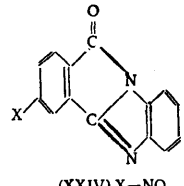


(XX) X=$NH_2$;
(XXI) X=$NHCOCH_3$

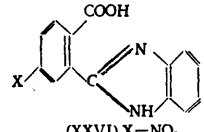


(XXII) X=$NH_2$;
(XXIII) X=$NHCOCH_3$

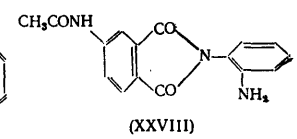
Paper chromatography indicates that six compounds are formed by the interaction of 4-acetamidophthalic anhydride and *o*-phenylenediamine, but of these only 4-acetamido--*N*-*o*-aminophenylphthalimide (XXVIII) could be isolated. From a chromatographic comparison of the reaction products with known specimens, the structure 4-amino--1,2-bisbenzimidazol-2'-ylbenzene (XVII) was assigned to the compound having $Rf$ = 0.6 and yellow fluorescence, the structure of its *N*-acetyl derivative (XVIII) to the compound having $Rf$ = 0.62 and green fluorescence, and the structure of 4-amino-2-benzimidazol-2'-ylbenzoic acid (XXVII) to the compound having $Rf$ = 0.89.



(XXIV) X=$NO_2$
(XXV) X=$NHCOCN_3$



(XXVI) X=$NO_2$
(XXVII) X=$NH_2$

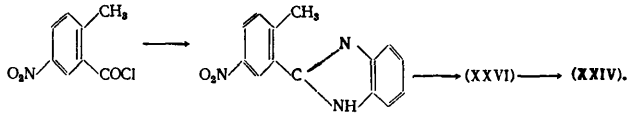


(XXVIII)

Comparison of the ultraviolet spectrum of 1,2-(6'-acetamidobenz-1',2'-oylene)benzimidazole (VIII), prepared by

reducing the 6'-nitro-derivative (VII), with that of the 3'-acetamido-derivative (XXIII) has demonstrated unequivocally that the nitro-group and the acetamido-group exert differently directed effects on the reaction of *o*-phenylenediamine with the corresponding substituted phthalic anhydrides.

The structure of 1,2-(4'-nitrobenz-1',2'-oylene)benzimidazole is supported by the difference between its ultraviolet spectrum and that of the 5'-nitro-derivative (XXIV), synthesised by the scheme

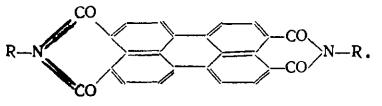



Reaction of 3- and 4-nitrophthalic anhydrides with *o*-phenylenediamine leads to the formation of intermediate products, which on subsequent treatment give 6'- and 4'-nitro-1,2-benz-1',2'-oylenebenzimidazole (VII) and (XIII) respectively. The acetamido-group, on the other hand, yields the opposite results, reaction of 3- and 4-acetamidophthalic anhydride with *o*-phenylenediamine giving 1,2-(3'-aminobenz-1',2'-oylene)benzimidazole (XXII) and 4-amino-2-benzimidazol-2'-ylbenzoic acid (XXVII).

## X. DYES BASED ON PERYLENE-3,4,9,10-TETRACARBOXYLIC ACID

Perylene-3,4,9,10-tetracarboxylic acid does not, on reaction with *ortho*-diamines, form compounds having desirable dyeing properties. With aliphatic and aromatic monoamines, however, interesting red dyes are obtained, which can be applied as vat dyes[137-139] or pigments[140].

Among vat dyes are known Indanthren Red 2G (R = $CH_3$) and Indanthren Scarlet R ( R = *p*-$CH_3OC_6H_4$).




Brilliant red vat dyes are obtained by introducing other vattable groups into the molecule[141,142]. Small changes in shade can be achieved by also introducing substituents into the dye, e.g. by chlorination or nitration[143,144].

The only dyes which differ in colour from the wide range of red dyes are those obtained by the reaction of perylene-3,4,9,10-tetracarboxylic acid with acrylonitrile and with aminopropionitrile, which are very good grey vat dyes[145].

A well-known pigment used for the colouring of plastics, especially poly(vinyl chloride)[140], is PV Fast Red B,[146] the bis-3,5-dimethylphenylimide of perylenetetracarboxylic acid, which is used for the mass coloration of poly(vinyl chloride)[140] and polyamides. It is employed under the name Permanent Red B Extra[147] for oil varnishes and cellulose nitrate varnishes.

## XI. DYES BASED ON VARIOUS DICARBOXYLIC ACIDS

Mainly browns have been obtained from other carboxylic acids which are capable of giving aroyleneimidazole dyes with *ortho*-diamines. The patent literature gives many such examples, but it is most likely that none of these dyes has yet been produced on an industrial scale. The most promising representatives of this group are dyes based on benzanthrone-3,4-dicarboxylic[148] and anthraquinone-2,3-dicarboxylic[125,149,150] acids. Dyes obtained from these acids can apparently be applied as vat and disperse dyes.

## XII. REACTIVE AROYLENEIMIDAZOLE DYES

Reactive yellow and red dyes have been obtained by reaction with cyanuryl chloride of both vattable and non-vattable aroyleneimidazoles of the naphthalene and perylene series containing an amino-group[126,127].

## XIII. AROYLENEIMIDAZOLE DYES FORMED ON THE FIBRE

In 1956 a process was patented for producing aroyleneimidazole dyes directly on the fibre[151]. A di- or tetracarboxylic acid is mixed with a diamine and a substance which will promote the reaction (a relatively non-volatile organic acid, e.g. lactic acid), the resulting paste is printed on cotton cloth, and the dye is developed by steaming the cloth or heating it to 120–130°.

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# CATALYTIC METHODS OF PREPARING ALIPHATIC AND ALICYCLIC AMINES

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## I. INTRODUCTION

The chemistry of amines has long attracted the attention of research workers. In particular there are numerous papers on the chemistry of the aromatic amines, but during the past decade more and more papers on the aliphatic and alicyclic amines and on catalytic methods of synthesising them have appeared. These compounds have been the object not only of theoretical investigations but also of a number of investigations connected with the solution of important scientific and technical problems. Information on the aliphatic and alicyclic amines has not been unified and there are no review papers on this important branch of chemistry in recent literature. The well known review paper of Emerson[1] appeared in 1949 and, of course, does not contain material published later.

Aliphatic amines were first discovered by Würtz in 1849 [2] in distilling isocyanates with potassium hydroxide:

$$R{-}N{=}C{=}O + 2KOH \longrightarrow RNH_2 + K_2CO_3.$$

At present there are a number of general and particular methods of synthesising amines. Catalytic methods are the most widely used. The methods are very diverse both with regard to the starting materials and to the catalysts employed; by changing the reaction conditions the yield of primary, secondary, and tertiary amine can be altered as required. Alcohols, ethers, halogen derivatives, aldehydes, ketones, nitrogen-containing compounds, and unsaturated hydrocarbons are used as starting materials for the synthesis of amines. Catalysts have been proposed with the aid of which some amines may be converted into others. Because of the extensive literature on this problem, we considered it expedient to deal only with problems connected with amines proper and not consider amino-derivatives with other functional groups.

Amines are produced in large tonnages by the basic organic synthesis industry. They are used in the production of plastics, explosives, dyes, artificial fibres, and in a number of other branches of industry. For example, vinylamines are used as inhibitors in the polymerisation of vinyl acetylene [3] and also as accelerators in vulcanisation [4] and in the dyeing of polyacrylic fibres [5]. Primary, secondary and tertiary amines are used as addition compounds with boranes in the reduction of organic compounds [6]. Secondary aliphatic amines are used in the synthesis of enamines, the polymerisation and copolymerisation of which yield auxiliary materials used in the textile industry and in the production of plastics [7]. Some higher primary amines, for example, palmitylamine and stearylamine, give auxiliary materials for the textile industry when condensed with hydroxymethylamides [8]. Primary and secondary aliphatic amines are used for the preparation of aminoacroleins [9]. Aliphatic amines with 2 to 20 carbon atoms in the molecule are used as additives to bind metallic impurities in the distillation of alcohols obtained by the hydroformylation of alkenes and subsequent reduction of the aldehydes formed by hydrogen on a nickel catalyst [10]. In connection with reports that some high-molecular primary alkylamines suppress the development of the tubercule bacillus, 1-aminododecane, 2-aminotridecane, and 3-aminotridecane have been synthesised and show the maximum activity *in vitro* [11]. It has been shown that primary amines containing no more than five carbon atoms in the molecule ignite on mixing rapidly with highly concentrated nitric acid and can be used as fuel for liquid reaction engines; branching of the hydrocarbon chain in the amine molecule reduces the rate of ignition [that is, increases the ignition delay (Ed. of Translation)]; on the other hand, an increase in the number of alkyl groups attached to the amino-group increases it. A solution of triethylamine in 2,6-xylidine was used by the Germans under the name "Tonka 250" as a fuel for rocket engines. A mixture of stereoisomeric 2,7-diaminooctanes is used for the preparation of polyamides from adipic acid. In the polycondensation, polyamides with a molecular weight of ~ 50 000 are formed [12]. The secondary diamines

$$C_2H_5NHCR_2(CH_2)_n\,CR_2NHC_2H_5$$

(where R = $CH_3$ or $C_2H_5$ and $n$ = 2–7) have been synthesised for tests of ganglionolytic activity; the greatest activity is found when $n$ = 4 and R = $C_2H_5$. [13] Aliphatic amines of the type $(CH_3)_2NH$ etc. are used for the synthesis of some ethanolamines with spasmolytic properties. For example,

4-methoxy-ω-chloroacetophenone and dimethylamine yield the effective 4-hydroxy-ω-dimethylaminoacetophenone[14].

Midzhoyan and coworkers[15] carried out investigations in the field of amines and their derivatives with the object of preparing some chloroacetamides and urethanes. Compounds of the general formula

$$p\text{-}ROC_6H_4CH_2CH_2NHCOCH_2Cl$$

where R = $CH_3$, $C_2H_5$, $C_3H_7$, iso-$C_3H_7$, $C_4H_9$, iso-$C_4H_9$, have been synthesised by the following scheme:

$$p\text{-}ROC_6H_4CH_2Cl + NaCN \longrightarrow p\text{-}ROC_6H_4CH_2CN,$$
$$p\text{-}ROC_6H_4CH_2CN + H_2 \longrightarrow p\text{-}ROC_6H_4CH_2CH_2NH_2;$$
$$p\text{-}ROC_6H_4CH_2CH_2NH_2 + ClCH_2COCl \longrightarrow p\text{-}ROC_6H_4CH_2CH_2NHCOCH_2Cl.$$

Changes in the anticonvulsant action of compounds of the type $p$-$ROC_6H_4CH_2CH_2NHCOCH_2Cl$ have been studied. With R increasing, amines of the type $p$-$ROC_6H_4CH_2CH_2NH_2$ have also been used for the synthesis of some urethanes of interest because of their cancerolytic activity.

Khorlin and coworkers synthesised tertiary aliphatic amines with ganglionolytic activity. The amines obtained were subjected to pharmacological examination[16].

Kyo Fujie[17] synthesised seven derivatives of 2-(diphenylmethoxy)ethylamine and six derivatives of 3-(diphenylmethoxy)propylamine and tested them for papaverine-like anticonvulsant activity. The tests were carried out on smooth muscle from the rat uterus, the mouse intestine, and tracheal muscles of the guinea-pig.

Bonvicino and coworkers synthesised the hypnotics xanthene- and thioxanthene-$\Delta^{9\gamma}$-propylamines and related compounds[18].

Ryan and coworkers synthesised halogenoethyl-derivatives of acetyleneamines and carried out pharmacological tests on rats[19]. The greatest activity was found in compounds having the t-butyl group on a nitrogen atom and also having a methyl group.

Björn[20], in a search for new anaesthetics and a study of the effect of structure on physiological activity, prepared s-butylaminoacetanilides. It was shown that the introduction of a methyl-group on the α-C-atom in the amine part of the molecule does not always increase the anaesthetic activity, but it always increases the toxicity; it was shown that replacement of the isopropyl by a s-butyl group on the nitrogen, with the remainder of the molecule unchanged, increases both the anaesthetic activity and the toxicity.

In the presence of small quantities of orthoboric acid, polyamides are obtained from diamines (trimethylenediamine, etc.) and high-molecular-weight fatty acids; these are used as antioxidants for plastics[21]. Resin amines are used for the preparation of effective inhibitors of the corrosion of steel and other metals[22]. *N*-Substituted acrylamides, required for polymerisation and copolymerisation, are obtained by the dehydration of *N*-substituted hydracrylamides, which are synthesised by the reaction of β-propiolactone with amines in the presence of water[23]. Some amines, for example methylamine, are used technically for condensation with *l*-acetylphenylmethanol in the presence of a platinum catalyst[24]. Amines are also used for the stabilisation of sorbic acid salts[25]. 1,4,7-Triazaheptane is used with ethylene oxide for the preparation of polyhydroxyethylated polyamino-compounds (1,11-dihydroxy-3,6,9-triazaundecane-*NN'N''*-triacetic acid) which form water-soluble complexes with the metals calcium, barium, strontium, magnesium, iron, cobalt, nickel, copper, zinc, manganese, and aluminium. The iron complex is used in agriculture for supplying iron to citrus plants growing on calcareous soil[26]. Accelerators for the dyeing of acrylonitrile fibres with anionic dyes are obtained by the reaction of acrylonitrile with mono-, di-, and poly-amines[27]. New complexes are synthesised from isocyanates and tertiary amines[28]. Diaminoalkenes are used commercially as additives to fuel to increase the rate of combustion[29]. Methylamines are used in the leather industry, for the preparation of rubber vulcanisation accelerators, and for the production of explosives, bactericides, and pharmaceutical preparations[30]. Cyclohexylamine is used in making emulsifiers, anticorrosion coatings, rubber vulcanisers, etc.[31] The literature cited on the uses of amines is not exhaustive, but it illustrates the great diversity of uses for amines in different branches of the economy.

## II. METHODS OF SYNTHESISING ALIPHATIC AMINES

The methods of synthesis of aliphatic amines and the conditions for the preparation of these reactive and labile compounds are very diverse. The methods differ substantially according to the nature of the starting materials and for this reason the methods are arranged here according to the nature of the materials being aminated.

### 1. Amination of Alcohols

Baum[32] considers that of all the dehydrating catalysts for the preparation of amines from alcohols or ethers the best catalyst is aluminium oxide. He studied the amination of n-propyl, n-butyl, isobutyl, and isopentyl alcohols and n-dibutyl ether at 220–550°. It was found that the optimal temperature lies within the range 200–350° for primary alcohols, 300–530° for secondary, and 400–550° for tertiary alcohols. The ratio of the quantity of ammonia to alcohol has a substantial effect on the relative amounts of amines formed. If primary amines are to predominate, the molar ratio alcohol:ammonia should be 4:1; for the formation of secondary amines from normal alcohols this ratio should be 2:1 or 3:1; and for iso-alcohols it should be 1:1. The contact time has a considerable effect on the amine yield. On the basis of his interpretations of the mechanism of catalytic amination, the author recommends that a small quantity of water should be introduced into the alcohol–ammonia or ether–ammonia system. It was found that this addition increases the yield of primary amines without affecting the total yield of amines. At temperatures up to 400° the aluminium oxide catalyst retains its activity practically indefinitely.

Goschorn[33] synthesised amines by the vapour-phase amination of aliphatic alcohols or ethers at 300–400° with a catalyst of oxides of metals of Groups II, III, or IV of the Periodic System, or silica gel on which oxides of metals of Groups V, VI, VII, or VIII have been deposited. Most frequently he used oxides of chromium, nickel, or cobalt. In a second patent[34], he obtained 24.9% of primary and 29.2% of secondary butylamine by the catalytic amination of butanol at 347° with a 1:4 molar ratio of butanol to ammonia. In a third patent[35], he aminated butanol at 320° in the presence of a catalyst based on ammonium molybdate, which enabled the reaction to be carried out at a lower temperature. The yield was 32.6% of primary and 23.6%

of secondary butylamine. Smith[36] recommends aluminium oxide as a catalyst in the reaction of methanol with ammonia at 450°; formation of trimethylamine may be kept to a minimum by the addition of 1–2 moles of water vapour.

Taylor and Raynolds[37] obtained amines from aliphatic alcohols with 2 to 13 carbon atoms in the molecule. Alcohol vapour together with ammonia and hydrogen was passed over a hydrogenation catalyst at 140–230°; the catalyst was an element of Group VIII of the Periodic System.

Doyvis and coworkers[38] proposed a method of preparing amines from aliphatic primary and secondary alcohols with 2–9 carbon atoms in the molecule or the corresponding aldehydes or ketones: the alcohol vapour with ammonia and hydrogen at 10–25 atm is passed over a copper catalyst at 240–300°.

Fowler[39] synthesised 1,2-diaminopropane from 1-aminopropan-2-ol by heating the latter with ammonia in the liquid phase at 150–250° and a pressure of 28–140 atm in the presence of a hydrogenation catalyst consisting of finely divided nickel or cobalt.

A Swiss patent[40] describes a method of preparing mono-, di-, and tri-alkylamines from primary and secondary aliphatic alcohols in the presence of a copper or aluminium/barium hydroxide catalyst at 240–300° and a pressure of 10–25 atm.

A French patent[41] describes a method of preparing primary amines from aliphatic alcohols in two stages. First alcohol vapour and excess of ammonia are passed over a catalyst of iron oxides at 360–420°. After the excess of ammonia has been removed from the condensate obtained, the latter is passed over a nickel hydrogenation catalyst at 100–130° and a pressure of 100–150 atm.

Popov and Shuikin[42] studied the amination of alcohols and were unable to confirm the views of Baum that aldehydes, ketones, ethers, or unstable compounds of alcohol with the catalyst are formed in this reaction. In their opinion amines are formed by the direct elimination of the elements of water from the molecules of alcohol and ammonia when they collide on the active surface of the catalyst.

Kozlov and Panova obtained aliphatic amines in high yield by the catalytic amination of ethers[43]. The vapour of dibutyl ether or diisobutyl ether was passed over alumina or thoria/alumina in a stream of ammonia under a pressure of 1–9 atm;[43] optimal results were obtained at 370–375° and a pressure of 9 atm; after distillation of the catalysate, mixtures of butylamine with dibutylamine and isobutylamine with diisobutylamine were obtained.

Bel'chev and Shuikin catalytically aminated n-butyl alcohol on a mixed oxide catalyst[44]; in the presence of 85% aluminia and 15% iron(III) oxide, which was the most active catalyst, at 405° and a volume flow of 0.75, amines were obtained in 42.8% yield (17.5% primary, 20.5% secondary, and 4.8% tertiary).

Kozlov and Panova[45] aminated butyl alcohols at 250–400° and a pressure of 1–10 atm in the presence of alumina. n-Butyl alcohol gave 89.9% of amines (62% primary, 29.8% secondary, and 8.2% tertiary); under the same conditions isobutyl alcohol gave 68.8% of amines and t-butyl alcohol gave 25.3%.

In a French patent[46] it is proposed to aminate primary or secondary aliphatic alcohols by gaseous ammonia on reduced metal catalysts (nickel, cobalt, copper, platinum, or palladium) in the presence of a hydrogen acceptor (the aldehyde or ketone corresponding to the alcohol). The yield of amines reaches 85%.

Rice and Kohn developed a method of preparing secondary and tertiary amines[47]; primary or secondary aliphatic amines are alkylated with alcohols in the presence of Raney nickel. Butylamine and anhydrous ethanol gave $C_2H_5N(n\text{-}C_4H_9)_2$ in 54% yield. Dibutylamine and anhydrous ethanol gave $C_2H_5N(n\text{-}C_4H_9)_2$ in 42% yield. Noeske and Kolling obtained amines from aliphatic alcohols through nitriles[48]. At first alcohol vapour and excess of ammonia were passed over an iron catalyst at 300–470°. After the excess of ammonia had been removed, the condensate obtained was hydrogenated on a nickel catalyst at 80–160° and a pressure of 100–150 atm. The yield of primary amines was 75–85%, and the yield of secondary and tertiary amines 5–15%.

Patnak and Rao synthesised methylamines, starting from methanol at 425° in the presence of alumina[49]. The yield was 50% of $CH_3NH_2$, 25% of $(CH_3)_2NH$, and 25% of $(CH_3)_3N$.

Bashkirov and coworkers[50] developed a method for the reductive amination of aliphatic alcohols or aldehydes at 230° and 100 atm pressure on $Fe_3O_4$ ($V_2O_5$). The yield of amines was 95–97%.

Bel'chev and coworkers[51] carried out the vapour-phase amination of primary alcohols (butyl and pentyl) on alumina and mixed catalysts; the highest yield of butylamines (80%) was obtained in the presence of 5% titanium dioxide/alumina.

Kochetkov and coworkers[52] synthesised secondary amines with a branched chain of the general formula:

$$C_2H_5NHCR_2[CH_2]_nCR_2NHC_2H_5,$$

where R = $CH_3$ or $C_2H_5$ and $n$ = 2–7. Diols of the type $HOCR_2[CH_2]_nCR_2OH$ were used as starting materials.

Kagan and coworkers[53] studied the amination of higher aliphatic alcohols in the presence of a promoted fused iron catalyst under the pressure of hydrogen. Using the amination of octyl alcohols as an example, they found the effect on this process of pressure, temperature, volume flow, composition of the starting gas, and also the effect of the structure of starting alcohols. In the amination of octan-1-ol when the temperature is raised from 230° to 270° the total degree of conversion is increased from 89.5 to 96.5% but the yield of by-products increases by a factor of 3; at 240–250° and 100 atm pressure the yield of amines passes through a maximum of 86%. In the amination of octan-2-ol the yield of primary amines increases to 92%. Branching of the carbon chain sharply reduces the yield of amines and leads to a reduction in the yield of secondary and tertiary amines in the catalysate. Thus, 2-methylheptan-4-ol is converted into amines with only 71.0% yield; the yield from octan-4-ol is 85.0%, that from 2-ethylhexan-2-ol 75%, and that from octan-1-ol 90%.

Kozlov[54] aminated primary, secondary, and tertiary aliphatic and alicyclic alcohols under pressure in the presence of alumina at 370–380°. Increasing the pressure of the ammonia to 8–10 atm suppresses side-reactions and in some cases increases the yield of amines to 90% of the theoretical, based on alcohol reacting.

## 2. Amination of Carbonyl Compounds

Carbonyl compounds as possible starting materials for the synthesis of amines difficult to obtain from other compounds have attracted the attention of a number of workers.

Grigorovskii and Margolina[55] studied the reductive amination of butanal in the liquid phase with finely divided nickel as catalyst. The yield of butylamine was 74–80%.

Olin and McKenna[56] studied the vapour-phase amination of aldehydes at 175–180° in the presence of hydrogen on nickel or cobalt. The yield of amines was 87.7–90.9%.

Bami and coworkers[57] carried out the reductive amination of ketones on finely divided nickel (5–10%). The yield of amines was over 80%. 2-Aminobutane, 2-aminopentane, 2-aminoheptane, 2-aminooctane, 3-aminopentane, and 2-aminohexane were obtained.

Alexander and Misegades[58] obtained primary amines by the reductive amination of ketones under pressure. They used platinum as a catalyst and they noted that the addition of ammonium chloride increases the yield of amines.

Popov and Shuikin[59] studied the possibility of aminating acetone under the action of hydrogen and ammonia in the gas phase in the presence of platinised silica gel. They found that acetone at 240° under these conditions gives up to 37.1% of primary amine.

In a later paper, Popov and coworkers[60] studied the effect on the yield of amines in catalytic amination of the nature of the hydrocarbon radicals in different ketones. It was found that aliphatic ketones with the same hydrocarbon groups are more easily aminated than ketones with different groups. Lengthening the carbon chain in one of the groups leads to a reduction in the yield of amines and the greater the difference between the number of carbon atoms in the two groups the greater will be the reduction in yield.

Hentrich and Kaiser[61] proposed a method for the preparation of aliphatic amines from unsaturated ketones and ammonia or a primary amine. The reaction is carried out in the presence of a nickel–manganese–iron catalyst at 120° and 80 atm.

Iffland and Yen Teh-Fu[62] obtained aliphatic amines by the reduction of the corresponding ketoximes on a Raney nickel catalyst at 20° and 4 atm. The yield of amines was 51–85% (2-aminopentane 85%, 2-aminooctane 51%, 2-aminoheptane 45%).

Teter[63] gives directions for preparing an amination catalyst for use in suspensions; it contains 30–70% of cobalt on a kieselguhr carrier with a small amount of alumina.

Skita and coworkers[64] recommend a method for preparing tertiary aliphatic amines by the catalytic reduction of carbonyl compounds in a liquid phase in a solution close to neutral at normal temperature and high pressure. In the presence of $Pt/BaSO_4$ at 20° and 3.4 atm, triethylamine, tributylamine, and other amines were obtained from an aqueous alcoholic solution of ammonium acetate and the corresponding aldehydes.

Reppe and coworkers[65] synthesised secondary and tertiary aliphatic amines (diethylamine, diethylisobutylamine, etc.) by interaction of aldehydes or ketones with ammonia or amines for 24 h in the presence of water at 160° and the introduction of carbon monoxide under a pressure of 120–200 atm in a stainless steel autoclave.

Treszczanowicz and coworkers[66] synthesised ethylamine from acetaldehyde, hydrogen, and ammonia in the presence of a dehydrating catalyst. Comparative studies were done in the presence of two different catalysts: (1) 1–7.9% nickel, 2.1% chromium(III) oxide and 90% pumice, and (2) 4.9% nickel and 51% alumina. The yield of amines was 58.7 and 64.5%.

In a British patent[67] a method of producing aliphatic or cycloaliphatic amines is based on the interaction of aldehydes with ammonia or amines in the presence of nickel or cobalt. The reaction is carried out in the liquid phase with a low-boiling solvent (alcohol, hydrocarbons). Subsequent hydrogenation is carried out at elevated temperature under pressure.

Schade and coworkers[68] have patented a method for the preparation of pure n-butylamine from commercial butyraldehyde containing ketones and ethers as impurities. The formation of dibutylamine depends on the amount of ammonia introduced into the reaction and the presence of ketones in the starting aldehyde; the reaction is carried out in the presence of 50% nickel on alumina.

Schade and Sperling[69] developed a method of converting mono- and tri-ethylamine into diethylamine. The mono- and tri-ethylamine are brought into reaction with one another at 150–180° in the presence of nickel/alumina and, hydrogen and ammonia under a pressure of 2–3 atm. The mixture of mono- and tri-ethylamine is formed as a by-product in the preparation of diethylamine by the reductive amination of acetaldehyde.

Tindall[70] obtained secondary aliphatic amines by hydrogenating a mixture of aliphatic ketones with anhydrous ammonia or primary amines containing from 1 to 8 carbon atoms. The reaction is carried out in the presence of cobalt on calcium or barium sulphate at 160° and a pressure of 70–105 atm. Diisopropylamine is obtained in 73% yield.

Rauch[71] has proposed a method for the preparation of alkylidenealkenylamines from isobutyraldehyde and ammonia at 200° with the use of a manganese–cobalt oxide catalyst on pumice (7.5% manganese and 1.5% cobalt). Isobutylideneisobutylenamine is obtained in 97.4% yield.

For the preparation of diethylamine from acetaldehyde, hydrogen, and ammonia, Treszczanowicz and coworkers[72] used a catalyst of 49% nickel on alumina reduced by hydrogen at 320°. The yield of diethylamine was 54.2%, based on acetaldehyde.

In a further patent, Treszczanowicz and coworkers[73] propose that the preparation of amines from aldehydes, ammonia, and hydrogen[68] should be improved by evaporating at ~40° before it is mixed with the hydrogen; this prevents the formation of resins and significantly lengthens the life of the catalyst.

Günter and Jutta[74] hydrogenated polyenealdoximes on Raney nickel under pressure and obtained the corresponding higher primary n-alkylamines in good yield; decylamine was obtained in 90% yield from decatetraenealdoxime.

Morris and coworkers[75] developed two methods of preparing cycloheptylamine. In the first method, cycloheptanone oxime is hydrogenated in methanol at 60° and 0.75–1 atm in the presence of rhodium on alumina; the yield is 80%. In the second method, cyclopentanone in a mixture with liquid ammonia and alcohol is hydrogenated at 70° and 100 atm; the yield is 61%. Saito Atsudzi[76] obtained hexamethylenediamine in 72% yield from hydroxyadipaldehyde; the aldehyde reacts with ammonia and hydrogen for 6 h with a small amount of alcohol in the presence of Raney nickel at 220–240°.

### 3. Amination of Halogen Derivatives

The synthesis of amines by the catalytic amination of halogen derivatives seems very attractive and promising in the first place because the haloalkanes are produced on a large scale and form a cheap raw material. Moreover, it should be borne in mind that at present it is possible to obtain haloalkanes of practically any given structure and therefore a great diversity of amines can be obtained from them.

Nekrasova and Shuikin[77] studied the catalytic alkylation of ammonia by halogen derivatives of alkanes and cyclanes in the vapour phase at atmospheric pressure. Chloroalkanes were aminated at 310° in contact with a catalyst based on magnesium oxide. The yield of amines in the catalysate changed from 60 to 78.6% as the length of the chain was increased from $C_4$ to $C_{10}$. Chlorocyclopentane, chlorocyclohexane, and bromocyclohexane were aminated at 340°;[78] the effect of the nature of the halogen and its position in the molecule on amination was also studied. The greatest yield of amines was obtained by amination of the chloro-derivative and the least by amination of the iodo-derivatives. The position of the halogen in the haloalkanes has a considerable effect on the yield of amines.

Brown and Lester[79] set out to synthesise primary alkylamines with a long carbon chain and also with different arrangements of the amino-group in the carbon chain. The amines were synthesised in three ways: by Hofmann's reaction, by Leuckart's reaction, and by the reduction of amides in ether in a Soxhlet apparatus. The yield of amines by the first method was 60–78%. The amines were prepared by Leuckart's reaction from the corresponding ketones in 50–63% yield. In the third method the amines were obtained by the reduction of amides with lithium aluminium hydride in ether in a heated Soxhlet apparatus; the yield varied between 50 and 62%.

Schulte and Goe[80] synthesised primary aliphatic amines with a triple bond from 1-haloalkynes and hexamethylenetetramine in chloroform with subsequent decomposition of the quaternary hexaminium salt by alcoholic solution of hydrogen chloride. The effect of chain length and the position of the triple bond was studied. The quaternary hexaminium salt readily forms at ~ 20° in 90% yield from 1-haloalk-2-ynes independently of the chain length. The quaternary hexaminium salt is not formed from 1-haloalk-1-ynes in the cold or with heating. The stability of the quaternary hexaminium salt decreases with increasing chain length.

Tkaczynski and Kotelko[81] obtained ethylenediamine in 45% yield by the reaction of dichloroethane with ammonia; at the same time 1,4,7-triazaheptane (34%) and 1,4,7,10-tetrazadecane (12%) were separated. Tkaczynski obtained 1,2-diaminopropane and other diamines in an analogous manner, starting from dihalo-derivatives[82].

Hennion and Hanzel[83] prepared amines that were difficult to synthesise for steric reasons. Primary and secondary amines were alkylated with t-alkynyl chlorides. *N*-Isopropyl-1,1-dimethylprop-2-ynylamine was obtained from isopropylamine and 3-chloro-3-methylbut-1-yne at 20° after 7 d; the yield was 58%. The alkynamines were reduced to the corresponding allyl and saturated amines. Thus, *N*-isopropyl-1,1-dimethylprop-2-ynylamine in petroleum ether containing 0.01 g 10% palladium on carbon was reduced under pressure over 7 h at 20°, and *N*-isopropyl-1,1-dimethylprop-2-enylamine was obtained in 71% yield.

Nelson and coworkers[84] obtained $ClC(R)(R')CH=CHCl$ by the interaction of $HOC(R)(R')C\equiv CH$ with HCl; with the appropriate amines this gives $R''NHC(R)(R')CH=CHCl$ in 10–35% yield. Dehydrohalogenation of the compound $R''NHC(R)(R')CH=CHCl$ leads to $R''NHC(R)(R')C\equiv CH$ in 50–70% yield.

### 4. Addition of Ammonia to Alkenes

The considerable development of the petrochemical industry in the past decade has led to alkenes becoming bulk raw materials in the basic organic synthesis industry. This is the main reason why, in the search for uses for alkenes, the addition of ammonia to alkenes to form amines was investigated.

Teter[85] has proposed nickel or cobalt on a carrier as a catalyst in the amination of unsaturated compounds or their conversion into nitriles. With this catalyst, propene reacts with ammonia at 343–427° and high pressure. He has also patented[86] a method for the preparation of a cobalt catalyst with the addition of magnesium silicate for the amination of unsaturated compounds. The addition of 1% magnesium oxide as a promoter to the cobalt catalyst suppresses side-reactions and prevents the formation of carbon. He has also proposed[87] a method for the preparation of a new catalyst for the conversion of alkenes into amines. For this purpose a reduced nickel or cobalt catalyst is prepared on bentonite clay; it contains 40–50% of metal. Teter also investigated the catalytic amination and cyanation of alkenes in the presence of a cobalt catalyst[88,89].

The use of sodium as a catalyst for the synthesis of amines from alkenes and ammonia is described in a British patent[90]. For example, when isobutylene is heated to 250–265° with liquid ammonia under a pressure of 650–700 atm in the presence of metallic sodium, t-butylamine is obtained.

Tindall[91] has proposed a method of preparing amines by the reduction of nitroalkenes of the type $R-CH=C(NO_2)-R'$, where R is alkyl or aryl and R' is alkyl. The reaction is carried out in the presence of Raney nickel catalyst under pressure in an inert organic solvent and in the presence of an organic acid with a dissociation constant between $1.86\times 10^{-5}$ and $1.1\times 10^{-3}$.

Thurston[92] prepared amines from alkenes containing a double bond inside or at the end of the carbon chain and an alkyl group on the second hydrogen atom. The alkenes are first brought into reaction with cyanogen chloride or cyanogen bromide in the presence of an acid catalyst in the liquid phase; the reaction mixture is then subjected to hydrolysis and amine separates.

Graf[93] synthesised aliphatic amines by condensing alkenes with hydrogen cyanide in the presence of a strongly acid catalyst and hydrolysing the reaction product. Thus, 3-formylamino-3-methylheptane is obtained by the condensation of 2-ethylhex-1-ene with hydrogen cyanide in the presence of concentrated sulphuric acid and hydrolysis of the reaction product with sodium hydroxide; hydrolysis of the 3-formylamino-3-methylheptane with concentrated sulphuric acid gives 3-amino-3-methylheptane. Octylamines, 4-aminoheptane, a mixture of dodecylamine isomers, 2-aminodecane, etc. are obtained in a similar way.

Howk and coworkers[94] have proposed a method for the catalytic amination of alkenes under the influence of alkali

metals. It has been shown that ammonia, primary amines, and secondary amines are converted into *N*-alkyl derivatives by reaction with ethylene, propene, 2-methylbut-1-ene, but-2-ene, hex-1-ene, butadiene, and cyclohexene in the presence of sodium, potassium, or lithium. The reaction is carried out in a steel autoclave at 200° and 800–1000 atm and the yield reaches 70%.

Urry[95] recommends a method of alkylating primary, secondary, and heterocyclic tertiary amines at the $\alpha$-carbon atom with the aid of alkenes. The reaction is initiated by alkyl peroxides at 90–130°, or under irradiation at 30–50°. When gaseous alkenes are used the reaction is carried out under pressure.

The alkenylamines are interesting compounds in their chemical possibilities, but there are only a few papers on this type of organic compound.

Engelhardt developed a method of preparing allene and acetylene amines by the interaction of 25% aqueous solutions of methylamine, diethylamine, morpholine, or n-butylamine with vinylacetylene under high pressure at a temperature of ~ 100°.[96]

Hasek and coworkers[97] synthesised allene amines by the following scheme:

$$(CH_3)_2CHCHO + NH_3 \longrightarrow (CH_3)_2CHCH[N{=}CHCH(CH_3)_2]_2 + H_2O$$
$$\downarrow$$
$$(CH_3)_2C{=}CHN{=}CHCH(CH_3)_2 + NH_3.$$

Nelson and coworkers[98] have proposed a method for the preparation of secondary alkynylamines by the interaction of $\alpha$-chloroalkynes and aliphatic amines in the presence of bronze at a temperature below 40°; the yield is 10–21%, depending on the nature of the hydrocarbon radical of the primary amine.

5. Synthesis of Amines and Diamines by Hydrogenation of Nitriles

a. Synthesis of amines. The synthesis of amines from nitriles is effected under conditions close to those used in the amination of alcohols and haloalkanes, but not quite identical. As a rule, the hydrogenation of nitriles is carried out in the presence of catalysts based on Group VIII elements under increased pressure of 10–60 atm and at temperatures of 150–300°. Since in the reduction of nitriles, especially dinitriles, a complex mixture of products may be formed, it is important to select those conditions under which the reaction will go mainly in the desired direction. It is possible to find the necessary conditions for the synthesis of amines from nitriles by making a rational selection of catalyst, temperature, and pressure and, in a number of cases, by introducing ammonia into the reaction zone. For example, the synthesis of hexamethylenediamine from adipodinitrile is carried out on an industrial scale in many countries.

Pratt and Norris[99] obtained lower secondary and tertiary amines by the action of hydrogen on a mixture of nitrile with aldehyde, ketone, or alcohol at 200–300° in the presence of pure copper, iron, cobalt, or nickel, or with the addition of oxides of thorium, silicon, aluminium, chromium, or cerium. Pumice, silica gel, or bauxite may be used as a carrier. The molar ratio of the nitrile to the other component depends on whether primary or secondary amines are desired. From acetonitrile and acetaldehyde with excess of hydrogen on a nickel catalyst at 200–230° 98% of amines is obtained, consisting of 12% monoethylamine, 24% diethylamine, and 62% triethylamine.

In a patent by Mell[100], a method is proposed for the preparation of primary, secondary, and tertiary amines by the cyanation of alcohols with ammonia at 200° in the presence of nickel on kieselguhr; immediately after this the reaction mixture is passed over a hydrogenating copper or nickel catalyst at 100–180°. A mixture of primary, secondary, and tertiary amines is obtained in close to 100% yield.

A patent of Hoffman recommends the preparation of primary amines from nitriles by the action of liquid ammonia and hydrogen at elevated pressure in the presence of nickel on kieselguhr or Raney nickel[101].

A method for the preparation of primary amines from nitriles of aliphatic acids with ten or more carbon atoms has been patented[102]. These nitriles are converted into the corresponding primary amines by the action of hydrogen and ammonia at 210° and high pressure in the presence of Raney nickel.

A method of preparing high-molecular-weight primary amines from nitriles of higher fatty acids (stearic, etc.) is described in a patent[103]. Hydrogenation is carried out at a pressure up to 20 atm in the presence of nickel and with the addition of a small amount of barium hydroxide solution, caustic alkalis, or a quaternary ammonium base; under these conditions 93.5% of primary octadecylamine is obtained from stearonitrile.

A method of preparing primary aliphatic amines with six or more carbon atoms is described in a patent[104]. The nitriles of the fatty acids of coconut and cottonseed oils are hydrogenated at 130–150° and 15 atm in the presence of ammonia and Raney-nickel catalyst. An aqueous solution of ammonia or sodium hydroxide is introduced into the reaction mixture in quantity sufficient to maintain an alkaline medium during the whole hydrogenation process; the yield of primary amines is 77.4%.

Sakakibara and coworkers[105] catalytically reduced nitriles of higher fatty acids in the presence of bases. Lauronitrile and stearonitrile were hydrogenated on Raney nickel in the presence of liquid ammonia, sodium hydroxide, methylamine, or furfurylamine. The reaction products were separated into primary and secondary amines. In the reduction of nitriles without the addition of bases 19% of secondary amines were obtained with the primary amines; the presence of any of the bases mentioned suppressed the formation of secondary amines.

Renfrew and Warner[106] developed a method for the preparation of aliphatic amines from nitriles containing 8 to 22 carbon atoms, which were hydrogenated at 110–170° and 10.5 atm. A nickel hydrogenation catalyst was used and 0.5 to 10% (based on nitrile) of aliphatic alcohol was introduced together with ammonia.

Komori Saburo and coworkers[107] synthesised saturated and unsaturated aliphatic amines containing 8 to 22 carbon atoms by the reduction of nitriles obtained from natural fats; the reduction is carried out in the presence of nickel on silica gel and liquid ammonia at 90–150° under a hydrogen pressure of 10–200 atm. The presence of ammonia suppresses the formation of secondary amines and increases the yield of primary amines; under these conditions the yield of primary amine is 73.5% and of secondary amine 26.5%.

Suganuma Tokumasa and coworkers[108] obtained a mixture of secondary and tertiary aliphatic amines from aliphatic nitriles containing 8 to 18 carbon atoms in the molecule; the nitriles were reduced at 150–300° at high pressure in the presence of saturated $C_1$ to $C_{18}$ alcohols and a nickel catalyst. A mixture of secondary and tertiary amines, depending on the quantity of alcohol, is formed according to the following scheme:

$$RCN + R'OH \xrightarrow{H_2} RCH_2NHR';$$
$$RCN + 2R'OH \xrightarrow{H_2} RCH_2NR'_2.$$

Tertiary amines with 20–30% of secondary amines are mainly formed by this method.

Sommers and Aaland[109] synthesised aliphatic amines by reduction of Schiff bases in the presence of lithium tetrahydroaluminate instead of a hydrogenation catalyst.

Kozlov and Panova[110] aminated carboxylic esters in the presence of alumina at 370°. The corresponding nitriles are formed as intermediates in the reaction.

Freifelder[111] synthesised primary amines of the type $R[CH_2]_n.CH_2NH_2$ by the catalytic reduction of the corresponding nitriles on a Raney rhodium–aluminium (Al–5%Rh) catalyst which is used in amounts 10–20% of the weight of nitrile. The reaction is carried out at 20° and 2–3 atm. The high selectivity of the catalyst is worthy of note. The reduction is carried out in the presence of ammonia to avoid the formation of secondary amines.

Yakushkin[112] hydrogenated a $C_8$–$C_{13}$ fraction of nitriles to the corresponding primary amines in the presence of Raney nickel. The reaction was carried out at 120–200° and a hydrogen pressure of 20–60 atm; it was noted that as the temperature was raised the yield of primary amines diminished. The hydrogenation of $n\text{-}C_5H_{11}CN$ showed that the addition of ammonia and absolute alcohol increases the yield of hexylamine.

In a patent Denis[113] describes the synthesis of primary amines by the catalytic hydrogenation at 200° of aliphatic nitriles containing from 6 to 22 carbon atoms. Selective hydrogenation catalysts, $Cr_2O_3$, ZnO, $ZnO(Cr_2O_3)$ with the addition of CuO are proposed; alumina and aluminosilicate are used as carriers. The yield of amines varies within the range 60–71.2%.

Gould and coworkers[114] studied the hydrogenation of nitriles in the presence of Raney catalysts (nickel, nickel–chromium, cobalt) in acetic anhydride with basic additives. When sodium acetate was added, the activity of the catalyst decreases after three cycles; with sodium hydroxide the catalyst retains its activity for a longer period and the rate of reduction is higher, but the reaction is strongly exothermic. The yield of amines reaches 100%.

b. Synthesis of diamines. In this section other methods are presented apart from the synthesis of diamines from nitriles.

A method of preparing diamines from dinitriles of higher fatty acids by hydrogenation under pressures up to 20 atm in the presence of a nickel catalyst is described in a patent[103]; a small quantity of aqueous barium hydroxide solution, caustic alkalis, or a quaternary ammonium base is added.

Whetstone and Ballard[115] have proposed a method for the preparation of diamines from aliphatic dialdehydes containing 6 to 12 carbon atoms in the molecule, ammonia, hydrogen, and primary or secondary amines in excess of stoichiometric requirements. The reaction is carried out in the presence of a hydrogenation catalyst. Under these conditions diamines were obtained by the condensation of $\alpha$-hydroxyadipaldehyde at 30–50° and 15–350 atm.

Schryer[116] synthesised 3-methylheptamethylenediamine from 5-methylhex-5-enenitrile. The nitrile was first treated with a mixture of carbon monoxide and hydrogen at 75–200° at a pressure not less than 50 atm in the presence of finely divided cobalt or its naphthenate, oxide, or carbonyl; the 6-cyano-3-methylhexenal obtained under those conditions at 75–250° was treated with a mixture of hydrogen and ammonia to give the diamine.

Roster and Schroeder[117] synthesised diamines by the reaction of the product of ozonization of a mixture of cyclohexene and a lower aliphatic alcohol with amines of the type NHRR′, where R and R′ are hydrocarbon groups with one to seven atoms of carbon; the reaction product was then hydrogenated in the presence of cobalt or nickel. To prepare the diamines (hexamethylenediamine, etc.), not less than two molecules of secondary amine or ammonia are used per molecule of cyclohexene.

Möller and Schröter[118] obtained tetramethylenediamine by the catalytic hydrogenation of succinodinitrile in an autoclave.

Regby[119] synthesised hexamethylenediamine by the reaction of adipaldehyde in solution with the secondary amine R′RNH and hydrogen at 25–150° in the presence of a hydrogenation catalyst; R and R′ are cyclohexyl or alkyl groups containing from 1 to 12 carbon atoms.

Larramona[120] studied the formation of diamines of the type $R''_2NCH_2NR_2$ in the cleavage of $\alpha$-vinylketones, $CH_2{=}CRCOR'$, by the action of secondary amines. The reaction proceeds through the intermediate formation of the $\beta$-aminoketone $R''_2NCH_2CHRCOR'$.

Swerdloff[121] obtained diamines by the catalytic hydrogenation of dinitriles in the presence of anhydrous ammonia and Raney nickel in a stainless steel autoclave.

Schreyer[122] developed a method of preparing di-primary aliphatic diamines. Glycols and aminoglycols containing 6–11 carbon atoms were used as starting materials; these reacted with ammonia at 150–250° and 400–700 atm in the presence of a ruthenium catalyst.

Adam[123] hydrogenated tetramethylenedinitrile in the presence of liquid ammonia and a catalyst containing 20% of cobalt and 0.3% orthophosphoric acid deposited on silicic acid at 85° and a hydrogen pressure of 300 atm. The yield of hexamethylenediamine is 90.9%.

A patent[124] describes the preparation of ethylenediamine from monoethanolamine or ethylene oxide with anhydrous ammonia at 180–210° and 145–150 atm in the presence of a hydrogenation catalyst. The yield of ethylenediamine reaches 80%.

In another patent[125] it is proposed to synthesise ethylenediamine from ethylene oxide or monoethanolamine in the presence of a specific catalyst consisting of finely ground nickel–magnesia. The use of such a catalyst in the proportion of 1–10% of the ethylene oxide or monoethanolamine allows the reaction temperature to be reduced to 150–180°, which reduces the formation of by-products and increases the yield of ethylenediamine.

Wiemann has patented a method of preparing 2,7-diaminooctane from octa-2,7-dione[12]. The reaction is

carried out in an atmosphere of hydrogen in the presence of Raney nickel and 30% ammonium hydroxide. A mixture of stereoisomers of 2,7-diaminooctane is formed.

Jefferson and coworkers[126] developed a detailed formula for the preparation of promoting catalysts based on cobalt oxide for the synthesis of hexamethylenediamine. The catalyst was partially reduced and silica (0.04–1%) and titanium dioxide (0.08–0.18%) were used as promoters.

Indest and Meyer[127] obtained hexamethylenediamine of high purity and in 96 to 99% yield by the continuous catalytic hydrogenation of adipodinitrile. Granulated nickel–aluminium alloy (40–60% nickel) was used as a catalyst. The catalyst retained its activity for 30–60 d, after which it was completely regenerated 7–10 times. The dinitrile was hydrogenated in the presence of a solvent (liquid ammonia, methanol, etc.) at 20–80° and a hydrogen pressure of 100–500 atm. The yield of hexamethylenediamine is 98.7%.

Polkovnikov and coworkers[128] have proposed a method for the preparation of hexamethylenediamine from adipodinitrile by hydrogenating the latter in the presence of cobalt boride at 100° and 130 atm. The yield of hexamethylenediamine is 92.6%.

Nakajima[129] studied the condensation of diethylaminoethanol with various imides; when the condensation product is hydrolysed by heating to 360° *NN*-diethylethylenediamine is formed. The yield is 85%.

Miva Itiro and coworkers[130] obtained diamines in a high degree of purity by the hydrogenation of nitriles in the presence of cobalt or nickel formates at 230° and increased pressure. The yield of hexamethylenediamine is 88.5%.

## 6. Other Methods of Preparing Amines

Bashkirov and coworkers[131] have developed a new method of preparing aliphatic amines in which a mixture (1 : 2) of carbon monoxide and hydrogen is passed with ammonia over a promoted iron catalyst. The yield of amines is 25% and 82–96% of these are primary amines. These workers have improved this method of synthesising amines from carbon monoxide, hydrogen, and ammonia[132]. As a result of the interaction of these gases in the presence of a fused iron catalyst, aliphatic amines, mainly primary, with one to 20 atoms and more in the carbon chain are formed. From one cubic metre of these gases 120 g of material is obtained containing 54% of alkylamines (33% liquid and 21% gaseous amines). n-Butylamine, n-pentylamine, n-hexylamine, n-heptylamine, and n-octylamine have been identified in the products of the synthesis.

Aygen and Wolfgang[133] have proposed a method of preparing primary, secondary, and tertiary amines by the methylation of ammonia, primary amines, and secondary amines with diazomethane. The reaction is carried out in the presence of halogen, halogenoalkyl, and alkoxy-derivatives of boron at -80° to 0° in an inert organic solvent. The yield of amines reaches 82%.

Dose[134] has developed a method of preparing aliphatic amines by the decarboxylation of $\alpha$-amino-acids in the presence of aromatic aldehydes, nitrobenzene, xylene, trichlorobenzene, etc. The presence of solvents in the reaction mixture suppresses the formation of by-products. The reaction is carried out according to the following scheme:

$$CH_3—CH_2—CH(NH_2)COOH \rightarrow CO_2 + CH_3(CH_2)_2NH_2.$$

Bashkirov and coworkers[135] studied the synthesis of amines from carbon monoxide, hydrogen, and ammonia on promoted iron catalysts. The best results were obtained by using a mixture of carbon monoxide 12%, hydrogen 68%, and ammonia 20% with a volume rate up to 100 $h^{-1}$ and temperatures up to 200°. The yield of amines reached 50%.

Johnston[136] synthesised amines from amides by reducing them with sodium tetrahydroborate.

Synthesis of alicyclic amines. There is much less information in the literature on the synthesis of alicyclic amines than on the preparation of aliphatic amines. In principle, the methods of synthesis of amines of these two classes of compounds are similar and differ only in the reaction conditions. Because of the limited amount of material it would not be useful to group it in several sections, as was done for the aliphatic amines; we shall confine ourselves to presenting it in chronological order.

Mousseron[138] obtained 3-methylcyclohexylamine in 60% yield (75% *trans* form) from 3-methylcyclohexanone in the presence of platinum(IV) chloride. 2-Methylcyclohexanone gave only 35% of 2-methylcyclohexylamine. The addition of a small quantity of hydrogen hexachloroplatinate(IV) to Harley's catalyst[138] in the amination of 3-methylcyclohexanone reduces the yield of the *trans* form.

Adkins and Billica[139] used a nickel catalyst and hydrogen under a pressure of 15–45 atm at 25–30° for the conversion of cyclohexanone oxime into cyclohexylamine. The yield is 90%.

Popov and Shuikin[140] studied the catalytic amination of cyclohexanol in the presence of hydrogenating and dehydrogenating catalysts. Of these, platinised silica gel was found to be the most active. In the presence of this catalyst at 320° the yield of cyclohexylamine reached 51.3%, calculated on the cyclohexanol consumed in the reaction.

Popov and Shuikin aminated cyclohexanol in the gas phase by the action of hydrogen and ammonia on platinised silica gel[59]. It was found that cyclohexanone at 200° gives up to 89.6% of primary amine.

Kozlov and Akhmetina[141] studied the catalytic amination of cyclohexanol on aluminium oxide in a flowthrough system at 150–380° and an ammonia pressure of 1–20 atm. At a pressure of 5–10 atm the amination predominates and the dehydration of the cyclohexanol almost ceases. It was established that the optimal temperature range is 260–300°; below this the reaction is extremely slow and at a higher temperature the cyclohexylamine decomposes into ammonia and cyclohexene. The yield of cyclohexylamine reaches 70–74%, based on cyclohexanol taken, or 90–95%, based on cyclohexanol consumed in the reaction.

Cairns and Gilbert[142] have proposed a method of preparing polycyclic tertiary amines. Cycloalkanols containing 5–7 carbon atoms and having at least one methylene group in the $\alpha$-position to the C–O group are used as starting materials.

Popov and Shuikin[143] have synthesised cyclopentylamine by passing a mixture of cyclopentanone with excess of ammonia and hydrogen over nickel on aluminium oxide or pumice. The optimal temperature is 150°; at higher

temperatures resin formation increases and the yield of amines decreases. The best yield of amines on nickel deposited on aluminium oxide was 66.6% (55.6% of cyclopentylamine and 11% of dicyclopentylamine).

Naumov and coworkers[144] studied the reaction for the preparation of cyclohexylamine by hydrogenating aniline on different catalysts in the gas phase at atmospheric pressure. Two reactions were studied:

$$C_6H_5NH_2+3H_2-C_6H_{11}NH_2, \quad (I)$$

$$2C_6H_{11}NH_2 \rightleftarrows NH_3+(C_6H_{11})_2NH. \quad (II)$$

An $Ni/Al_2O_3$ catalyst promotes the second reaction. A mixed CoO/CaO catalyst at 190–200° is active only in the formation of cyclohexylamine. The ease with which reaction (II) proceeds and its reversibility on a nickel–alumina catalyst makes it possible to convert aniline almost completely into cyclohexylamine and dicyclohexylamine.

Noeske and Kolling[145] have patented a method of preparing alicyclic amines. Saturated alicyclic mono- and di-aldehydes, hydroxyaldehydes, and products of the oxo-synthesis containing alicyclic aldehydes may be used as starting materials. Hydrogenation is carried out in the presence of nickel on magnesium oxide with kieselguhr at 120° and 90 atm. The yield of (tricyclodecylmethyl)-amine from tricyclodecylmethylal is 83%.

Kost[146] studied the possibility of using Raney nickel and cobalt catalysts in the synthesis of amines. It was shown that cobalt catalysts are less effective, but more convenient in practice, because the change of colour of the reaction mass enables the end of the hydroamination to be determined. Methods of preparing mono- and di-cyclohexylamine from cyclohexanol by the Leuckart reaction have been studied and it has been shown that dicyclohexylamine is sometimes contaminated with formylcyclohexylamine formed by hydrolysis.

Naumov and coworkers[147] proposed a synthesis of cyclohexylamine by hydrogenating aniline at 120–170° in contact with cobalt(III) oxide or mixed oxides, hydroxides, or carbonates of magnesium or strontium. The maximal yield of cyclohexylamine is 96–98% with an admixture of 2% of dicyclohexylamine.

Ivanova[148] obtained cyclohexylamine in 97% yield by hydrogenating nitrocyclohexane on a Raney nickel catalyst.

Illick and Robinson[149] have proposed the preparation of cyclohexylamine by hydrogenating aniline in the presence of a rubidium catalyst. The yield of cyclohexylamine is 81.6%.

Zienty obtained substituted amines (2-cyclopentyl-1-methylethylamine, 1-cyclopentyl-2-aminopropane, 2-cyclohexyl- and 2-cycloheptyl-1-methylethylamine) by hydrogenating the corresponding carbonyl derivatives of cyclopentyl-, cyclohexyl-, and cycloheptyl-acetone, etc. in the presence of a nickel catalyst (70% nickel)[150].

Nisimura Keidzo synthesised cyclohexylamine by the hydrogenation of aniline and acetanilide in the presence of Raney nickel–aluminium catalyst; the catalyst was prepared by treating an alloy of nickel–aluminium and a metal of variable valency with a solution of sodium carbonate and barium hydroxide[151]. The hydrogenation was carried out at 200° and 70 atm.

Wheaton obtained cyclohexylamine in 50% yield by the reaction of cyclohexane with ammonia under the action of ionising radiation with energy ≥ 15 eV.[152]

McKeever and Washburne[154] have proposed a substantial improvement in a method of preparing 1,8-diaminomenthane[153]. As starting material they used limonene, terpin hydrate, dipentene, etc. Reaction with hydrogen cyanide, sulphuric acid, and water was carried out at 50–55° and the 1,8-diaminomenthane was separated; the yield was 57%, calculated on dipentene.

From the great amount of literature material quoted here it is quite clear that for the synthesis of the simplest amines the greatest attention is being devoted to the development of methods based on the catalytic vapour-phase amination of alcohols or alkyl halides. These methods are most promising from the point of view of both production technology and the use of cheap raw materials available in bulk. As far as the catalytic synthesis of more complex amines is concerned, this is often carried out by aminating nitriles or carbonyl compounds in the liquid phase. Metals of Group VIII of the Periodic Table are widely used as catalysts. In recent years papers have begun to appear on the reductive amination of a number of compounds with the aid of aluminium and boron hydrides, fused iron catalysts, and promoted oxides of an acidic and amphoteric character, for example, vanadium pentoxide.


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# PROGRESS IN THE STUDY OF THE AGING OF FIBROUS CELLULOSIC MATERIALS

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## 1. INTRODUCTION

Cellulose is the most common natural organic substance and forms the basis of the cell walls in higher plants. Man uses vast quantities of cellulose (~ 500 million tonnes per annum) in the form of various fibrous materials; this tremendous consumption is compensated annually almost entirely by the process of photosynthesis [1,2].

Cellulose plays an important part in the national economy, and a number of organic manufacturing industries are based on the processing of this natural polymer; cellulose is used to prepare various types of paper, synthetic fibres, cotton fabrics, cine film, lacquers, explosives, etc.

The chief sources of cellulose are wood and cotton. Cellulose obtained from annual vegetation (flax, ramie, hemp, reeds, and straw from various grasses) is also of considerable importance. The technological process of cellulose production and purification may be accompanied by degradation resulting from processing. Certain necessary oxidising operations (for example, the pre-ripening of alkali cellulose in the manufacture of viscose rayon, bleaching, scouring, and dyeing) lead to undesirable and harmful consequences. The continuous degrading action of the atmosphere, heat, light, and moisture is shown spontaneously during the storage or exploitation of fibrous cellulosic materials, leading to premature wear and breakdown. All this introduces into the economy considerable losses, which exceed the losses due to the corrosion of metals [3].

In the chemistry of macromolecular compounds, the term *degradation* signifies the entire range of phenomena leading to a decrease in the length of the macromolecules. The decrease in the length of the molecular chains under the influence of internal or external factors takes place spontaneously and leads to *aging* of the polymer, that is, it leads to a decrease in the mechanical strength of the material and a decrease in its period of serviceability.

Degradation processes are usually complex, since it is difficult to determine the factors directly responsible; in general, these processes are brought about by the action of heat, light, and atmospheric oxygen. These factors operate simultaneously in the form of thermal, photochemical, and oxidative processes. There are several classifications of the different types of cellulose degradation [4,5].

Although the importance of the study of the mechanism of degradation is obvious from the practical and scientific viewpoints, many aspects of this mechanism have not been touched upon, despite the rising increase in the number of papers devoted to this problem. The degradation of cellulose leads to the formation of complex reaction products containing, in addition to the original hydroxyl groups, other non-hydroxyl functional groups produced as a result of oxidative degradation, and a certain number of broken units may be present together with unchanged elementary cellulose units: all these changes labilise the $\beta$-glucoside bonds of the chains and lead finally to a decrease in the length of the macromolecules.

In the study of the chemical changes, use is made of physical, physicochemical, and chemical methods, and also methods of artificial aging, in order to estimate the nature, direction, and intensity of the degradation processes, the durability of the manufactured products, the mechanisms of the reactions, etc.

The aim of the present review is to summarise the progress made in the recognition of the nature and mechanism of the processes involved in the degradation and aging of fibrous cellulosic materials, and also to point out the most rational methods for preventing the degradation of these materials.

## 2. THE DURABILITY OF PAPER

The durability of a fibrous material (paper, cardboard, cellulose fibres, or cotton fabric) is determined by its ability to withstand the action of the internal and external factors bringing about degradation during prolonged storage or under conditions of use, when the material is subjected to various mechanical treatments (folding, crumpling, elongation, etc.)[6]. The durability depends on the ability of the material to withstand the action of the surrounding medium, that is, the action of light, moisture, heat, and harmful atmospheres containing industrial gases. Decrease in the durability of fibrous materials, in particular paper, is usually accompanied by a decrease in the degree of whiteness.

Chemical analysis of the fibrous material (for example, paper) may give interesting information on its durability; the approximate period of resistance to wear shown by papers can be found from the data in Table 1.[7-9] Chemical analysis cannot always characterise the durability, however. For example, old Chinese papers (500–925 years old) and European documents (400 years old) have been found in good condition, although the $\alpha$-cellulose content of these papers amounted to only 65–67%.[11] Thus other factors (for example, pH) play an important part.

The exceptional stability of papers manufactured in ancient times can be attributed to their preparation from an exceptional form of raw material (cotton or flax fibres or rags), the mild digesting conditions, the use of starch and gelatin for sizing, use of the minimum amounts of fillers, bleaching in sunlight, and drying under natural conditions. The change to the production of paper from wood cellulose, with mechanical processing on paper-making machines, led to a sharp decrease in the stability of the paper [12]. Modern forms of paper are not durable, and this is due not only to the use of fibres from wood cellulose but also to other technological factors.

The best method for estimating the durability of paper is apparently by *natural aging* under conditions of prolonged storage. This method is applicable to paper which is many centuries old; for modern papers, use is usually made of *artificial (accelerated) aging* methods, based on the fact that

TABLE 1. Estimation of the durability of papers from data obtained by chemical analysis [10].

| Minimum period of use, a | Minimal $\alpha$-cellulose content, % | Copper number | Minimal resin content, % | pH | Lignin |
|---|---|---|---|---|---|
| 500 | 90 | 1.0—1.5 | 1.0 | 5 | absent |
| 100 | 80 | 2.0—2.5 | 1.5 | 5 | absent |
| 50 | 70 | 3.5—5.0 | 2.0 | 4.5 | absent |
| Less than 50 | no limit | | | | present |

damage to paper under natural conditions is due to the action of atmospheric oxygen, heat, and sunlight (direct or diffuse), the degradation being hydrolytic and oxidative in character. In artificial aging, the same factors as in natural aging are used, but under more severe conditions. The most important methods of artificial aging are given below[13-15].

1. Thermal treatment at 105° for 3 d in a drying oven with natural or controlled circulation of air.

2. Treatment with ultraviolet radiation.

3. Hydrolytic degradation in an atmosphere containing sulphur dioxide.

4. Oxidative aging in an atmosphere of oxygen at 15 atm pressure and 50–60°.

5. Aging in air with relative humidity 45% at 38° for 200 h.

6. Aging in air with relative humidity 75–80% at 30–40° for 45–180 d in the presence of definite quantities of oxygen and sulphur dioxide.

Irrespective of the method used, the change in the same physicochemical properties (tensile strength, number of double folds, elongation, bursting strength, etc.) and physicochemical properties (concentration of $\alpha$-, $\beta$-, and $\gamma$-celluloses, degree of polymerisation, degree of whiteness, concentration of functional groups, etc.) is followed. Of particular importance is the determination of the degree of polymerisation (DP): the higher the molecular weight of the cellulose, other conditions being equal, the more stable the paper prepared from it.

The technological factors decreasing the durability of modern forms of paper include the following[16,17]: (1) the decrease in the DP resulting from digesting, beating, and bleaching; it is possible to develop operating conditions under which the change in DP will be a minimum; (2) sizing in acid medium (coagulation of rosin by aluminium sulphate); of considerable promise in this respect are neutral and alkaline sizing procedures, which give papers with increased durability[18,19]; (3) the addition of fillers, which may facilitate degradation processes, although they

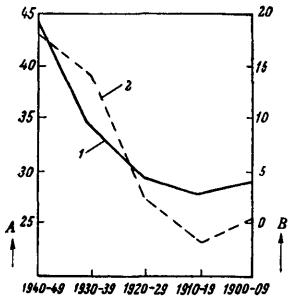



Fig.1. Comparison of the strength of modern printing papers prepared in the past 50 years.
*A*) Mean values of the resistance to tearing; 1) ditto.
*B*) Mean values of the resistance to folding; 2) ditto.
The values of the strength of modern papers, prepared in 1960, lie outside the diagram.

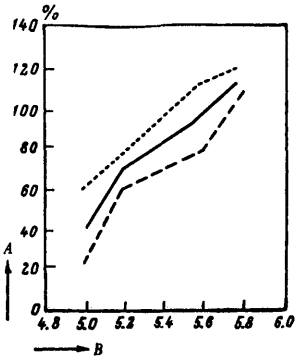



Fig.2. Effect of the pH of paper sheet on the decrease in strength under the influence of artificial aging.
*A*) Mean values of the resistance to folding as a percentage of the original values.
*B*) pH of cold aqueous extract.
The effect of artificial aging is equivalent to natural aging for 25 years. Photographic paper base was used.

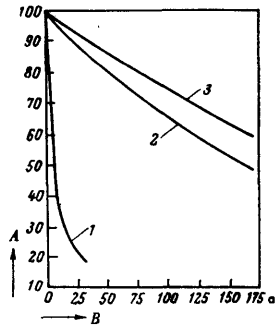



Fig.3. Comparison of the decrease in stability under the influence of artificial aging for old and modern printing papers.
*A*) Values of the resistance to folding as a percentage of the original values.
*B*) The durability of the papers (in years) established by artificial aging.
1) Modern printing papers wear rapidly; 2) the same papers treated with hydrogen carbonate solution; 3) mean value for seven old papers 250–400 years old.

may also, on the contrary, retard these processes[19]. The conditions necessary for the production of papers with increased durability have been described[20-22]. By using alkaline fillers, for example, $CaCO_3$, it is possible to reduce the acidity of paper and increase its durability (Figs. 1–3)[22].

Cellulose fibres can be arranged in the following order of decreasing stability[10]: (cotton, flax, hemp) > (sulphite and soda cellulose) > (esparto and straw) > (wood pulp).

The compositions used in paper manufacture are classified as follows[23] (in order of decreasing stability): (a) pulped rags (100%), (b) pulped rags (50%) + wood cellulose

(50%), (c) wood cellulose (100%), (d) wood cellulose + wood pulp (in different proportions).

Variations of different compositions using cellulose from annual vegetation (reeds and straw) have been put forward[24].

The durability of paper also depends on the conditions of storage and use[25]. Thus during storage, special measures are taken to protect papers from chemical[26], physical[27-29], or biological[30-33] agents.

The literature contains data on the appreciable depolymerisation of cellulose during bleaching, leading to a decrease in the stability of papers[34]. Uchastkina[35] and later Dixon and Nelson[36,37] developed equations for determining the relationship between durability and the physico-mechanical characteristics of the original material. Finally, mention may be made of methods and apparatus for treating old papers for purposes of regeneration[38,39] or methods of chemical modification to increase resistance to heat and light[40].

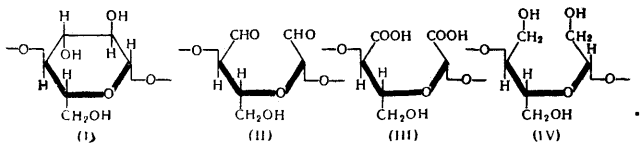
## 3. THE AGING OF FIBROUS MATERIALS

During storage and use, polymers show a continuous change in a number of variable properties — rigidity, elasticity, durability, and colour — usually referred to as aging[41]. In cellulosic materials, in particular paper, aging is accompanied by a decrease in the degree of whiteness (*yellowing*). The first quantitative observations were made as early as 1918.[42]

The sensitivity of cellulosic fibres to degradation depends on a number of factors. According to certain data[43,44], this is due to the presence of so-called "weak points" in the cellulose structure, appearing as a result of the stresses undergone by, for example, a single macromolecule taking part in the formation of two separate crystalline regions. The number of such weak points may be revealed by oxidative reactions and determined by chemical methods. According to other data[45], these stresses in cellulose appear as a result of repeated drying processes during the technological processing of the material, leading to the irreversible physical phenomena of aging (decrease in viscosity, physiocomechanical characteristics, sorption of dyestuffs, etc.). All these phenomena are described as *internal defects in physical structure*.

Another internal factor is the presence of *defects in chemical structure*. Ivanov and coworkers[46] attribute departures from the normal structure in cellulose to the presence of carboxyl and carbonyl groups, leading to the production of "weak points". Rånby[47] states that some of these non-hydroxyl groups appear as a result of chemical treatment, whereas a certain proportion (one group per 100 glucoside residues) are already present in the wood[47].

Other authors[48,49] have established the following order of stability of the elementary unit in cellulose in degradation processes, for functional groups of different kinds in positions 2 and 3:




The rate of hydrolysis increases in the order I < II < III < < IV.

Korshak and coworkers[50] showed that the resistance of polymers to degradation increases with increase in the length of the macromolecules.

Of the other main factors responsible for aging, *external factors* require emphasis. Cellulose is almost completely stable at room temperature in the dark[51], but with increase in temperature to 100–120° in the presence of air, oxidation processes begin to take place, the rate of these processes increasing in the presence of moisture[52]. Rheological determinations have shown that degradation takes place even at room temperature (the long-chain cellulose macromolecules disappear)[53].

Aging is also favoured by the fact that the weak points referred to above are extremely susceptible to the action of oxygen[54,55], oxidation taking place by a chain reaction[56]. The rate of hydrolysis of cellulose at these "weak points" is 300 times the rate of hydrolytic rupture of an ordinary β-glucoside bond; it should be borne in mind that one weak unit is found for every 400–500 anhydroglucoside units[57]. The rate of hydrolysis of wood cellulose is reduced considerably by preliminary treatment with sodium tetrahydroborate[58].

Mathematical equations describing qualitatively the effect of aging in various grades of paper under the influence of heat, light, or wear have been put forward[59-64]. The rate of these effects, including photo-oxidation or thermal oxidation, is determined by the temperature, the presence of atmospheric oxygen, light, ultraviolet radiation, etc. Thus characteristic features of photo-oxidation are the photochemical initiation of the reactions and the stability of the peroxides formed, whereas characteristic features of thermal oxidation are the chain reactions of peroxo-compounds formed under the influence of heat[65,66].

It has been shown for the example of rubber[67] that aging depends on the number of active reaction centres: degradation under the influence of ultraviolet radiation, despite the superficial nature of the irradiation, is much more intensive than the effect of heat, although with the latter the reaction takes place throughout the entire bulk of the polymer[68-70].

The phenomenon of keratinisation, manifested as a decrease in the reactivity of the fibres as a result of drying above 100°, is observed during the aging of cellulose. Keratinisation is attributed to merging of the fibrils to form characteristic aggregates, with subsequent bonding by hydrogen bonds, leading to a decrease in the physico-mechanical characteristics[71,72].

The aging of various documents or books in libraries in large industrial cities results from the action of the atmosphere, which contains sulphur dioxide. Study of the absorption of sulphur dioxide by papers[73] shows that the reaction of this compound is catalysed by traces of heavy metal ions (Fe, Cu, Cr, V, Co, Ni, or Mn); Na, K, Ca, Ba, and Al ions have no catalytic action. A number of inhibitors (disodium hydrogen phosphate, 8-hydroxyquinoline, or ammonium oxalate) have been proposed for suppressing the action of these metals[74].

The influence of metal ions on the aging of papers has been studied by many workers. Stübchen-Kirchner[75] showed, for example, that the presence of the ions $Fe^{3+}$ > > $Fe^{2+}$ > $Cu^{2+}$ causes yellowing of paper, whereas other ions stabilise the colour of paper, in the following order:

$Cd^{2+} > La^{3+} > Mg^{2+}$. Similar phenomena were observed by other authors [76-79], who emphasise the importance of iron ions in the formation of coloured complexes with rosin during sizing. Similar effects of yellowing in paper have been noted when gelatin and starch were used as sizing agents [80,81].

In the study of the yellowing of monocarboxycellulose under the influence of sodium, calcium, manganese, and aluminium salts, it was established [82] that the free carboxy--groups show a tendency to form anhydrides, lactones, and salts; the formation of salts intensifies the colour. Czepiel [83] arranged metal ions in the following order of decreasing action on the stability of the whiteness of papers: $Fe^{3+} > Fe^{2+} \geq Cu^{2+} > Al^{3+} \geq$ control specimen without ions $\geq$ $\geq Cd^{2+} \geq La^{3+} \geq Mg^{2+} \geq Mn^{2+}$. Manganese salts retard aging. Analogous results were reported by other authors [84-86]. Wultsch and coworkers [87] proposed preliminary treatment of the paper pulp with complex salts of the Trilon B or sodium polyphosphate type (in concentrations of 0.06–0.08%) to remove traces of metals (Fe, Cu, Mn, Co, Al, Cd, and Mg) and increase the whiteness of paper.

The yellowing of paper is an extremely undesirable phenomenon, particularly since paper with a high degree of whiteness can now be produced. The degree of yellowing is defined by the PC number (post colour number). [88] Most authors consider that yellowing is a natural consequence of the accumulation of carbonyl compounds in the cellulose or paper [88-99]. Okada and Ida [99] even established a direct relationship between the degree of yellowing and the quantity of carbonyl groups.

Sikhtol and Virkol [100] made a detailed study of the influence of various functional groups in cellulose on the phenomenon of yellowing, and established that: (1) a formyl group at $C_{(1)}$ in the elementary unit does not cause yellowing, whereas at $C_{(2)}$ and $C_{(3)}$ it favours this process; (2) hydroxyl groups in positions $C_{(2)}$ and $C_{(3)}$ do not cause yellowing; and (3) carboxy-groups in positions $C_{(2)}$ and $C_{(3)}$ bring about the same yellowing effect as formyl groups; the intensity of the yellow colour is greater when these groups are present in the form of the sodium salts, and weaker in the case of the calcium salts.

Sikhtol [100] points out that yellowing is accompanied by a decrease in the DP of cellulose and an increase in the value of the copper number; in the latter case, an increase in the copper number from 5 to 50 has no influence on the yellowing of such celluloses as sulphate cellulose, bisulphite cellulose, cotton cellulose, and hemicellulose.

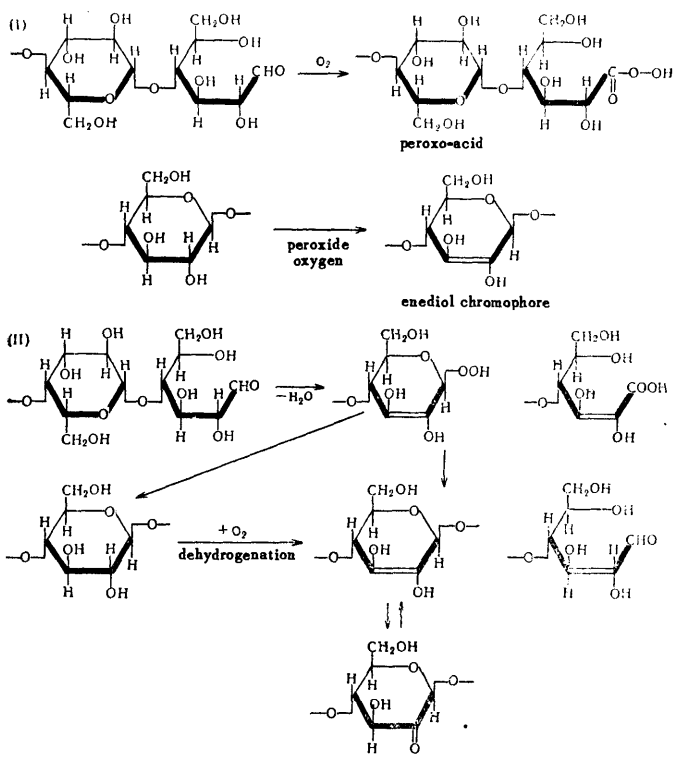
The yellowing of celluloses decreases with removal of the hemicelluloses, since the presence of the latter facilitates the hydrolytic formation of low-molecular-weight compounds of the oligosaccharide type or even monosaccharides, which condense under the influence of pectic substances and are converted into brown humic products [101-111]. Some authors relate the phenomenon of aging to the concentration of hemicelluloses [112] and, in particular, $\gamma$-cellulose [113].

Celluloses obtained by use of an ammonium hydrogen sulphite cooking liquor undergo yellowing more rapidly than those obtained using a calcium hydrogen sulphite liquor [114]. The stability of the whiteness may also depend on other technological factors, for example, the methods used to bleach the celluloses [115], the best results being obtained by bleaching with chloride dioxide [116]. In all, preliminary treatment with sodium tetrahydroborate can be used to increase the whiteness [117,118].

Roudier and coworkers distinguished two successive stages in the aging and yellowing of papers: (1) *hydrolysis* (as a result of chemical technological treatment or the action of moisture after preparation of the papers), and (2) *degradation* (which is more marked, the higher the concentration of hemicelluloses); the latter also leads to aging [119-122]. Similar conclusions were reached by other authors [123,124].

In an examination of the influence of soluble substances on the increase in the rate of aging of cellulose, Treffers [125] found, among the degradation products, organic acids which have a hydrolytic influence on the separation of hemicelluloses with the formation of free pentoses and oligosaccharides. Under the influence of the same acids, sugars are converted into dark humic products.

Here, mention must be made of an attempt by Kleinert and Marraccini [126] to establish the chemical mechanism of the aging and yellowing of celluloses under the influence of heat. They showed that peroxides are formed during aging [112]. In the presence of air (I), peroxo-groups and enediol compounds are formed, and in the absence of air (II), polyacetal groups are formed; in both cases unsaturated chromophoric groups are produced.




The individual stages of this mechanism were established chromatographically but the scheme is nevertheless fairly speculative.

A similar study was made of the aging of cotton cellulose in 0.5 *N* NaOH in the absence of air at elevated temperatures; the formation of saccharic acids was established chromatographically [127]. Under the influence of atmospheric oxygen and light, cotton cellulose shows a change in DP during ripening in the cotton-plant bolls under conditions of natural and accelerated aging [128]. Different mechanisms of degradation in the presence of oxidising agents of different types have been pointed out [129], together

with the unique part played by the carbonyl groups in this process [130].

In a comparison of natural aging (for 4, 8, 22, and 26 years) with accelerated methods (72 h at 100°), Wilson [131] found good agreement between the results obtained by the two methods for the change in the concentration of $\alpha$-, $\beta$-, and $\gamma$-celluloses, the acidity of the aqueous extract, and the mechanical characteristics of the papers; he established that accelerated aging under the above conditions is equivalent to the effect of natural aging for 25 years. The method of artificial aging has also been used to study the durability of textile fibres [132]. The resistance of fibrous materials to aging is usually established by determining their viscosity [133]; no difference in the concentration of carbonyl and carboxyl groups has been observed for a given DP value [134].

Papers containing wood pulp undergo aging more rapidly because of the increased lignin content. There are reports of a direct relationship between aging and the lignin concentration [135-141]. The phenomenon of aging has also been studied for papers produced from linen and cotton rags [142] and also for papers prepared from wood and straw celluloses [143] or from jute [144]. In all, it was found that aging is accompanied by oxidative and hydrolytic reactions.

## 4. THE THERMAL DEGRADATION OF FIBROUS MATERIALS

Most work on degradation has been carried out by thermal treatment of the cellulose or paper. Yabrova [145] subjected newsprint to thermal aging (at 80° and 20° and a relative humidity of 60%) and observed a decrease in the number of double folds on the fifth day of treatment; at the same time, the solubility of the fibrous material in 7.4% sodium hydroxide solution increased, with a simultaneous increase in the concentration of carboxy-groups.

In a comparison of artificial aging (100° for 72 h) with natural aging, Royen [146] attributed the oxidative degradation of papers to the presence of hemicelluloses. Gluchowska and Winczakiewicz [147] equated the action of thermal treatment under these conditions for different grades of paper prepared from sulphite cellulose to only six years of natural aging (instead of 25 years, as is generally assumed). The presence of carboxy-groups in cellulose leads to a decrease in the heat-resistance of papers [148].

Simionescu and coworkers [19,149] studied the effects of artificial aging for more than 50 grades of writing, printing, and technical papers manufactured in various Roumanian factories, determined the most stable grades, and the technological factors favouring the production of durable paper. The addition, to the fibrous composition of the papers, of cellulose from annual vegetation (reeds and straw) in quantities up to 30–50% in mixtures with spruce cellulose did not lead to any significant intensification in the degradation; this is of practical importance for Roumanian conditions [150].

The most important factors influencing the heat-resistance of cellulose and papers are the DP, the molecular composition of the fractions, and the active acidity of the material; the most stable celluloses are cotton cellulose and sulphate celluloses, and the least stable are bleached (non-purified) sulphite celluloses [151]. The parameters most sensitive to the action of heat are the whiteness, viscosity, and number of double folds [152].

Sulphate cellulose has been shown to have a high heat resistance. In the case of bleached kraft cellulose, it has been established that there is a difference in the behaviour during artificial aging, depending on the temperature and the presence or absence of moisture [153]; other conditions being equal, the presence of lignin and hemicelluloses intensifies degradation [154,155]. Intermediate drying of cellulose for paper-making to a moisture content of 25% leads to a decrease in the mechanical characteristics of the paper [156]. Papers prepared from kraft cellulose, thanks to their heat-resistance, are better than the corresponding grades of paper prepared from rags [157-160], so that they are preferred for work on the restoration of documents [161] or for the production of capacitor papers [162-164]. Fabre [165] recommends chemical methods for the analysis of sulphate papers, in order to examine their aging in electrical transformers.

Cardboard becomes sensitive to the influence of heat only at a relatively high temperature (200°) [166].

Comparison of the aging of cellulosic fibres from cotton [167] or from artificial silk under the influence of heat with that for natural silk [168], and also comparison of the aging of natural fibres [169] with that of synthetic fibres [170], are of practical interest. The heat-resistance of fibres is increased by the addition of antioxidants [171]. In a study of the action of high temperatures (100–160°) on viscose fibres, Agster established that the following stages are involved in the degradation: up to 140° hydrolytic processes predominate, in the range 140–150° oxidative processes predominate, and in the range 150–160° thermal cracking begins [172,173]. At 145° the strength of viscose fibres decreases by 45% relative to the original value [174].

Interesting results have been obtained in the pyrolytic degradation of cellulose. Thus at 172°, [175] a number of gaseous products (CO, $CO_2$, and $H_2O$) were obtained, and saccharic acids, aldehydes, ketones, and glucose were determined by paper chromatography in the residue. In the presence of air, the reactions take place initially in the amorphous regions and then continue in all regions with a simultaneous decrease in the DP to a constant value [176]. At higher temperatures, for example, at 350–375°, a residue containing 55% water, 12.5% laevoglucosan, 15% carbonyl compounds, and 7.5% of various acids is obtained [177].

In the absence of air [178], the thermal degradation of cellulose takes place with an activation energy of the order of 26 kcal mole$^{-1}$. The pyrolysis of fibrous vegetable materials has been studied in the presence of mineral salts [179] under different temperature conditions [180-186]. In all, the formation of laevoglucosan with 1,5 and 1,6 oxygen bridges was established [187]. A relationship was established between the reactivity of celluloses and their behaviour during pyrolytic degradation [188]. In the degradation of cellulose with a molecular weight of approximately one million for 10 h at 130°, one chain unit in every 18 units underwent a change, even in the absence of air [189]. Analogous data on the degradation of various native celluloses have been given by other authors [190-193].

An important contribution to the study of various aspects of thermal degradation has been made by Golova and coworkers. On the assumption that $\beta$-glucose is an intermediate product in the formation of laevoglucosan [194,195], they showed [196] the possibility of the direct formation of the latter from cellobiose [197,198], pectic substances [199], and polygalacturonic acids [200] by splitting at the 1-4-$\beta$-glucoside

bond and isomerisation of the chain fragments. The yield of laevoglucosan depends on the original structure of the cellulosic material[201], high yields being obtained where the density of packing of the molecular chains is high. Similar conclusions were reached by other authors[202,203].

The extent of degradation depends not only on temperature but also on the duration of treatment, the degree of polymerisation of the cellulose, and the composition and nature of the medium in which the degradation takes place. For example, moderate heating (up to 120°) is accompanied by depolymerisation, but at elevated temperatures (240°) dehydration begins with a subsequent change in the chemical composition of the elementary unit[204].

A review by Sergeeva[205] gave data obtained in a study of the changes and degradation undergone by wood vegetable fibres, and also the macromolecular components of wood, under the influence of thermal treatment. In particular, it was reported that the degradation of the cell walls of holocellulose takes place in stages: degradation of the hemicelluloses and the loose regions of the cellulose takes place at 155–260°, degradation of the secondary layer of cellulose begins at 280–285°, and at 280–300° the secondary layer of cellulose decomposes completely and degradation of the cellulose of the cambial layer begins; under these conditions, only the cellulose of the tertiary layer remains stable.

The degradation of cellulose has been carried out in various liquid media. For example, cellulose has been heated in petrol, benzene, pyridine, dioxan, and various alcohols, for 3 h at 200°; a decrease in the DP was observed[206]. Depolymerisation is more extensive in non-polar liquids (kerosene, benzene) than in polar liquids[207-209]. Heating for 1 h at 240° in anhydrous glycerol leads to an increase in the density of packing of the cellulose (the density of the specimen changed from 1.531 to 1.551). This led Sharkov and Shchleglova[206] to establish a direct relationship between the changes in the density of cellulose specimens and the changes in the infrared spectra of the specimens in the range 3000–3600 $cm^{-1}$. Usmanov and coworkers[210] established that thermal treatment of cotton cellulose leads to a decrease in the integral heat of wetting, and that a unique type of structural change takes place, leading to an increase in the ability to undergo changes in packing and an increase in molecular packing. The action of pure water on cellulose at elevated temperature has also been studied[211,212]; on treatment with water, the concentration of carboxy-groups increases, the water becomes acidic, and the cellulose undergoes extensive depolymerisation.

Degradation has been carried out in sodium hydroxide solutions at 170°,[213,216] sodium hypobromite solutions[214], liquid paraffin, superheated steam, sulphuric acid, and salt solutions in the range 130–250°, in order to establish the approximate mechanism of degradation[217].

The changes undergone by cotton cellulose during thermal degradation were described by Aubry[218]. Thus at 90° there is a moderate decrease in such parameters as the moisture content, mechanical strength, degree of whiteness, and DP, after treatment for only 4 h; at 110° these characteristics also decrease slightly (from the start in this instance), the rate of decrease in these characteristics increasing considerably only at 130–150° (the DP decreases from 3000 to 1200); the same rates are observed for the change in solubility in sodium hydroxide, the acidity of the aqueous extract, the copper number, the degree of whiteness, and the concentration of carboxyl groups in the cellulosic material. Hydrocellulose is distinguished by an increased heat-resistance; this is attributed to a difference in the number of "weak points" (one per 1000 glucoside residues for cotton fibre and one per 500 or 250 glucoside residues respectively for hydrate cellulose)[219-221].

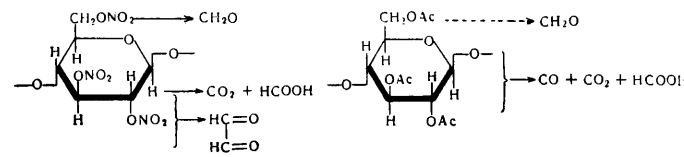
Significant changes are also observed in the X-ray diffraction patterns for native and mercerised cellulose as a result of thermal treatment; at moderate temperatures there is a change in the reflections corresponding to the (002) planes, and the (101) and (10$\bar{1}$) planes show irreversible broadening; in the case of cellulose-II the reflections of the (101) plane show gradual fogging[222]. At 300° the texture of both celluloses disappears completely from the X-ray diffraction patterns[224].

When the degradation of cellulose is carried out by increasing the temperature gradually (5.5 deg $min^{-1}$), dehydration is observed at 200–230°, and at 300° the water is removed completely and structural changes begin, with partial loss of carbon; above 300° combustion begins, with partial decarbonisation and formation of amorphous carbon[224].

The thermal decomposition of cellulose in a vacuum is accompanied by the production of carbonyl and carboxyl groups, with a simultaneous change in elemental composition[225]. Structural changes resulting from thermal treatment have also been described for mercerised cellulose[226,227].

The method of thermal degradation has been extended to cellulose derivatives. Thus the thermal decomposition of nitrocellulose[228,229] (which takes place by a chain reaction), cellulose acetate[230-234], ethylcellulose[235], or cellulosic fibres thermostabilised by partial acetylation[236] or cyanoethylation[237-239] has been described. Acetylcellulose was found to be more stable under conditions of thermal aging than other derivatives, its thermal stability being several times that of cellulose[240].

The thermal decomposition of nitrocellulose leads to the formation of oxides of nitrogen, volatile organic substances, carbon dioxide, carbon monoxide, formic acid, formaldehyde, glyoxal, and hydrogen cyanide[241]. On the basis of data obtained using tracer atoms, the following schemes were proposed for the degradation of cellulose nitrate[100] and cellulose acetate[235]:




It should be emphasised that in the last scheme the degradation products appear chiefly as a result of the rupture of the pyranose ring, and not by removal of the acetyl (Ac) groups of the macromolecule, as was previously generally accepted.

Thermal degradation, as a method of studying the structure of cellulose, provides extensive factual material and gives additional information on the overall mechanism of the decomposition. Different versions of the method are still used by many authors.

## 5. THE PHOTOCHEMICAL DEGRADATION OF CELLULOSE

During use, cellulosic materials always undergo aging under the direct influence of *sunlight.* Diffuse light (day--light, the light from "white" incandescent lamps or fluorescent sources) also leads to aging, although it rarely contains appreciable proportions of the ultraviolet range of the spectrum [242,243].

The influence of sunlight on cellulose fibres during the bleaching of flax and hemp in bleaching greens has been known for long: this action was attributed to the influence of heat and light [244,245]. The prolonged action of sunlight on various grades of paper (exposure for 5-120 d) produced different changes in the concentration of $\alpha$-cellulose and in the value of the copper number [246,247]. Yellowing has been attributed to the presence of rosin size [248-251]. The bleaching of paper under the influence of sunlight filtered through window-glass has also been noted [252]. The aging of papers from bisulphite bleached and unbleached celluloses exposed to sunlight depends on the concentration of lignin present [253]. Since the spectrum of sunlight contains radiation with wavelength from 290 m$\mu$ to 700 m$\mu$, it should be noted that cellulose absorbs radiation with $\lambda < 400$ m$\mu$; [254,255] the presence of lignin [256-259] displaces the absorption to the range 280–400 m$\mu$; the use of rosin as size intensifies the absorption in the range 330–440 m$\mu$. [260]

Marini [261] compared the action of sunlight in the yellowing of papers with that of illumination by a mercury lamp; the results of exposure to the two different light sources are different, due to the difference in the energy distribution of the spectra. Analogous experiments were carried out by others [262].

Photochemical degradation is generally studied using *ultraviolet irradiation.* Under the influence of this illumination, simple sugars decompose with the formation of volatile products. Fructose [263] gives carbon dioxide, carbon monoxide, formaldehyde, methanol, and various acids; aqueous solutions of glucose and fructose gave carbon monoxide, methane, hydrogen, carbon dioxide. The rate of decomposition of fructose is seven times that of glucose [264]. In the case of cellulose irradiated in a vacuum ($\lambda$ = 253.7 m$\mu$ at 40°), liberation of a gas mixture with characteristic composition (87.5% $H_2$ + 8.2% CO and 4.3% $CO_2$) is also observed; [265] depolymerisation (DP 1710 → 690) and an increase in the concentration of nonhydroxyl functional groups takes place simultaneously. The degradation is attributed to the conversion of alcoholic groups into carbonyl groups, accompanied by the liberation of hydrogen: a stoichiometric relationship was established between the number of broken glucoside bonds and the number of carboxy-groups.

The effects of ultraviolet irradiation on cellulose and paper depend on the wavelength. Irradiation with narrow ranges of the ultraviolet spectrum established a difference between the behaviour of papers with high lignin content (from wood pulp) and that of papers containing almost no lignin. Liberation of gases was observed always [266]; after an interval, the liberation of gases stopped, as a result of the screening effect of the carbonyl groups [267]. Radiation with wavelength 290–395 m$\mu$ was most effective [60,268]; according to data obtained by other authors, the active radiation is displaced towards 250 m$\mu$. [269] A systematic study by Spinner [270] of the dependence of the degradation on the spectrum of the ultraviolet radiation showed that a unique part in the photodegradation is played by lignin, the moisture content of the medium, atmospheric oxygen, and the temperature of the medium. The phenomena of photolytic after-effects are also observed. These data are given in Table 2.

Emphasising the importance of physical bonds between the components of paper for the development of durable grades, Richter and Wells [273] developed a method of artificial aging by ultraviolet irradiation. Ultraviolet radiation was also used to determine the degree of decomposition of sulphite and sulphate celluloses and to establish the nature of fillers and contaminants [274].

McClaren and coworkers [275] studied the action of ultraviolet radiation ($\lambda$ = 253.7–365.4 m$\mu$) on paper prepared from bisulphite kraft celluloses, and established that rapid yellowing of the specimens takes place in the initial stages of exposure. A curious feature is that according to the results of these authors, the behaviour of the materials is independent of the humidity of the atmosphere or the presence of carbon dioxide or sulphur dioxide; the effect of exposure is restricted to a depth of 0.15 mm. According to the results of other authors [276], the light sensitivity of paper depends on the method of bleaching: papers bleached with sodium tetrahydroborate were found to be most stable, and celluloses bleached with calcium hypochlorite were found to be most sensitive to the action of heat and light.

The light sensitivity of bleached celluloses is closely related to the nature of the fibrous raw material, the method of digestion, and the use to which the material is put. Rozmarin and Simionescu [277] studied the chemical changes undergone by different celluloses under the influence of ultraviolet radiation, and established that for chemical celluloses the concentration of $\alpha$-cellulose decreases with a marked increase in the concentration of hemicelluloses and a simultaneous decrease in the degree of whiteness. It was noted that the rate of formation of keto-groups is greater than the rates of formation of aldehyde and carboxyl groups. Papermaking grades of cellulose show an approximate analogous change in chemical composition. The degradation of cellulose from beech and reeds is more intensive than that of cellulose from spruce.

Spectroscopic study of photodegradation confirmed these conclusions; under the influence of ultraviolet radiation, cellulose and its derivatives undergo chemical and structural changes (new absorption bands due to carbonyl groups appear in the range 1720–1760 $cm^{-1}$, and the 3400 $cm^{-1}$ band corresponding to the hydroxyl groups is displaced towards smaller wave numbers). These results also show that the oxidative changes involve the direct participation of atmospheric oxygen [277].

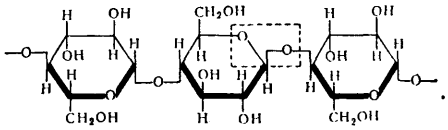
Cellulose can be regarded as transparent to radiation with $\lambda > 200$ m$\mu$. Carboxy-groups absorb radiation of

TABLE 2. Influence of ultraviolet irradiation on cellulose.

| Wavelength of radiation $\lambda$, m$\mu$ | Action on cellulose or paper containing no lignin | Action on cellulose or paper containing appreciable quantities of lignin | References |
|---|---|---|---|
| 200–300 | *Yellowing*: the presence of water inhibits the process; yellowing may begin during the after effect; temperature has no direct effect on the process | *Yellowing*: more intensive in the presence of air, moisture, and heat; moderate in their absence | 266, 267 |
| 300–400 | *Bleaching*: appreciable in the presence of moisture and air; heat causes yellowing | *Yellowing*: bleaching takes place in the absence of moisture and heat | 258, 268, 271, 272 |
| 400–500 | – | Bleaching may take place | 258, 270 |

very short wavelength, whereas the C–O–C group does not absorb radiation with $\lambda > 220$ mμ.[278-280] Sippel[60] established that the energy corresponding to radiation with $\lambda = 350$ mμ, equal to 82 kcal mole$^{-1}$, is quite sufficient for the rupture of chemical bonds in polymers. It has been established that other wavelengths also correspond to appreciable energies[281].

From the above data it follows that the splitting of the $C_{(1)}-C_{(2)}$ and $C_{(1)}-O$ bonds of the elementary unit of cellulose may take place in different ways under the influence of ultraviolet radiation. Chromatographic determination of the corresponding cellulose degradation products confirmed, in particular, the mechanism of labilisation of these bonds, as shown below[282]:



By measuring the polydispersity, Page[283] proved that significant changes are undergone by cellulose subjected to ultraviolet irradiation for a prolonged period (500–2000 h). Recently, Rozmarin and Simionescu[284] established that appreciable changes take place in the polydispersity of celluloses as a result of shorter exposures (100–240 h); in all cases the maximum of the differential molecular-distribution curves was displaced towards lower DP values (papermaking celluloses acquire a more regular molecular composition under the influence of irradiation, but chemical celluloses, with more regular initial fraction composition, show a much greater increase in the degree of polydispersity). These changes are illustrated schematically in Fig. 4.

The above data confirm the theory (put forward as early as 1943[285]) that photolytic splitting of the cellulose chains takes place under the influence of ultraviolet radiation, with simultaneous photo-oxidation phenomena[286]. On the other hand, for cellulose and its derivatives, Tichener[287] found no relationship between the polydispersity and the course of the photolytic reactions.

Photochemical degradation involves free-radical chain reactions[288]. This was proved for cellulose by Simionescu and Poppel[289], who observed that solutions of hydroquinone and gallic acid inhibit the photodecomposition completely; this revealed that the reaction involved free radicals[19,290]. Zapol'skii[291] also confirmed this suggestion for the case of Cellophane, on the basis of spectroscopic data.

A mathematical method has been developed for calculating the number of cellulose chains split during photolysis from the concentration of aldehyde groups formed and the quantity of hydrogen liberated during the reaction[292].

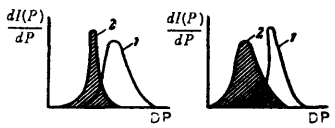



Fig. 4. Change in the molecular composition of paper-forming (left) and viscose (right) celluloses under the influence of ultraviolet radiation.
1) Control specimens; 2) irradiated specimens.

Flieder[293] used the ultraviolet light from bactericidal lamps to bleach old papers, and Belaya[294] used the same light to determine the durability of grades of paper used for printing. Simionescu and Poppel[295,296], on the basis of the artificial aging of papers by ultraviolet irradiation, recommended the use of kauri gum for the preservation of papers. A large number of versions of new methods of bleaching, using chlorine dioxide, sodium tetrahydroborate, sodium peroxide, and hydrogen peroxide, have been proposed, to increase the stability of the whiteness of papers[297] and reduce the effects of photodegradation[298,299].

Centola[300] established the following order of photo-stability for cellulosic materials: cotton > flax > hemp > > jute and linter > spruce viscose cellulose > spruce papermaking cellulose > spruce cellulose > sulphate cellulose > spruce semi-chemical cellulose > straw cellulose.

Using the numerical criterion of Geller and Meskin[301] for determining the degree of polydispersity, Rozmarin and Simionescu[284] gave another version of the order of photo-stability of bleached celluloses: spruce papermaking kraft cellulose > spruce bisulphite papermaking cellulose > > viscose sulphate cellulose from reeds > papermaking sulphate cellulose from reeds > viscose bisulphite spruce cellulose.

It has been shown that lignin facilitates the photodecomposition of cellulose, although it has also been reported[302] that lignin is able to retard oxidation processes. Papers sized with natural rosin are less stable to the action of light than papers sized with completely saponified rosin[303]. No appreciable yellowing effect is observed for cardboard[304].

Titanium dioxide fillers have a catalytic action. Atomic oxygen is formed, according to the reaction[305]:

$$2TiO_2 + h\nu = Ti_2O_3 + O,$$

and this oxidises hydrated cellulose[306] or cellulose derivatives[307] (for example, acetate rayon) preferentially. Under the influence of ultraviolet light, titanium dioxide acts an an oxidising agent on disaccharides (maltose, lactose, saccharose, and cellobiose) with the formation of the corresponding acids, but no splitting of the heterocyclic rings or acetal bonds was observed[308].

The presence of hemicelluloses and oxycelluloses does not play any significant part in the photolytic yellowing of cellulose from jute[309,310].

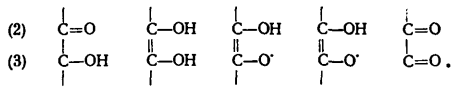
Zinc oxide increases the sensitivity to photochemical reactions, but glycerol, glucose, benzidine, etc. have a retarding influence[302]. More than 1% titanium dioxide may exert a protective influence on cellulosic materials[311-313]. A catalytic action is shown by Fe, Cu, Cr, Mn, U, Ti, and Mg ions[314]. Similar observations were made for synthetic[315,316] and artificial[311-313] fibres and on mixed fibres from cotton and Lavsan [Dacron, Ed. of Translation)][317].

Mention must be made of work on the influence of photodecomposition on the formation of cellulose ethers[318], which established a decrease in the reactivity of cellulose and also work on cellulose nitrate[319-321] and cellulose acetate[322].

Various schemes for the mechanism of the photodecomposition of cellulose have been proposed. Mention has already been made of the theories of Wilson and coworkers[265-267], Beelik and Hamilton[282], and Simionescu and coworkers[18,19,277,284,289,296]. In the opinion of these authors, ultraviolet radiation has a *photolytic* action on

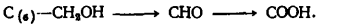
the bonds formed by the carbon atoms in positions 1 and 2[282] and an *oxidative* action on the carbon atoms in positions 2, 3, and 6[265,277]. The reactions take place with the participation of atmospheric oxygen[277] by oxidative chain reactions[19,289].

Work by other authors has confirmed these suggestions. Schurz and coworkers[323] studied the ultraviolet absorption spectra of the soluble products of the yellowing of celluloses and found the following chromophoric groups in positions 2 and 3 of the elementary unit:

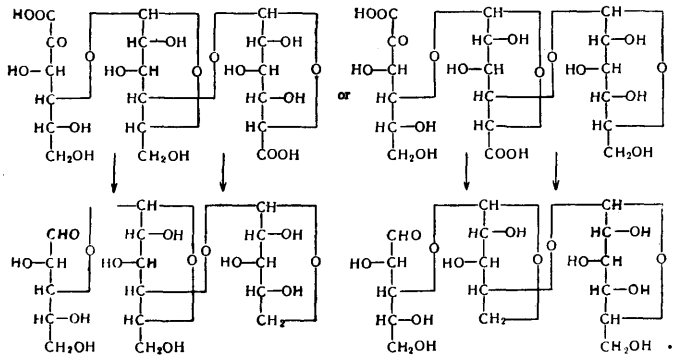


These groups undergo a number of changes, leading finally to splitting of the $C_{(2)}-C_{(3)}$ bond and the pentylene oxide bond 1–5 with the formation of brown products.

Zapol'skii[324] subjected Cellophane to the action of ultraviolet light and established an increase in the concentration of carboxy-groups as a result of the oxidation of primary alcoholic groups. On the basis of a study of the infrared absorption spectra, he suggested the following mechanism of photodegradation:



On the basis of data obtained by chromatographic separation of the products of the photodecomposition of cellulose, Bera and coworkers[325,326] concluded that cellulose decomposes to monosaccharides (xylose, arabinose, and glucose), cellobiose, and oligosaccharides (cellotriose and cellotetrose), which are converted into simple sugars by decarboxylation and splitting of the glucoside bonds:



The formation of xylose, arabinose, and glucose proves that photolysis of the β-glucoside bond takes place initially; the products are oxidised by atmospheric oxygen and decarboxylated under the influence of irradiation. It is difficult, however, to explain the formation of dark brown decomposition products by this scheme.

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The above published data indicate the considerable interest shown by scientists in the study of the degradation of cellulose under the influence of a variety of factors. The phenomenon of aging, which accompanies degradation processes, has also attracted the attention of research workers. Examination of the above results makes it possible to determine the progress made in each branch of the study of the degradation of cellulose and to establish the nature of the problems requiring further examination.

It follows from this review that in thermal degradation and photodegradation, cellulose exhibits dual behaviour: oxidation and depolymerisation. The heat- and light--stability of cellulosic materials depends on the nature of the cellulosic raw material, the processes of digestion and bleaching, and the conditions of use. It may also be taken as established that the two types of degradation (under the influence of heat and light) differ essentially only in the superficial action of light and the bulk action of heat. In both, the decomposition involves chemical changes in the cellulose macromolecules (under the influence of atmospheric oxygen or the oxygen atoms of the molecules itself) and rupture of the chains.

The mechanisms proposed by different authors for the decomposition of cellulose have thrown light on a large number of individual aspects of the chemical changes undergone by cellulose but all possibilities in this field have not yet been exhausted. In the solutions of these problems, use must be made of the more promising methods of study, for example, chromatographic and spectroscopic methods.

Among methods leading to an improvement in the durability of cellulosic materials, particular attention should be paid to the development of milder conditions for the technological processes involved in the preparation, purification, bleaching, and finishing of cellulose. Mention may be made, for example, of the harmful effects of beating, bleaching, and sizing in acid medium in the manufacture of paper. Methods involving the addition of various inhibitors to prevent the degrading action of air, heat, and light, and also methods for the chemical partial modification of celluloses[327] appear promising.

Finally, it should be noted that in the study of artificial aging, the contradictory results which have been obtained can be attributed to the fact that the conditions of humidity and temperature have not been strictly controlled. In this field it is necessary to determine the factors responsible for the decrease in the whiteness of cellulosic materials, to develop standard methods of accelerated aging, and to establish the part played by non hydroxyl functional groups. In this connection the development of accurate methods for determining the different functional groups of cellulose is of considerable importance.


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# THE PHYSICOCHEMICAL PROPERTIES OF OXYETHYLATED NON-IONIC SURFACE-ACTIVE SUBSTANCES

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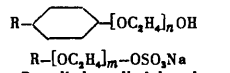
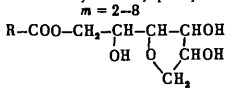
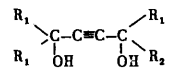
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## I. INTRODUCTION

The production of non-ionic surface-active substances (NSAS) began in 1929–1935, when for the first time products were obtained by the addition of ethylene oxide to organic compounds containing at least one reactive hydrogen atom, such as the higher aliphatic acids, their amides, higher aliphatic alcohols, thiols, alkylphenols, amines, etc. These products are characterised by the number of ethylene oxide groups attached to one mole of the organic substance. It should be noted that the oxyethylene chains in the compounds are almost never of equal length, their distribution with respect to dimensions being described by a classical Poisson curve[1,2]. At the present time, methods are available for separating a mixture of polymer-homologues into individual products[3] and also for obtaining certain individual NSAS using particular chemical reactions[4].

As a result of the slightly hydrophilic character of ethylene oxide, the addition products usually have a higher solubility in water than the original substances. A significant advantage of oxyethylated substances is the possibility of controlling their hydrophilic nature by altering the quantity of attached ethylene oxide, and also the number of carbon atoms in the hydrophobic chain. This makes it possible to obtain substances with optimal properties for any given field of application. Another important characteristic feature of oxyethylated substances is that they cannot form salts, so that they are stable in hard water and can be used in combination with both anion-active and cation-active SAS.

TABLE 1. Main classes of NSAS.[10]

| Type | Chemical structure | Trade name and firm** |
|---|---|---|
| Oxyethylated aliphatic acids and products of the oxyethylation of tall oil* | $R-CO[OC_2H_4]_nOH$ | Soromine SG<br>Emulsifier A<br>Sterox CD (Monsanto)<br>Prevocel (Buna) |
| Oxyethylated amides | $R-CON\begin{matrix}[C_2H_4O]_xH\\[C_2H_4O]_yH\end{matrix}$ | Dionyl (Hulz) |
| Oxyethylated alcohols | $R-[OC_2H_4]_nOH$ | Peregal O, Bunegal O (Buna) |
| Oxyethylated alkylphenols |  | Igepal C and W, Sapal (Buna) |
| Sulphonated oxyethylated alcohols | $R-[OC_2H_4]_m-OSO_3Na$<br>R = alkyl or alkylphenyl<br>$m = 2-8$ | Alipal<br>Igepal B |
| Esters of sorbitan and aliphatic acids |  | Span |
| Oxyethylated esters of sorbitan and aliphatic acids | the same, polyglycol ester | Tween |
| Monoethanolamides | $R-CO-NH-C_2H_4OH$ | Ninol |
| Diethanolamides | $R-CON\begin{matrix}C_2H_4OH\\C_2H_4OH\end{matrix}$ | Ninol |
| Oxyethylated poly(propylene glycol)s | $H[OC_2H_4]_x-[OC_3H_6]_n-[OC_2H_4]_y-OH$;<br>$R-[OC_3H_6]_n-[OC_2H_4]_xOH$ | Pluronic |
| Oxyethylated (ethylenediaminopolypropylene glycol)s | $CH_2-N\{[C_3H_6O]_n-[C_2H_4O]_xH\}_2$<br>$CH_2-N\{[C_3H_6O]_n-[C_2H_4O]_xH\}_2$ | Tetronic |
| Dialkyldihydroxyacetylene |  | Surfynol |
| Esters of saccharose and aliphatic acids | R–CO–(saccharose) | Sacrodet |
| Saccharose alkylurethanes | R–NH–CO–(saccharose) | |

* Tall oil is a by-product of sulphate cellulose production, containing chiefly a mixture of aliphatic and resin acids.

** See Ref. 10.

The combination of valuable technical properties shown by NSAS and the continuous decrease in the cost of their production has recently led to their extensive application in many branches of technology, including the textile industry, the manufacture of wetting agents[5], the processing of petroleum[6], etc.

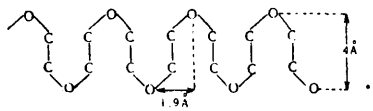
As well as increased production of these substances, the production of oxyethylated substances of the block copolymer type – oxyethylated poly(propylene glycol)s[7,8] and oxyethylated ethylenediaminopoly(propylene glycol)s[8,9] – has been developed in recent years.

Since 1935, NSAS of the sorbitan ester, ethanolamide, saccharose–aliphatic acid ester, dialkyldihydroxyacetylene, etc., type have been prepared in addition to oxyethylated NSAS. Some of the most commonly encountered classes of NSAS are listed in Table 1.

The aim of the present review is to summarise data on the properties of oxyethylated non-ionic surface-active substances and to indicate some of their fields of application.

## II. STRUCTURE OF NON-IONIC SURFACE-ACTIVE SUBSTANCES (NSAS)

In a study of the structure of polyoxyethylene chains, Staudinger[11] suggested that the retarded increase in chain length with increase in the number of oxyethylene groups can be explained by assuming that the polyoxyethylene chain has a winding shape (caterpillar shape):




The winding shape of the polyoxyethylene chain is generally assumed to be due to the mutual attraction of the oxygen atoms in the chain to one another. The chain strives to become shorter under the influence of the forces of attraction. At a low degree of polymerisation, these forces are insufficiently strong to lead to a decrease in the length of the chain, and the chain retains its usual zigzag shape[12].

Comparison of the observed and calculated specific viscosities of polyoxyethylene diacetates established that the chains have a zigzag shape up to a degree of polymerisation of 9 and that they acquire a winding shape only at higher degrees of polymerisation.

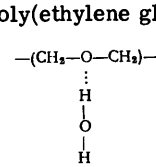
Many studies have been made of the structure of the polyoxyethylene chain[13–16]. Rösch[16] explains the winding shape of the polyoxyethylene chain on the basis of the general concepts of valency theory. He represents the structure of the polyoxyethylene chains as a zigzag structure, in which, because of the presence of $CH_2-CH_2-O$ and $CH_2-O-CH_2$ groups, oblique-angled and equilateral triangles alternate in the ratio 2:1. Each ethylene oxide group forms a dipole with a moment of 1.88, in which the $CH_2$ is the positive pole and the O the negative pole. The distance between the dipoles is 2.3 Å. The $CH_2$ groups of the ethylene oxide repel one another and the oxygen atoms attract neighbouring $CH_2$ groups. This produces stresses which increase with increase in the length of the zigzag chain. When the degree of oxyethylation reaches 9–11, the magnitude of the stresses becomes sufficiently high to produce a change in structure, and the zigzag shape is converted into the winding shape. The change in the structure leads to contraction of the oxyethylene chain.

In aqueous solutions of oxyethylated substances, as a result of the formation of polyoxonium complexes, an increase in the polarisation of the CO bond takes place and this may also lead to a change in structure.

Uchida and coworkers[17], on the basis of the dipole moments in dioxan solution, established that the polyoxyethylene chain consists of a mixture of both structures, although the winding shape of the chain predominates in aqueous solution.

## III. SOLUBILITY AND TEMPERATURE OF APPEARANCE OF TURBIDITY IN SOLUTIONS

The solubility of oxyethylated substances in water is due to the formation of hydrates as a result of the production of hydrogen bonds between the water molecules and the ether oxygen atoms of the poly(ethylene glycol) residue:




With increase in the number of oxyethylene groups, there is an increase in the number of water molecules attached to the ether oxygen atoms, and the hydrophilic

nature of the oxyethylated substance increases. Thus the polyoxyethylene chain can be regarded as "sheathed" with water molecules throughout its length. One or more of these water molecules may take up a proton from the surrounding solvent, with the formation of a hydroxonium ion. When this is so, each molecule of the oxyethylated substance is surrounded by an electrical double layer of ions. The ethylene oxide oxonium group can be represented as follows:

$$[-(CH_2-\underset{\displaystyle H_3O}{\underset{|}{O}}-CH_2)]^+OH^- .$$

The formation of charged groups increases the hydration of the substance. The presence of the charge was confirmed indirectly by the analytical studies of Wurzschmidt[18], who showed that in aqueous solutions, oxyethylated substances behave as weakly cation-active polyoxonium compounds. Only a small proportion of the ether oxygen atoms usually form oxonium salts. Studies by Schick[19], however, showed that oxonium salt formation increases on acidification, and that in strongly acidic media every ether oxygen atom forms an oxonium ion.

Scheller[5] established a rule which makes it possible to find the relationship between the number of carbon atoms in the hydrophobic fraction of oxyethylated substances and the number of oxyethylene groups necessary to make these substances soluble in water. If the hydrophobic fraction contains $n$ carbon groups, $n/3$ oxyethylene groups are required to give minimum solubility in water, $n/2$ oxyethylene groups are required to give moderate solubility in water, and between $n$ and $3n/2$ oxyethylene groups are required to give ready solubility in water.

According to the ideas of Cohen and Smith[20], one hydroxyl group or one ether oxygen atom is sufficient to overcome the hydrophobic character given to a substance by three methylene groups. Since the ethylene oxide molecule contains two $CH_2$ groups, the oxyethylated substance should contain one oxyethylene group in the hydrophilic fraction for every $CH_2$ group in the hydrophobic fraction if the substance is to dissolve in water. Thus a substance with general formula $H[CH_2]_x[OCH_2CH_2]_yOH$ is soluble in water if $y \geq x - 3$.

Shakhovskii[5] prepared oxyethylated $C_4-C_{12}$ alcohols and established that the substances obtained dissolved in water when they contained $M/44.05$ oxyethylene groups, where $M$ is the molecular weight of the aliphatic alcohol.

The solubility of oxyethylated substances in water decreases with increase in temperature, and since the energy of the hydrogen bond is low (7 kcal mole$^{-1}$), dehydration takes place so that the non-ionic substance loses its ability to dissolve in water. With decrease in temperature, the hydrate is reformed and the substance dissolves. The solubility of oxyethylated substances in water at elevated temperatures is characterised by the temperature at which turbidity appears in the solution (the cloud point). This temperature provides an important analytical indication of the degree of polyoxyethylation of the product and to some extent makes it possible to characterise NSAS. If the poly(ethylene glycol) residue contains a sufficiently large number of $CH_2-CH_2-O$ groups, the ability of these compounds to undergo hydration is so great that their aqueous solutions do not become cloudy even on boiling. Table 2 gives the cloud points of aqueous solutions of polyoxyethylated poly(propylene glycol)s.

TABLE 2. Cloud points ($t_c$) of 10% aqueous solutions of Pluronics[6].

| Pluronic symbol | Characteristics of Pluronic | Mean molecular weight of polyoxypropylene taken for oxyethylation | % polyoxyethylene in Pluronic molecule | $t_c$, °C |
|---|---|---|---|---|
| L-62 | liquid | 1750 | 20 | 20 |
| L-64 | liquid | 1750 | 40 | 70 |
| L-44 | liquid | 1200 | 40 | 78 |
| F-68 | flakes | 1750 | 80 | 100 |

Table 2 shows that the longer the oxyethylene chain, the greater the degree of hydration and the higher the temperature necessary for dehydration of the non-ionic molecules of the substance. The properties of Pluronics have been described in detail[21].

Raphael[5] determined the dependence of the cloud points of oxyethylated alcohols and octylcresols on the degree of oxyethylation at different concentrations. He showed that increase in the degree of oxyethylation leads to a linear increase in the cloud point, and that for a given degree of oxyethylation the cloud points are higher in concentrated solutions.

The cloud point depends on the chain-length distribution of the oxyethylene chains. If the oxyethylated substance contains a large proportion of low-molecular-weight products, the cloud point is low, whereas substances with a narrow distribution are more hydrophilic and have high cloud points[22].

The addition of certain electrolytes to solutions of oxyethylated substances leads to a marked decrease in the solubility and cloud points. Thus Knowles and Krupin[23], in a study of the cloud points of aqueous solutions of nonylphenols with different degrees of oxyethylation in the presence of electrolytes, obtained the results given in Table 3.

The influence of electrolytes involves chiefly a dehydrating action resulting from rupture of the hydrogen bonds. Sometimes, however, electrolytes exhibit a stabilising action related to the cation-active nature of the oxyethylated substances. Hydrochloric acid raises the cloud point (Table 3). This is due to the fact that in acid medium there is an increase in the possibility of formation of oxonium ions and hence in the hydration. Sulphuric acid has a very weak dehydrating action, since the increase in hydration resulting from oxonium ion formation is compensated by the desolvating action of the bivalent $SO_4^{2-}$ anion. Bases bring about particularly extensive dehydration. The cation-active nature of NSAS is also shown by the fact that the solubility is little influenced by the nature of the cation but is influenced to a marked extent by the nature of the anion[24].

TABLE 3. Influence of electrolytes on the cloud point of oxyethylated nonylphenols[28].

| Degree of oxyethylation of nonylphenol | Cloud point, °C | | | | | | |
|---|---|---|---|---|---|---|---|
| | distilled water | 3% NaCl | 3% $Na_2CO_3$ | 3% NaOH | 3% HCl | 3% $H_2SO_4$ | 3% $Na_3PO_4$ |
| 9 | 55 | 45 | 32 | 31 | 60.5 | 51 | 43 |
| 10.5 | 72 | 61 | 48 | 45.5 | 78 | 69 | 60 |
| 15 | 98 | 84.5 | 70 | 67 | 100 | 96 | 83.5 |
| 20 | 100 | 95 | 78 | 73 | 100 | 100 | 92 |

Doscher and coworkers[25] showed that salts of the alkaline earth metals, for example, calcium, have no dehydrating action and even facilitate the dissolution of NSAS. The $Ca^{2+}$ ions are strongly hydrated and the dipoles of the water are orientated around the $Ca^{2+}$ ions with their positive pole directed outwards. This orientation favours the formation of a coordinate bond between the hydrated ions and the negative ether oxygen atoms, leading to an increase in the hydration of the NSAS. This may explain the high efficiency of non-ionic wetting agents in hard water.

The addition of small quantities of anionic surface-active substances increases the cloud point by 10–20 deg. Maclay[26] attributed this phenomenon to the formation of mixed micelles of anionic and non-ionic SAS. At the cloud points, the non-ionic detergents are solubilised in these micelles.

The addition of aromatic or polar aliphatic substances (benzene, phenol, aniline) leads to a marked lowering of the cloud point[26–28]. The lowering of the cloud point in the presence of polar additives is attributed to the fact that these substances are solubilised in the micelles of non-ionic detergent and, as it were, increase the relative part played by the hydrophobic fraction of the detergent, with a consequent decrease in hydration and lowering of the cloud point.

## IV. SURFACE ACTIVITY AND SURFACE FILMS

It has been shown for the case of oxyethylated aliphatic alcohols[5,29], alkylphenols[5,30], and Pluronics[31] that within a given series, the minimal surface tension of the aqueous solutions increases with increase in the degree of oxyethylation and decreases with increase in the number of carbon atoms in the hydrophobic chain. The change in surface activity shows qualitative agreement with Traube's rule, that is, the surface activity increases with increase in the number of carbon atoms in the hydrophobic chain. The surface activity decreases with increase in the degree of oxyethylation. Data for Pluronics, confirming these general features, are given in Table 4.

With increase in temperature, the minimal surface tension of aqueous solutions of NSAS decreases and the surface activity of the non-ionic substances increases. This characteristic feature is related to the dehydration of the NSAS molecules with increase in temperature.

Crook and coworkers[30] recorded the surface tension isotherms for *p*-t-octylphenols with normal distribution and for individual *p*-t-octylphenols prepared by special methods[4]. Using these isotherms, they determined the dependence of the minimal surface tension $\sigma_{c_k}$ and the areas occupied by the molecules in a layer with maximum

TABLE 4. Dependence of the surface tension (dyn $cm^{-1}$) of a series of Pluronics at 30° on the concentration of the aqueous solutions[31].

| Pluronic symbol | Concentration, % | | | |
|---|---|---|---|---|
| | 1 | 0.1 | 0.01 | 0.001 |
| L-44 | 41.2 | 45.2 | 47.2 | 52.5 |
| L-62 | 34.5 | 37.1 | 42.0 | 45.6 |
| L-64 | 36.0 | 40.0 | 43.8 | 48.6 |
| F-68 | 43.6 | 46.6 | 47.4 | 64.0 |

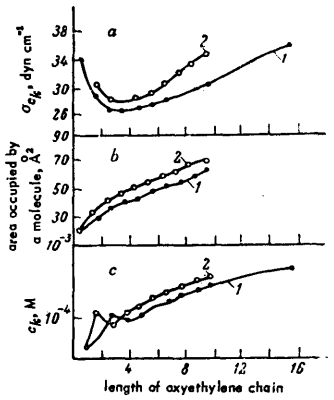



Fig. 1. Dependence of the surface tension at $c_k$ (*a*), area occupied by a molecule (*b*), and $c_k$ (*c*) on the chain length of individual OP SAS (2) and mixtures with normal distribution (1).[39]

saturation on the degree of oxyethylation (Figs. 1*a* and 1*b*). It can be seen from Fig. 1*a* that the surface tension corresponding to $c_k$ for the individual products is greater than that for the mixtures with normal distribution, since in the latter case preferential adsorption of the more highly surface-active components with lower degree of oxyethylation takes place at the solution–air boundary.

On the basis of a comparison of the surface activity of oxyethylated substances of different classes, Schönfeldt concluded that oxyethylated alcohols and phenols exhibit the highest surface activity. Wrigley and coworkers[31] studied the surface tension of 1% solutions of oxyethylated aliphatic acids and aliphatic alcohols with oxyethylated chains of different length. With equal numbers of carbon atoms in the hydrophobic fraction and equal numbers of oxyethylene groups in the hydrophilic fraction, the surface tension is greater for the oxyethylated alcohols. For example, the values of the surface tension (dyn $cm^{-1}$) for hexadecanol specimens with degree of oxyethylation equal to 15, 20, and 30, are 36.4, 38.2, and 40.2 respectively, whereas the values for palmitic acid specimens with the same degree of oxyethylation are 34.2, 35.8, and 38.4.

To determine the nature of the orientation of non-ionic surface-active substances at an air–water boundary, a number of workers have studied surface films of aqueous solutions of polyoxyethylated aliphatic alcohols[32] and alkylphenols[19,28,33–36].

The nature of the packing and orientation of the polar groups in these surface films was established from the surface tension and surface potentials, and also by recording two-dimensional phase diagrams for the films[32]. Schick[33] used the Gibbs equation and surface tension isotherms to establish the dependence of the area of the adsorbed surface film on the surface pressure $\pi$ for two homologous series of oxyethylated NSAS.

The areas occupied by the molecules in the adsorbed films at $\pi = 20$ dyn $cm^{-1}$ are given in Table 5. This table also gives the data obtained by Lange[35] for a saturated adsorbed film, and Schick's data for insoluble surface films of the same NSAS. It can be seen from Table 5 that the area occupied by a molecule of oxyethylated n-dodecanol and n-octadecanol is much greater than the cross-sectional area of aliphatic hydrocarbons (20 Å²) or the benzene

TABLE 5. Areas occupied by the molecules in the surface films of non-ionic detergents.

| Hydrophobic group | Degree of oxyethylation | Area occupied by a molecule, Å² | | |
|---|---|---|---|---|
| | | adsorbed film | | insoluble film |
| | | $\pi$=20 dyn cm$^{-1}$ | $\pi_{max}$ | $\pi$=20 dyn cm$^{-1}$ |
| n-Dodecanol | 0 | — | — | 25 |
| | 4 | 44 | — | — |
| | 5 | — | 54 | — |
| | 7 | 48 | 59 | 65 |
| | 9 | — | 71 | — |
| | 12 | — | 77 | — |
| | 14 | 65 | — | 160 |
| | 23 | 82 | — | — |
| | 30 | 107 | — | 265 |
| n-Octadecanol | 0 | — | — | 20 |
| | 5 | 42 | — | 70 |
| | 14 | 94 | — | 160 |
| | 100 | 150 | — | 960 |

ring (25 Å²) and increases with increase in the length of the oxyethylated chain. Thus vertical orientation of the oxyethylene chain is excluded. Changes in the structure of the hydrophobic groups at constant molar concentration of ethylene oxide have little influence on the area occupied by the molecule. On the basis of these results, two possible configurations can be suggested for the NSAS molecules in adsorbed surface films: the molecules are orientated in such a way that the hydrophobic groups lie above the interface, and the oxyethylene groups either lie on the surface of the phases or form coils in the aqueous phase. In order to select one of the two possible orientations, a comparison was made of the molecular areas occupied by the molecules of non-ionic detergents in adsorbed surface layers and the corresponding molecular areas in insoluble surface films[35]. In the latter, the substrate consisted of a saturated solution of sodium nitrate or 29% sodium chloride solution.

In both homologous series, the areas occupied by the molecules at comparable surface pressures increase with increase in the length of the oxyethylene chain, whereas the difference in the structures of the hydrophobic groups at constant degree of oxyethylation has little influence on the areas of the molecules in the saturated films. From this it should have followed that the hydrophobic groups are orientated above the interface, and the oxyethylene chains lie on the surface. The molecular areas in insoluble surface films, however, are very much greater than the corresponding values in adsorbed surface films, so that the horizontal orientation is also excluded. These considerations led the authors to the conclusion that the molecules of the surface-active substance are orientated at the air–water interface with their hydrophobic groups above the interface and with the oxyethylene chains forming coils in the aqueous phase. The dimensions of the coils increase with increase in the number of segments in the oxyethylated chain.

These conclusions were confirmed and extended in a study of the surface potentials for polyoxyethylated n-dodecanols and n-octadecanols containing oxyethylated chains of different length[19].

It was found that the increase in surface potential and hence the increase in the dimensions of the coils decreases with increase in the degree of oxyethylation. This is related to the polymeric nature of the oxyethylene chain. Figure 1*b* gives the dependence of the area occupied by a molecule of *p*-t-octylphenol on the length of the oxyethylene chain. The increase in area is non-linear, although

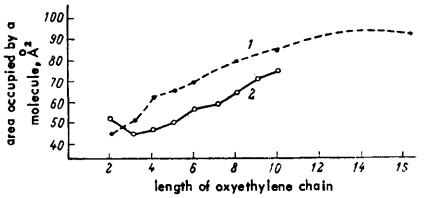



Fig. 2. Dependence of the area occupied by a molecule at the solution–isooctane boundary on the chain length of individual OP SAS (2) and mixtures with normal distribution (1).[39]

the deviation from linearity is slight in the range from 3 to 10 oxyethylene groups. On the basis of the assumption that the hydrated molecules of oxyethylated substances in adsorption layers form statistical configurations, Van Voorst-Vader[37] concluded that the area of the molecule at saturation is proportional to $\sqrt{m}$, where $m$ is the degree of oxyethylation. This was confirmed for the case of oxyethylated alkylphenols. Lange[32] obtained the same relationship for oxyethylated dodecanol.

By measuring the interfacial tension at the interface between isooctane and an aqueous solution of NSAS, Crook[30] determined the dependence of the area occupied by a molecule at the interface on its degree of oxyethylation (Fig. 2). For individual substances, the areas occupied by a molecule on the solution–hydrocarbon boundary are close to the corresponding values for a solution–air boundary. For mixtures with normal distribution, the area of the molecule at the solution–air boundary (Fig. 1*b*) is smaller, and the area at the solution–hydrocarbon boundary (Fig. 2) greater, than the value for the corresponding individual products. As already described, the former is due to the preferential adsorption of the more highly surface-active components of the mixture at the solution–air boundary. The second result is due to the fact that for mixtures with normal distribution it is necessary to make allowance for the specific solubility of the different components of the mixture in isooctane. Since the components with lower degree of oxyethylation are more soluble in isooctane, they are concentrated in the hydrocarbon phase, so that the average molecular weight of the NSAS dissolved in water increases, leading to an increase in the area of the molecule at the interface. Becher[34] put forward suggestions regarding the orientation of non-ionic surface-active substances at an oil–water interface for the polyoxyethylated lauryl alcohols and nonylphenols, and the part played by hydrogen bonds in this orientation.

## V. MICELLE FORMATION. THE SHAPE AND DIMENSIONS OF MICELLES

Micelle formation by NSAS has been fairly fully studied. The studies have been carried out chiefly using oxyethylated aliphatic alcohols and alkylphenols. Several methods have been used to determine the critical concentration of micelle formation ($c_k$) of non-ionic surface-active substances: the surface tension method[38-43], the dye solubilisation method, a method based on the change in the absorption spectrum[40,43-50], the light scattering method[40,41,50-55], and the viscosity method[51,55].

Unlike the case of ionogenic surface-active substances, in which the hydrophilic fraction of the molecule is much

TABLE 6. $c_k$ and the micellar weights of non-ionic detergents in aqueous solutions[56].

| Hydrophobic groups | Degree of oxyethylation | Number of C atoms in the hydrophobic fraction | $c_k$, μmole litre$^{-1}$ | Micellar weight × $10^{-3}$, $M_m$ | Degree of association (n) |
|---|---|---|---|---|---|
| Nonylphenol (branched) | 10 | 10.5 | 75 | 182 | 276 |
| | 15 | | 110 | 70 | 80 |
| | 20 | | 140 | 68 | 62 |
| | 30 | | 185 | 67 | 44 |
| | 50 | | 280 | 48 | 20 |
| n-Dodecanol | 7 | 12 | 50 | | |
| | 14 | | 55 | 100 | 125 |
| | 23 | | 60 | | |
| | 30 | | 80 | 82 | 55 |
| n-Octadecanol | 14 | 18 | 60 | 330 | 370 |
| | 100 | | 20 | 465 | 100 |

smaller than the hydrophobic fraction, the hydrophilic fraction may be greater than the hydrophobic fraction in non-ionic oxyethylated substances. With non-ionic substances, the absence of electric charge facilitates micelle formation, so that $c_k$ for NSAS is much lower than $c_k$ for ionic surface-active substances, as can be seen from Table 6, which gives the values of $c_k$ for several homologous series of non-ionic detergents in aqueous solutions. For comparison, it may be noted that for sodium dodecyl sulphate, $c_k$ = 8100 μmole litre$^{-1}$.[5]

From the results obtained it follows that $c_k$ increases with increase in the length of the oxyethylene chain, that is, increase in hydration or solubility hinders the aggregation of the non-ionic surface-active substances. The low values of $c_k$ for n-octadecanol-100, compared with those for n-octadecanol-14, can be attributed to the decrease in the solubility of the oxyethylene fraction of the chain at very high degrees of oxyethylation. Thus with increase in the length of the oxyethylene chain, the overall solubility of non-ionic detergents passes through a maximum. It has been shown[38,39] that the increase in $c_k$ with increase in the length of the oxyethylene chain is given by the equation

$$\ln c_k = BR + K \qquad (1)$$

where $R$ is the average number of oxyethylene groups in the chain, $B$ a constant which depends on the nature of the hydrophobic group and decreases with increase in the length of the hydrophobic chain, and $K$ a constant which depends on the nature and concentration of the electrolyte present.

For oxyethylated nonylphenols in water, $B$ = 0.056 and $K$ = 3.87. It then follows from formula (1) that the value of $c_k$ is doubled when $R$ increases by 12. Approximately the same relationship is applicable for oxyethylated substances of other classes (Fig. 1c)[39].

For oxyethylene chains of constant length, the values of $c_k$ for NSAS, like those for ionogenic detergents, decrease with increase in the length of the hydrocarbon chain, due to the increase in the interaction between the hydrocarbon chains, facilitating aggregation. According to recent work by Schinoda[57], the influence of the length of the hydrocarbon chain on $c_k$ is given by the formula

$$\log c_k = -\frac{m\omega}{kT} + \text{const}, \qquad (2)$$

where $m$ is the number of carbon atoms in the chain and $\omega$ the change in cohesion energy for the transfer of one methylene group from aqueous solution into the micelle.

The values of $c_k$ are approximately doubled when the hydrophobic chain is reduced by one $CH_2$ group. Thus the influence of 12 ethylene oxide groups on $c_k$ is equivalent to that of one methylene group.

The influence of temperature on $c_k$ for NSAS solutions is opposite to the usual influence of temperature on micelle formation. Since thermal movement hinders micelle formation, the latter should decrease with increase in temperature, and the values of $c_k$ should increase. This is the usual relationship observed, with certain exceptions, in solutions of ionogenic SAS. For NSAS, $c_k$ decreases with increase in temperature, that is, micelle formation shows negative thermal effects.

Schick[58] used the Clausius–Clapeyron equation to determine the enthalpy change on micelle formation ($\Delta H_m$) from the temperature dependence of $c_k$. The dependence of $\log c_k$ on $1/T$ for oxyethylated alcohols is shown in Fig. 3. As shown in Fig. 3 and in other papers[41,59,60], this relationship is strictly linear for NSAS, and the enthalpy increases on micelle formation. The fact that the Clausius–Clapeyron equation is applicable to micelle formation means that in NSAS solutions this process must be regarded as involving phase separation. This approach is also applicable to ionic detergents in the presence of salting-out electrolytes[60,61]. From the conditions for equilibrium at $c_k$, it follows that the free energy change $\Delta\bar{G}_m$ is equal to zero, and the entropy of micelle formation can be calculated from the equation

$$\Delta\bar{S}_m = \frac{\Delta\bar{H}_m}{T}. \qquad (3)$$

The quantity $\Delta\bar{H}_m$ is positive, so that the entropy change on micelle formation in NSAS solutions is also positive. A positive entropy change means an increase in disorder. Since it cannot be that aggregation of monomeric detergent molecules to form micelles is accompanied by an increase in the disorder of the system, it is necessary to find other reasons for the positive change in entropy. Studies have shown[33,56,58,62] that the chief reason for the increase in entropy on micelle formation may be the desolvation of the NSAS molecules on aggregation. This is confirmed by the data in Table 7.

The greater the concentration of electrolyte and hydration of the anion ($CNS^- < Cl^- < SO_4^{2-}$), the greater the increase in entropy. The part played by dehydration can

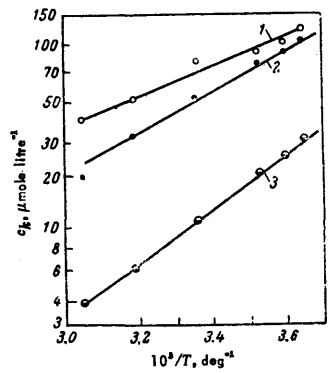



Fig. 3. Straight lines obtained by plotting $\log c_k = f(1/T)$ for aqueous solutions of non-ionic detergents[68]:
1) n-$C_{12}H_{25}(OC_2H_4)_{30}OH$; 2) n-$C_{12}H_{25}(OC_2H_4)_7OH$;
3) n-$C_{16}H_{33}(OC_2H_4)_{30}OH$.

TABLE 7. Partial values of the enthalpy and entropy of micelle formation for non-ionic detergents*.[58]

| Hydrophobic group | Degree of oxyethylation | Solvent | $\Delta\bar{H}_m$, kcal mole$^{-1}$ | $\Delta\bar{S}_m$, cal × ×mole$^{-1}$ deg$^{-1}$ |
|---|---|---|---|---|
| n-Dodecanol | 30 | $H_2O$ | 3.7 | 12.3 |
| n-Dodecanol | 7 | $H_2O$ | 5.0 | 16.6 |
| n-Hexadecanol | 30 | $H_2O$ | 6.6 | 21.9 |
| n-Dodecanol | 30 | 0.43 M NaCl | 6.0 | 19.9 |
| n-Dodecanol | 30 | 0.86 M NaCl | 6.5 | 21.6 |
| n-Dodecanol | 30 | 0.86 M NaCNS | 4.1 | 13.6 |
| n-Dodecanol | 30 | 0.86 M $^1/_2Na_2SO_4$ | 9.1 | 30.2 |

* Values obtained in the range 1–55°.

also be seen by comparing the values of $\Delta\bar{S}_m$ for substances with different hydrophilic character (n-dodecanol-30, n-dodecanol-7, and n-hexadecanol-30). The greater the hydrophilic character, the more difficult the process of dehydration and the smaller the increase in entropy on aggregation.

In addition to desolvation, another factor increasing the entropy may be an increase in the configurational entropy of the hydrocarbon chain of the detergent molecule inside the micelle[36,64]. To counterbalance this, the configurational entropy of the oxyethylene chain in the outer sheath of the micelle is smaller than its entropy in solution. Since the experimentally-observed entropy change is positive, the decrease in entropy taking place on aggregation of the molecules of non-ionic detergents is compensated by desolvation and to some extent by an increase in the entropy of the hydrocarbon chain.

Tables 6 and 8 give values of the micellar weights and corresponding values of $c_k$ for non-ionic detergents in aqueous solutions, obtained by the light scattering and ultracentrifuge methods[54]. Similar results were obtained by Mankowich[65], Dwiggins and coworkers[66-68], and Elworthy and Macfarlane[55].

Low values of $c_k$ correspond to the highest values of the micellar weights, and vice versa, as is usually the case in micellar solutions. The degree of association or the number of molecules in the micelle is defined as the ratio of the micellar weight to the molecular weight of the surface-active substance. No allowance is made for the degree of hydration since this is unknown.

It can be seen from Table 6 that when the degree of oxyethylation is constant (for example, 14 or 15 $CH_2-CH_2-O$ groups), the micellar weights and degree of aggregation increase with increase in the chain length of the hydrophobic fraction of the molecule. With increase in the number of oxyethylene groups, however (Tables 6 and 8), the micellar weights decrease, and for substances with a low degree of oxyethylation, small changes in the ethylene oxide content bring about the most marked changes in the micellar weights. Study of a mixture of fractions with different degree of oxyethylation showed that the change in the micellar weight for fractions with high ethylene oxide content is much greater than that for fractions with low degree of oxyethylation. Thus change in the conditions of preparation of polyoxyethylated surface-active substances may have a marked influence on their micellar weight in solutions.

TABLE 8. Average micellar weights and degree of association of oxyethylated lauryl alcohol and nonylphenols[53].

| Hydrophobic fraction | Degree of oxyethylation | $10^3 c_k$, g litre$^{-1}$ | Micellar weight × $10^{-3}$, $M_m$ | Degree of association, $n$ |
|---|---|---|---|---|
| Lauryl alcohol | 8 | 59 | 68.2 | 123 |
| | 12 | 65 | 58.9 | 81 |
| | 18 | 80 | 50.6 | 51 |
| | 23 | 110 | 48.9 | 40 |
| Nonylphenol | 10 | 64 | 66.3 | 100 |
| | 15 | 77 | 45.0 | 52 |
| | 30 | 236 | 29.7 | 19 |

The degree of association decreases with increase in the length of the oxyethylene chain. With n-octadecanols (Table 6), the degree of association also decreases with increase in the length of the oxyethylated chain, but the micellar weight increases, due to an increase in the molecular weight of the surface-active substance. Becher[53] found a linear relationship between the degree of association and the degree of oxyethylation. For derivatives of lauryl alcohol and nonylphenol, the equations for the straight lines are of the form

$$n = 1025/R - 5.1 \quad (4)$$

and

$$n = 1215/R - 22.5 \quad (5)$$

respectively, where $n$ is the degree of association and $R$ the number of oxyethylene groups in the chain.

A decrease in the degree of association with increase in the length of the oxyethylene chain was also observed by Kushner et al.[69] for polyoxyethylated isooctylphenols and by Stauff and Rasper[70] for polyoxyethylated dodecanol. This work[69,70] was carried out with fractionated specimens, however, and since the polymer distributions are different in the fractionated specimen and in the industrial product with the same average molecular weight, these results are of mainly theoretical importance.

Work by Balambra and coworkers[54] and Mankowich[47] showed that the micellar weights increase exponentially with increase in temperature.

A number of authors have put forward suggestions regarding the shape of the micelles in NSAS solutions[53,56,71-74]. As for ionic detergents, the existence of spherical, lamellar, and cylindrical micelles has been suggested. On the basis of calculations of the surface area of micelles of different types for oxyethylated nonylphenols and lauryl alcohol, Becher[53] showed that the cylindrical shape is the most probable.

Ermilov[48] suggests that there exist two critical concentrations for micelle formation: $c'_k$, at which small spherical micelles are formed, and $c''_k$, at which large lamellar micelles are formed. Levitskii and coworkers[49], however, consider that only the spherical micelles postulated by Hartley exist at $c'_k$ and $c''_k$, but that the quantity of these micelles is smaller at $c'_k$ and greater at $c''_k$. The final equilibrium distribution of the structural units of different type (molecules and micelles), both in the bulk of the micellar solutions and between the bulk and the adsorption layers, is established at $c''_k$, and this distribution remains unchanged over a wide concentration range until another form of micelle is produced in the solution.

Schick and coworkers[56] determined the shape of micelles formed by non-ionic surface-active substances, by the light-scattering method and from the rate of sedimentation. They suggest that in the micellar weight range 45 000–100 000 the micelles are most probably spherical, whereas

at higher micellar weights they have the shapes of discs and rods. Similar results were obtained by Gorkill[74].

The addition of electrolytes influences $c_k$ and the dimensions of the micelles in solutions of non-ionic detergents. This influence is analogous to the influence of electrolytes on $c_k$ for ionic SAS, established by Corrin and Harkins[75] and Klevens[76]. Addition of electrolytes leads to a decrease in $c_k$ and an increase in the micelle dimensions. The influence of electrolytes on $c_k$ for non-ionic detergents has been studied in detail by Hsiao and coworkers[39], Becher[38], Kuriyama[77], and Schick[33].

It can be seen from Table 9 that increase in the NaCl concentration leads to a marked increase in $c_k$ for solutions of polyoxyethylated nonylphenols in water (the increase is greater than that for ionic surface-active substances).

In a study of the influence of added electrolytes on micelle dimensions for oxyethylated derivatives of lauryl alcohol, nonylphenol, and tridecanol in the presence of Na and Ca chlorides, Na sulphate, and Na citrate $Na_3C_6H_5O_7$, Becher[38] showed that replacement of the univalent $Na^+$ cation by the bivalent $Ca^{2+}$ cation has no significant influence on the micelle dimensions or degree of association; change in the anion, however, has a more marked influence on these quantities. The anions can be arranged in the following order of decreasing activity:

sulphate > citrate > chloride.

TABLE 9. Influence of electrolyte concentration on $c_k$ for solutions of polyoxyethylated nonylphenols[33].

| NaCl concentration, M | Decrease in $c_k$, $\mu$mole litre$^{-1}$ | |
|---|---|---|
| | nonylphenol + $+15CH_2CH_2O$ | nonylphenol + $+50CH_2CH_2O$ |
| 0.43 | 45 | 80 |
| 0.86 | 55 | 130 |
| 1.29 | 65 | 180 |

The data which they obtained on the influence of electrolytes are given in Table 10. The micellar weights $M_m$ were calculated from the Debye equation, and the degree of association $n$ was calculated from the micellar weight and the average molecular weight of the surface-active substance. The increase in the degree of association is due to the decrease in the hydration of the oxyethylene chain resulting from the desolvating action of the electrolytes. It can be seen from Table 10, however, that this influence of electrolytes is shown only in solutions of substances with low degree of oxyethylation. For substances with a high degree of oxyethylation, the addition of electrolytes sometimes leads to a decrease in the degree of association, although the addition of electrolytes leads to a decrease in $c_k$ even at high degrees of oxyethylation, as can be seen from Table 9. Becher suggests that the effect of electrolytes involves not only their action on the hydrophilic nature of the polyoxyethylene chain but also their action on the charge of the micelles resulting from the formation of the hydroxonium ion.

## VI. FORMATION OF MIXED MICELLES. SOLUBILISATION

Kuriyama and coworkers[78] determined the micellar weight for mixtures of non-ionic and ionic surface-active substances in 0.2 M sodium chloride solution at different temperatures. The results are given in Table 11.

The micellar weight of non-ionic surface-active substances increases with increase in temperature, whereas that of ionic surface-active substances decreases.

In mixtures of non-ionic and ionic surface-active substances, the increase in the micellar weight of the non-ionic detergents is suppressed with increase in the quantity of ionic SAS added. When the quantity of added ionic SAS exceeds a definite value (~20%), the micellar weights decrease with increase in temperature. This relationship was explained as follows[78]. The formation of micelles in solutions of non-ionic surface-active substances is determined by two factors: the forces of cohesion between the oleophilic groups and the affinity of the hydrophilic groups

TABLE 10. Influence of electrolytes on the micellar weight ($M_m$) and average degree of association ($n$).[38]

| Original products | $10^{-4} M_m$ | | | | | | | | $n$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | degree of oxyethylation | | | | | | | | degree of oxyethylation | | | | | | | |
| | 8 | 10 | 12 | 15 | 18 | 22 | 23 | 30 | 8 | 10 | 12 | 15 | 18 | 22 | 23 | 30 |
| Polyoxyethylated lauryl alcohol | | | | | | | | | | | | | | | | |
| without electrolytes | 68.2 | — | 58.9 | — | 50.6 | — | 48.8 | — | 123 | — | 81 | — | 51 | — | 40 | — |
| NaCl 0.30 *N* | 70.0 | — | 57.6 | — | 52.9 | — | 42.2 | — | 127 | — | 79 | — | 53 | — | 35 | — |
| 0.50 *N* | 77.0 | — | 50.0 | — | 45.4 | — | 40.3 | — | 140 | — | 69 | — | 46 | — | 33 | — |
| $CaCl_2$ 0.30 *N* | 66.1 | — | 52.4 | — | 45.0 | — | 40.2 | — | 120 | — | 72 | — | 45 | — | 33 | — |
| 0.50 *N* | 82.0 | — | 46.9 | — | 43.2 | — | 38.8 | — | 149 | — | 63 | — | 44 | — | 32 | — |
| $Na_3C_6H_5O_7$ 0.30 *N* | 97.0 | — | 46.3 | — | 38.3 | — | 34.5 | — | 176 | — | 64 | — | 39 | — | 28 | — |
| 0.50 *N* | 87.2 | — | 48.0 | — | 40.2 | — | 34.3 | — | 158 | — | 66 | — | 40 | — | 28 | — |
| $Na_2SO_4$ 0.30 *N* | 171 | — | 53.5 | — | 45.8 | — | 47.2 | — | 310 | — | 73 | — | 46 | — | 39 | — |
| 0.50 *N* | 472 | — | 53.5 | — | 49.5 | — | 45.0 | — | 856 | — | 73 | — | 50 | — | 37 | — |
| Polyoxyethylated nonylphenol | | | | | | | | | | | | | | | | |
| without electrolytes | — | 66.3 | — | 45 | — | — | — | 29.7 | — | 100 | — | 52 | — | — | — | 19 |
| NaCl 0.30 *N* | — | 75 | — | 51 | — | — | — | 30.7 | — | 113 | — | 58 | — | — | — | 20 |
| 0.50 *N* | — | 82.9 | — | 46.5 | — | — | — | 24.0 | — | 126 | — | 53 | — | — | — | 16 |
| Polyoxyethylated tridecanol | | | | | | | | | | | | | | | | |
| without electrolytes | — | 58.7 | — | 32.8 | — | 32.5 | — | — | — | 92 | — | 38 | — | 28 | — | — |
| NaCl 0.30 *N* | — | 70.0 | — | 40.5 | — | 33.5 | — | — | — | 110 | — | 47 | — | 29 | — | — |
| 0.50 *N* | — | 90.3 | — | 40.0 | — | 32.8 | — | — | — | 141 | — | 47 | — | 28 | — | — |

for water molecules. At a given temperature, a corresponding balance is established between the forces of hydration and cohesion, and micelles with definite dimensions are formed. In the case of ionic SAS, the formation of micelles is associated with a balance between the electric forces of the ionised groups and the forces of cohesion of the hydrocarbon chain.

In mixtures of ionic and non-ionic detergents in solution, mixed micelles are formed. The balance between the electric forces and the forces of cohesion and hydration may be altered in either direction with increase in temperature, depending on the ratio of the quantities of ionic and non-ionic detergents. It follows from the results obtained (Table 11) that the micellar weights increase with increase in temperature until a definite composition is reached in the mixture of ionic and non-ionic SAS, after which the micellar weights decrease.

The ionogenic substances added to a solution of non-ionic detergents may influence the equilibrium between the forces of cohesion and the electric forces in two ways: (1) by penetrating into the micelle and altering its structure, and (2) by dissolving in the aqueous phase and thus altering the medium surrounding the micelles[25].

The solubilisation of n-decane and n-decanol in solutions of oxyethylated decanols with general formula $C_{10}H_{21}[OC_2H_4]_nOCH_3$, where $n$ = 8 or 12, at different temperatures, was studied by Kuriyama[79,80]. The solubilisation was estimated from the change in micellar weights, as shown in Table 12.

TABLE 11. Micellar weights of mixed micelles of sodium dodecyl sulphate and methoxypoly(oxyethylene)-dodecyl ether[78].

| Temperature, °C | Wt. % of sodium dodecyl sulphate in the detergent mixture | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 | 5 | 20 | 40 | 60 | 80 | 100 |
| 30 | 61 000 | 60 200 | 53 600 | 45 500 | 40 000 | 37 600 | 31 800 |
| 50 | 71 000 | 66 900 | 54 000 | 41 700 | 36 200 | 31 700 | 26 600 |
| 70 | 92 200 | 86 100 | 57 300 | 43 900 | 33 800 | 28 300 | 23 100 |

TABLE 12. Influence of substance being solubilised on the structure of micelles[80].

| Surface-active substance (S) | Substance being solubilised (H) | H/S, wt. % | Critical concentration of micelle formation, $c_k \times 10^4$, g per 100 ml | Micellar weights $\times 10^{-3}$, $M_m$ | Number of molecules of NSAS in the micelle | Number of molecules of substance being solubilised in the micelle |
|---|---|---|---|---|---|---|
| $C_{10}H_{21}[OC_2H_4]_8OCH_3$ | n-decane | 0 | 6.0 | 43.1 | 83 | 0 |
| | | 1.32 | 5.7 | 45.6 | 87 | 4 |
| | | 2.33 | 5.4 | 47.8 | 90 | 8 |
| | | 3.16 | 5.2 | 50.5 | 94 | 11 |
| | | 3.78 | 5.1 | 52.0 | 96 | 13 |
| | | 4.93 | 4.8 | 57.5 | 105 | 19 |
| | | (12.0) | 4.0 | 88.5 | 158 | 46 |
| | | (150) | 4.0 | 90.7 | 162 | 47 |
| | n-decanol | 3.40 | 5.2 | 47.8 | 89 | 10 |
| | | 6.19 | 4.5 | 51.3 | 93 | 19 |
| | | 8.50 | 4.0 | 61.3 | 109 | 30 |
| | | 11.42 | 3.3 | 90.9 | 157 | 59 |
| | | 16.61 | 2.0 | 21.3 | 351 | 192 |
| $C_{10}H_{21}[OC_2H_4]_{12}OCH_3$ | n-decane | 0 | 9.5 | 42.9 | 65 | 0 |
| | | 1.4 | 9.2 | 44.8 | 67 | 4 |
| | | 2.58 | 9.0 | 51.5 | 76 | 9 |
| | | 3.31 | 8.8 | 54.3 | 80 | 12 |
| | n-decanol | 5.67 | 8.4 | 52.6 | 75 | 18 |
| | | 10.18 | 7.5 | 62.9 | 86 | 37 |
| | | 17.12 | 6.3 | 12.2 | 158 | 113 |

With n-decane, the micellar weights increase with increase in its solubilisation up to a definite saturation limit and then remain unchanged. The data obtained indicate that the increase in micellar weights is due not to simple introduction of the molecules of the substance being solubilised into existing micelles but also to an increase in the number of molecules of surface-active substance making up the micelle. Thus the solubilisation process is associated with a change in the structure of the micelles. These results agree with data given by Mattoon[81].

Mankowich[47], in a study of the micellar solubilisation of oxyethylated alkylphenols, found that the temperature dependence of this process is exponential.

## VII. HYDROPHILIC-LIPOPHILIC BALANCE (HLB)

Of decisive importance for the surface and bulk properties of the non-ionic SAS described in the preceding sections and hence for their application, is the relative efficiency of the two opposed groups of the molecule — the hydrophilic and hydrophobic (or lipophilic) groups — the so-called hydrophilic-lipophilic balance (HLB). Unlike the case of ionic SAS, whose HLB depends to a marked extent on the concentration of electrolytes in the medium, the HLB of non-ionic SAS is comparatively constant and depends only on the structure of the molecule.

An empirical quantitative characterisation of the HLB was derived in 1949 by Griffin[82] and this has been used extensively in the last decade as a guiding principle in the preparation of emulsions and for other applications of SAS. The HLB system was described briefly by Schönfeldt[5] and in more detail by Jalina and Goǒjila[83]. According to Griffin's classification, each SAS is characterised by a definite value for the HLB number, which may vary from 1 to 40. The higher the HLB number, the greater the hydrophilic character of the SAS. The smallest HLB number, 1, is shown by oleic acid, and the highest, 40, by Na lauryl sulphate. The HLB number determines the range of application of the SAS, as follows:

| HLB number | Application |
|---|---|
| 3–6 | water/oil emulsions |
| 7–9 | wetting agents |
| 8–18 | oil/water emulsions |
| 13–15 | wetting agents |
| 15–18 | solubilising agents |

It should be emphasised that the value of the HLB number, which determines the range of application of the SAS, does not characterise its efficiency sufficiently completely. SAS with different chemical structures, some of which are more effective than others, may have the same HLB number. The HLB system makes it possible to define the parameter required for a given process and thus to limit the range of substances studied. The HLB number is determined from the emulsifying action. Here it must be borne in mind that the HLB number characterises not only the emulsifier but also the "oil" being emulsified. The so-called necessary HLB number of the "oil" is taken as the value of the HLB number of the emulsifier which forms the most stable emulsion with this oil. To determine the necessary HLB number of the "oil", use is made of the fact that the change in HLB number, when a mixture of two SAS is used, is additive. If a series of emulsions of a given "oil" is prepared, using as emulsifiers a mixture of two SAS for both of which the HLB numbers are known, and the stability of the resulting emulsions is determined, it

is possible to calculate the HLB number of the optimal mixture (the necessary HLB number of the "oil") using the formula:

$$HLB_1X + HLB_2(1-X) = HLB_0\dagger, \quad (6)$$

where $X$ is the weight fraction of the first emulsifier in the mixture.

By emulsifying an "oil" with known necessary HLB number $HLB_o$, using a mixture of two emulsifying agents, for one of which the value of the HLB number $HLB_1$ is known, while that of the other requires to be determined, it is possible to find the optimal ratio of these emulsifying agents and to calculate from formula (6) the value of the HLB number $HLB_2$ in which we are interested. The values of the experimentally determined HLB numbers for various emulsifying agents and oils are given in Table 13.

Griffin's procedure for determining HLB numbers is very tedious, so that a method for the rapid determination of the HLB numbers of emulsifying agents and the necessary HLB of "oils", using a centrifuge, has been proposed[84].

In the experimental determination of HLB numbers by these methods, use is made of a high concentration of emulsifying agent (5% of the total volume of the disperse phase and dispersion medium) so that this number makes allowance for the influence of the structure of the molecule of the emulsifying agent and the nature of the disperse phase on the stability of the emulsion but it does not characterise the influence of the emulsifying agent concentration.

In later work, using different pairs of NSAS for the emulsification of the same oil, Griffin[85] was able to show that in all the experiments, maximum stability is observed at the same weight percentage of hydrophilic substance in the mixture. Thus the HLB of NSAS is essentially a function of the weight fraction of the hydrophilic part of the molecule. On the basis of this observation, it was possible to derive formulae for calculating HLB numbers; these were found to be different for substances of different chemical character. For example, the HLB number of esters is calculated from the formula

$$HLB = 20\left(1 - \frac{s}{A}\right), \quad (7)$$

where $s$ is the saponification number and $A$ the acid number.

TABLE 13. HLB numbers[82].

| Emulsifying agent | HLB No. | Oil | HLB No. |
|---|---|---|---|
| Na oleate | 18 | Carbon tetrachloride | 9 |
| K oleate | 20 | Paraffin | 9 |
| Oleic acid | 1.8 | Kerosene | 12.5 |
| Span 80 | 4.3 | Cetyl alcohol | 13 |
| Span 60 | 4.7 | Dimethyl phthalate | 15 |
| Span 20 | 8.6 | *o*-Phenylphenol | 15.5 |
| Tween 81 | 10.0 | Stearic acid | 17.0 |
| Tween 60 | 14.9 | | |
| Tween 80 | 15.0 | | |
| Tween 20 | 16.7 | | |
| Oxyethylated nonylphenol-7 | 9.9 | | |
| Oxyethylated nonylphenol-15 | 16.1 | | |

† In this and all subsequent formulae, the symbol HLB denotes the HLB number of the corresponding substances.

For oxyethylated products, whose hydrophilic fraction consists of ethylene oxide, the following formula is applicable:

$$HLB = \frac{E}{5}, \quad (8)$$

where $E$ is the wt. % of ethylene oxide groups.

A paper by Davies[86] gave a convenient method proposed by Griffin for calculating HLB numbers from chemical composition by means of so-called group numbers. The calculation uses the formula

$$HLB = \Sigma N_{\text{hydrophilic}} - nN_{CH_2} + 7, \quad (9)$$

where $\Sigma N_{\text{hydrophilic}}$ is the sum of the group numbers of the hydrophilic groups, $n$ the number of $CH_2$ groups in the molecule, and $N_{CH_2}$ the group number for $CH_2$. The values of the group numbers are given in Table 14.

The numbers given are not suitable for very large molecules of oxyethylated substances; in practice, a degree of oxyethylation equal to 20 represents the upper limit of the value of the HLB number for these molecules. The values of the HLB number calculated from formula (9) for a number of substances show good agreement with the values found experimentally. Sometimes[87], instead of the HLB numbers, the so-called approximate HLB number is calculated. The approximate HLB number is the ratio of the number of ethylene oxide groups in the hydrophilic chain to the number of carbon atoms in the straight chain of the hydrophobic group. In these calculation a benzene ring is taken as equivalent to 3.5 carbon atoms. It should be borne in mind that an unsatisfactory feature of all the formulae used for the calculations is that they are based on the stoichiometric composition and make no allowance for isomerism.

A large number of papers have been devoted to establishing the relationship between the empirical HLB number characterising the range of application of SAS, and their physicochemical properties, such as the solubility in water and other solvents[5], the distribution between the two phases of an emulsion[86], the formation of insoluble complexes[88], the cloud point[4], the surface tension and interfacial tension[89,90], $c_k$,[42] the hydration energy, and the electric potential[86].

Table 15 shows that the solubility in water is an extremely approximate characteristic of the HLB. It has been pointed out[90] that there is no direct relationship between solubility and the HLB number. Two emulsifying agents with the same HLB number may exhibit different solubilities.

TABLE 14. Group numbers for calculating HLB numbers[86].

| Groups | Group No. | Groups | Group No. |
|---|---|---|---|
| Hydrophilic groups | | Lipophilic groups | |
| $-SO_4Na^+$ | 38.7 | $-CH-$ | −0.475 |
| $-COOK^+$ | 21.1 | $-CH_2-$ | −0.475 |
| $-COONa^+$ | 19.1 | $CH_3-$ | −0.475 |
| N (tertiary amines) | 9.4 | $CH-$ | −0.475 |
| Ester group (sorbitan ring) | 6.8 | | |
| Ester group | 2.4 | Complex groups | |
| $-COOH$ | 2.1 | | |
| Hydroxyl | 1.9 | $-(CH_2-CH_2-O)-$ | 0.33 |
| $-O-$ | 1.3 | $-(CH_2-CH_2-CH_2-O)-$ | −0.15 |
| Hydroxyl (sorbitan ring) | 0.5 | | |

TABLE 15. Approximate values for the HLB numbers of SAS with different solubilities in water.

| Solubility in water | HLB No. |
|---|---|
| Not dispersed | 1–4 |
| Slightly dispersed | 3–6 |
| Milky dispersion formed after vigorous shaking | 8–10 |
| Spontaneous formation of milky dispersion | 10–13 |
| Transparent solutions | 13 |

‡ The solubility of water in a mixture of organic solvents, for example, dioxan and benzene, is altered in the presence of NSAS. The water number characterises the number of millilitres of distilled water which must be added to a mixture of solvents containing NSAS until a permanent turbidity is produced. The water numbers of SAS mixtures are algebraically additive and directly proportional to the HLB numbers for the given class of substance. The coefficients in the equations of the straight line are different for different classes of substance.

The HLB of individual SAS can also be characterised by the distribution constant $R_f$ for distribution between a stationary aqueous phase and a mobile organic phase for chromatography on paper or on paper which has been made hydrophobic[90]. There is a direct relationship between $R_f$ and the HLB number. Unfortunately, this method is not suitable for a mixture of emulsifying agents, since separation into individual components takes place[2].

In an examination of the relationship between the rate of coalescence of an emulsion of oil in water and an emulsion of water in oil, the HLB number, and the solubility of the emulsifying agent in each of the emulsion phases, Davies[86] concluded that the HLB number is related to the distribution of the emulsifying agent between the two phases by the expression

$$\text{HLB} - 7 = 0.36 \ln \frac{c_w}{c_o}, \qquad (10)$$

where $c_w$ and $c_o$ are the solubilities of the emulsifying agent in water and oil.

If the emulsifying agent dissolves preferentially in water, the HLB number is greater than 7, and if the emulsifying agent dissolves preferentially in the oil, the HLB number is less than 7.

The methods used by Karabinos and Jutaka Tanaka to characterise the HLB, described in a paper by the latter[88], are based on the fact that when aqueous or alcoholic solutions of NSAS are titrated with a phenol solution, an insoluble complex of these two substances is formed and the solution becomes cloudy. The quantity of phenol solution used up at the end of the titration is called the cloud number. The cloud numbers increase with increase in the length of the oxyethylene chain. An interesting feature is that Jukata Tanaka's cloud number is directly proportional to the HLB number, irrespective of the class of compound. The equation of the corresponding straight line is

$$\text{HLB} = 0.89A + 1.11, \qquad (11)$$

where $A$ is the cloud number.

‡ The beginning of this paragraph is missing from the Russian text (first two lines of preceding paragraph repeated instead) (Ed. of Translation).

For a given class of compounds, the HLB may be characterised by the cloud point, which is higher, the greater the hydrophilic character of the substance.

It might be suggested that the necessary HLB number of an oil is equal to the HLB number of the emulsifying agent which produces the greatest decrease in the interfacial tension. Wachs and Reusche[90] studied the stability of emulsions of undecane in water in the presence of mixtures of emulsifying agents with HLB from 2 to 17 and the interfacial tension at the boundary between the undecane and solutions of the corresponding mixtures of emulsifying agents, and found that the optimal value of the HLB number was equal to 9.5, irrespective of the composition of the mixture of emulsifying agents. In some systems the interfacial tension at this value of the HLB number passes through a minimum. In others, however, the interfacial tension changes continuously with change in the HLB, without passing through extreme values. Becher[34] obtained the same results in a study of the dependence of the interfacial tension on the degree of oxyethylation. Thus the interfacial tension is not the only factor determining the stability of an emulsion and the necessary HLB number of the oil. Ross and coworkers[89] concluded that the influence of the interfacial energy on the energetic balance in the formation of emulsions cannot be denied. Low interfacial tension, however, is a necessary but insufficient condition for stability. Another condition for stability in an emulsion of the type formed by oil in water is that the spreading coefficient $S_1$ should have a low negative value (from 0 to -5). The spreading coefficient indicates the way in which the oil spreads over the surface of a 1% solution of the emulsifying agent in water, and is calculated from the formula

$$S_1 = \sigma_{\text{solution}} - (\sigma_o + \sigma_{i.f.}), \qquad (12)$$

where $\sigma_{\text{solution}}$ is the surface tension of the solution of the emulsifying agent in water, $\sigma_o$ the surface tension of the oil, and $\sigma_{i.f.}$ the interfacial tension at the boundary between the oil and the solution of the emulsifying agent in water.

It follows from Ross's data that the spreading coefficient is directly proportional to the HLB number of the emulsifying agent. The results for the boundary between castor oil and an aqueous solution of an emulsifying agent are given in Fig. 4. This makes it possible to replace

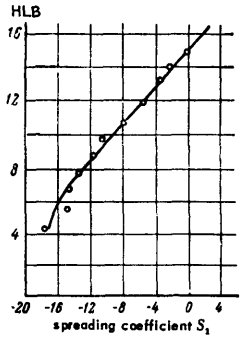



Fig. 4. Spreading coefficient $S_1$ for castor oil on the surface of 1% solution of SAS with different HLB.[99]

the tedious and sometimes inaccurate method of determining the HLB number of an emulsifying agent by measurements of the physicochemical constants of the system formed by the disperse phase with a solution of the emulsifying agent in the dispersion medium.

Wachs and Hyano[42] found experimentally for the monoesters of saccharose and saturated aliphatic acids that the HLB of this class of compound is directly proportional to the logarithm of $c_k$. These authors derived the same equation by calculation based on a comparison of the above equations used by Griffin[85] for calculating the HLB, on the one hand, with the empirical equation (2) giving the dependence of $c_k$ on the length of the hydrocarbon chain, on the other hand. This showed the applicability of Griffin's equation. The observed relationship between the HLB number and $c_k$ makes it possible to determine the HLB numbers of the stereoisomers of the monoesters; as pointed out above, this cannot be done using the calculation formulae.

In a paper presented at the Second Congress on Surface-Active Substances in London, Davies[86] tried to provide a quantitative kinetic basis for the HLB system. Davies' conclusion was based on the suggestion put forward by Rebinder[92] that both oil/water and water/oil emulsions are formed during emulsification, the nature of the final emulsion depending on which of the emulsions formed undergoes more rapid coalescence. Davies considered the rate of coalescence ($R_1$) of two drops of oil separated by water, and the rate of coalescence ($R_2$) of two drops of water separated by oil in the presence of the emulsifying agent. He assumed that the rate $R_1$ depends on a hydrodynamic factor $A_1$, an energy barrier related to the electric potential $\psi_0$, and an energy barrier $\Sigma\epsilon_h$, equal to the sum of the energies of hydration of the polar groups, which must be overcome in order to remove the hydration layers of water from the surface. In general, the rate of coalescence of oil drops decreases both as a result of charging and as a result of hydration, and the equation is of the form

$$R_1 = A_1 e^{-\frac{0.24\psi_0^2 - \theta\Sigma\varepsilon_h}{RT}}, \qquad (13)$$

where $\theta$ is the fraction of the surface occupied.

The opposite system consisting of two drops of water in a non-polar oil will undergo coalescence if the intermediate layer of oil is squeezed out as the drops of water approach one another. The rate of coalescence $R_2$ will depend on a hydrodynamic factor $A_2$, the barrier created by each $CH_2$ group on movement into water (equal to 300 cal[93]), the number $n$ of $CH_2$ groups, and the proportion $\theta$ of the surface occupied by the emulsifying agent

$$R_2 = A_2 e^{-2n\theta\frac{300}{RT}}. \qquad (14)$$

By combining Eqns. (13) and (14) and assuming that $A_1 = A_2$ (i.e. that the viscosities and phase volumes of the oil and water are equal), we obtain the equation

$$RT\ln\frac{R_2}{R_1} = 0.24\psi_0^2 + \theta\Sigma\varepsilon_h - 600n\theta. \qquad (15)$$

Separating $n$ from Eqns. (9) and (15) and comparing the right-hand sides of the resulting equations term by term, Davies arrived at a system of three equations:

$$\ln\frac{R_2}{R_1} = 2.2\theta(\mathrm{HLB} - 7), \qquad (16)$$

$$\Sigma N_{\substack{\text{hydrophilic}\\ \text{hydrated}}} = \frac{\Sigma\epsilon_h}{1260}, \qquad (17)$$

$$\Sigma N_{\substack{\text{hydrophilic}\\ \text{charged}}} = 1.9\times10^{-4}\frac{\psi_0^2}{\theta}, \qquad (18)$$

where $\Sigma N_{\substack{\text{hydrophilic}\\ \text{hydrated}}}$ is the sum of the group numbers of the hydrophilic hydrated groups, and $\Sigma N_{\substack{\text{hydrophilic}\\ \text{charged}}}$ the sum of the group numbers of the hydrophilic charged groups.

These equations show that the HLB system has a firm kinetic basis. The HLB determines the rate of coalescence. For oil/water emulsions the HLB numbers are greater than 7 and for water/oil emulsions the HLB numbers are less than 7. For an HLB number equal to 7 or values of $\theta$ close to zero, neither of the emulsions is stable. Eqns. (17) and (18) show the part played by the hydration energy and charge in the characterisation of the HLB of surface-active substances. It can be seen from Eqn. (18) that the HLB of a charged group depends on $\psi_0$, and the latter changes with even a small change in the concentration of electrolytes in the system. Thus the contribution made by the charged groups to the HLB numbers of anion-active and cation-active SAS, as already noted, is not strictly constant, so that the HLB numbers are not constant. In the case of non-ionic SAS, the values of the HLB numbers are less dependent on the electrolyte concentration.

Deryagin[94], in the discussion of Davies' paper, pointed out that it is incorrect to express the influence of the hydrophilic groups of the emulsifying agents on the stability of an emulsion of oil in water as the simple sum of the hydration energies of these groups. In actual fact, the action of the hydrophilic groups is determined by the forces of repulsion produced under the general influence of these groups in the aqueous polymolecular layers surrounding the surface of the drops.

These studies make it possible to estimate the part played by the HLB as a factor characterising the relationship between the structure of the molecule of the emulsifying agent and its affinity for the disperse phase and the dispersion medium of the emulsion. It should be emphasised that the HLB numbers of SAS, as shown at the start of the present section, play an important part not only in emulsification, but also in other processes taking place in dispersion systems. For example, Schick and Beyer[87] showed that the HLB number of a non-ionic stabiliser characterises the stability of foams. In each homologous series of NSAS, the stability of the foams passes through a maximum at a certain critical value of the HLB number. This is due to the fact that the resistance to rupture shown by the film of stabiliser depends on the magnitude of the cohesion of the adsorbed molecules, and the latter passes through a maximum with increase in the degree of oxyethylation.

Examples of the use of HLB numbers for the selection of emulsifying agents for emulsion polymerisation have been given[95]. A study was made of the dependence of the stability of the latices, the dimensions of the particles, the viscosity, and the rate of conversion on the HLB numbers for the emulsion polymerisation of styrene and vinyl acetate. An anionic emulsifying agent (an alkyl aryl sulphonate), non-ionic emulsifying agents (polyoxyethylated esters of oleic, lauric, steric, palmitic, and other acids), and their mixtures were used for this purpose. A high rate of conversion and the most stable polystyrene emulsions were obtained using polyoxyethylated stearate, with HLB

number equal to 15. With mixtures of anionic and non-ionic SAS, the greatest stability of the emulsions lies at HLB numbers of about 14–15. With vinyl acetate, this range is broader and extends from 16.2 to 17.5.

## VIII. REASONS FOR THE STABILISING ACTION OF NSAS

When NSAS are used, the stabilising action cannot be due to the electrical double layer. In this case, other thermodynamic stability factors are operating, such as hydration of the molecules of stabiliser, the entropy factor[96], and the associated splitting pressure. In addition to these thermodynamic factors, the structural-mechanical properties of the adsorption layer may be of considerable importance for the aggregate stability[97,98].

It has been shown[99,100] that dispersion systems stabilised by non-ionic SAS may exhibit a small electrokinetic potential. For example, 1% polychloroprene latices stabilised by the oxyethylated products OP-4, OP-7, and OP-10, at pH 9, had electrokinetic potentials from -35 mV to -55 mV. The magnitude of the electrokinetic potential decreased with increase in the degree of oxyethylation. Butadiene–styrene latices stabilised with the SAS OP-7, OP-10, and OP-18, and prepared with precautions to reduce the concentration of electrolytes in the system, showed much smaller electrokinetic potentials. The potential varied from -9 mV for the latex stabilised by OP-7 to -5 mV for the latex stabilised by OP-18. These results show that here the electrokinetic potential is due to the selective adsorption of anions which are present, for one reason or another, in the system. The negative charge produced by the adsorption of anions may be partly neutralised by adsorbed molecules of oxyethylated SAS, exhibiting cation-active character. The longer the chain, the greater the extent to which the negative charge of the globules is reduced. None of the resulting latices coagulated when electrolytes were added, although the electrokinetic potential decreased to zero. The aggregative stability of the polychloroprene latices in the isoelectric state decreased slightly relative to that of the original latices. These results confirm the part played by non-electric stability factors, for example, according to the authors cited, hydration of the adsorption layers.

The importance of hydration of the stabiliser and its affinity for the dispersion phase of the emulsion was examined by Davies[86] and was reflected in the HLB system. As shown above, however, this examination did not make allowance for the possibility that hydration of the hydrophilic groups of the stabiliser molecules leads to the formation of polymolecular hydrate sheaths and the production of a splitting pressure when the particles approach one another. The splitting pressure is positive, that is, it prevents approach, if the interaction between the hydrophilic groups of the stabiliser molecules and the molecules of the solvate layer is greater than the interaction between the molecules of the solvate layer and the molecules of the medium, Duyvis and Overbeek[101] showed that for foam films formed by solutions of NSAS of the type OP-7, OP-10, and OP-20 in the presence of an electrolyte (NaCl), there exist two ranges of equilibrium film thickness: one very small, of the order of 100 Å, which is close to twice the length of the stabiliser molecule, and the other much greater, observed only at NaCl concentrations less than $10^{-4}$ *N*. The first thickness corresponds to the repulsion caused by steric hindrance, whereas the second is related to the splitting pressure. Analogous results were obtained by Sheludko and coworkers[102], who also worked with free liquid films. On the basis of the existence of equilibrium film thicknesses of the order of 100 Å, with stability related to the steric hindrance arising in the interaction of the adsorption layers, it was concluded that in order to obtain thermodynamically stable films, it is necessary that the adsorption monolayer have a sufficiently high stability (an arbitrary term denoting the presence of adequate tangential forces of cohesion in the monolayer).

Deryagin and coworkers[103] studied free films of solutions of the NSAS OP-10 and oxyethylated di-t-butylphenol at an NaCl concentration of $10^{-2}$ *N*. The equilibrium film thickness, equal to approximately 120 Å, is independent of the electrolyte concentration and temperature. The observed splitting pressure, which prevents further decrease in the thickness of the film, was attributed to interaction between the adsorbed monolayers and adjoining water layers with a thickness of 10–20 molecules. If, however, these results are compared with the results obtained by Duyvis and Overbeek, the phenomena observed by Deryagin and coworkers must be attributed not to the splitting pressure but to steric hindrance provided by the adsorbed molecules of the monolayer. The splitting pressure associated with the polymolecular hydrate layers apparently could not be observed in this work because of the relatively high concentration of electrolytes in the system. The absence of a splitting pressure due to hydration is also confirmed by the fact that the observed effects were independent of temperature, whereas increase in temperature should have a dehydrating action.

The existence of a splitting pressure in stabilisation by non-ionic SAS can be related not only to hydration in the true sense of the term, but also to osmotic forces developing during the swelling of the adsorbed layer of stabiliser, as suggested for protective colloids by Bromberg[104]. This possibility is confirmed by the above results obtained by Schick[58], from which it follows that the oxyethylated chains are present in the form of a coil in the dispersion medium, so that they exhibit the properties of a flexible polymeric chain capable of undergoing micro-Brownian movement. The micro-Brownian movement, which causes the dispersion medium to be forced into the space between approaching particles, can also be regarded as the entropy component of the splitting pressure (the entropy stability factor). The mobility of a chain usually increases with increase in temperature, but here the mobility decreases with increase in temperature, since dehydration takes place, causing the oxyethylene chains to adhere to one another with a consequent loss of mobility. Thus increase in temperature should lead to a decrease in both the hydration and the entropy components of the splitting pressure. The same influence on the splitting pressure should be shown by the addition of electrolytes. The part played by hydration as a factor influencing the stability of dispersion systems in the presence of NSAS is confirmed by the fact that dehydration, produced for example by an increase in temperature, leads to separation of the phases and, in the case of latices, to gelatinisation. This last result was shown by Panich and coworkers[100] for the case of butadiene–styrene latices stabilised by the non-ionic oxyethylated products OP-7, OP-10, and OP-18. Work by Orr and coworkers[105,106] showed that the addition of a non-ionic stabiliser to latices containing an anion-active soap leads to a decrease in the area occupied by a molecule of the latter. This was attributed to a decrease in the electrostatic repulsion of the soap ions as a result of the presence of the molecules of

the non-ionic stabilising agent between the ions in the adsorption layer. Sometimes, however, non-ionic soaps produce the opposite effect. Van Voorst-Vader[37], in a study of a solution—air interface, showed that the area occupied by the molecule of an ionic soap increases in the presence of non-ionic soaps. He attributed this phenomenon to the fact that in the presence of two different hydrophilic groups, the water molecules may be orientated in such a way that the ionic soap is more readily hydrated. This leads to attraction of the ionic soap into the water, increases the area occupied by the molecule, and thus decreases the affinity of the soap for the surface. Thus the addition of NSAS to disperse systems containing ionic soaps may either increase or decrease the affinity of the ionic soap for the dispersion phase with a corresponding influence on the aggregative stability of the system.

Neiman and coworkers[107] showed that the addition of NSAS of the OP type to an adsorptively unsaturated latex stabilised by an ionic soap increases its stability to the action of electrolytes until saturation of the adsorption layer takes place. Further addition of NSAS has no influence on the stability. The results obtained are readily explained by the fact that on the addition of NSAS, an important part begins to be played by the non-electric latex--stability factor, and the influence of electrolytes becomes less marked.

Aleksandrova and coworkers[108] studied the influence of NSAS on the stability to mechanical treatment shown by adsorptively saturated and unsaturated polystyrene latices stabilised by an ionic emulsifying agent (sodium oleate) and found that the addition of non-ionic emulsifying agents leads to an increase in the aggregative stability only for the adsorptively saturated latex. With the unsaturated latices, the addition of non-ionic surface-active substances is accompanied by a decrease in the aggregative stability until adsorptive saturation of the surface of the latex globules takes place, after which the stability increases, as for the adsorptively saturated latices. The observed phenomena were explained as follows. When small quantities of NSAS are added to adsorptively unsaturated latices, the molecules of the non-ionic emulsifying agents are distributed on the free areas of the surface of the polymeric globules, screening the sodium oleate molecules and leading to a deterioration in the protective properties of the adsorption monolayer. Increase in the quantity of NSAS leads to an even sharper decrease in stability as a result of the formation of a fragile saturated monolayer consisting of alternating associates of NSAS and sodium oleate. A sharp increase in stability is observed only when the excess of NSAS is sufficient for the formation of a single--layer protective sheath. The theory that a polymolecular protective sheath is formed on the surface of the latex globules is not undisputed. Kuznetsov and Lebedev[109] showed, on the basis of viscosity measurements, that soaps of aliphatic acids form a monomolecular interfacial layer on the surface of globules of butadiene–styrene latex.

Shits and Trapeznikov[110] studied the structural-mechanical properties of adsorption layers of the NSAS Xylital O-10, OP-7, OP-10, OP-20, Tween-20, and OS-20 at the boundaries with air and styrene. They found that only OS-20 forms a stable adsorption film at the boundary with air. At the boundary with styrene, in the initial period of existence of the interfacial surface, the SAS studied do not produce a high surface viscosity. The process of solubilisation, accompanied by the spontaneous formation of a styrene micro-emulsion, takes place gradually and facilitates structure-formation in the volume adjoining the interface on the aqueous-solution side.

Taubman and coworkers[111] studied the stability of adsorption layers of non-ionic stabilisers (OP-10 and Pluronic L-64) at the boundary with xylene, and also the stability of emulsions of xylene in water and the stability to freezing shown by polystyrene latices in the presence of the same substances. The stability of the emulsions and latices was greatest when protective layers of high stability were formed. High stability of the protective layers is associated with the formation, at the interface, of two liquid phases consisting of complex supermolecular structures in the form of fairly thick multi-layer films. It has been shown[112-114] that these structures are formed as a result of a hydrodynamic effect associated with the surface turbulence and convection leading to unidirectional transfer of the hydrocarbon phase into the aqueous phase in the form of an ultramicro-emulsion. It can be seen that Taubman and coworkers[111] studied not the structural--mechanical properties of the adsorbed films but the structure-mechanical properties of the supermolecular structures. The formation of the latter represents a particular case and cannot be taken into account in the development of a general theory of the stability of disperse systems. This was confirmed by Sonntag and Klare[115], who pointed out particularly that in the characterisation of the specific protective action of SAS, it is necessary to consider only those concentrations at which the interfacial tension is greater than the critical value, and at which spontaneous emulsification does not take place.

## IX. THE USE OF NSAS FOR EMULSION POLYMERISATION AND FOR INCREASING THE STABILITY OF LATICES

As noted in the Introduction, extremely varied use is made of NSAS in the modern economy. The use of NSAS in various branches of technology was examined in detail in the well-known monograph by Schönfeldt[5], to which the reader is referred. In this section we shall review briefly only the application of NSAS as stabilisers in emulsion polymerisation and for increasing the stability of latices — the fields which are of greatest interest to the authors of the present review.

Polymerisation in emulsions has found extensive application in industry, since it has a number of important advantages over other methods of polymerisation under the influence of free radicals. The high rates of the processes compared with those in homogeneous systems, the wider temperature range in which the polymerisation processes can be carried out, and the possibility of varying the nature and concentration of emulsifying agents are of considerable importance for the control of the polymer properties.

A large number of papers[116-120] have been devoted to the problems of studying the complex heterogeneous process represented by emulsion polymerisation. Several recently published papers have dealt with the problems of studying the characteristic features of the mechanism of emulsion polymerisation in the presence of non-ionic emulsifying agents. Thus French[121] studied the emulsion polymerisation of vinyl acetate with the non-ionic emulsifying agent Pluronic F-68 (a block copolymer of ethylene oxide and propylene oxide) in the presence of potassium persulphate. Parts and Moore[122] studied the polymerisation of

vinyl stearate with oxyethylated octylphenol as emulsifying agent. Neither of these papers, however, give any conclusions regarding the characteristic features of this process.

The problems of selecting different emulsifying agents (anionic, cationic, and non-ionic) for emulsion polymerisation were examined by Helin and coworkers[123], who recommended a number of emulsifying agents and their mixtures on the basis of a study of the kinetics of polymerisation and stability of latices.

Gritskova and coworkers[124-126] studied the emulsion polymerisation of styrene in aqueous solutions of non-ionic emulsifying agents (Pluronic F-68 and oxyethylated octylphenol and octadecanol) and point out a number of characteristic features distinguishing these processes from the analogous processes taking place "in bulk" and in the presence of ionic emulsifying agents.

NSAS are often used as additives to latices for increasing their stability to the action of electrolytes. This is particularly important in the production of latex pigments. Many grades of NSAS are produced especially for this purpose[5]. It has been shown[5,110] that NSAS added to latices increase their stability to low temperatures. Finally, NSAS can be used for the thermo-sensitisation of latex mixtures[127]: the NSAS give the latices stability at low temperatures, whereas with increase in temperature they separate as an individual phase, are solubilised in the adsorption layers of the ionogenic stabiliser and decrease their protective properties, leading to gelatinisation of the latices.


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# MECHANISM AND KINETICS OF TOPOCHEMICAL REACTIONS TAKING PLACE WITH DECREASE IN THE VOLUME OF THE SOLID PHASES

E. S. Vorontsov

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## I. INTRODUCTION

There is a large class of reactions which can be described by the equations:

$$A(solid) = B(solid) + D(gas), \quad (1)$$

$$A(solid) + C(gas) = B(solid) + D(gas), \quad (2)$$

in which the volume of the newly formed solid phase B is less than the volume of phase A which is undergoing the conversion. This very important condition, which brings about the distinctive features of the mechanism and kinetics of the process, can be expressed by the inequality:

$$V_B < V_A. \quad (3)$$

Such reactions include: the dissociation of carbonates, oxides, sulphates; the reduction of most commercially important metals from their oxides by gaseous reductants; the dehydration of crystal hydrates; and many other processes.

Relation (3) usually leads to the appearance of a finely disperse, very porous, new solid phase. It is well-known that the dissociation of massive calcite yields calcium oxide with a very porous, finely disperse structure, and in the production of iron by the reduction of crystals of its oxides "sponge" iron is produced. Metals reduced at moderate temperatures can be pyrophoric. These facts already suggest that in processes (1) and (2) the formation of the new phase B is accompanied by its continuous breaking-away or scaling off from the initial material.

The general theory of the nucleation and growth of a new phase from an old one was created by Gibbs and developed in the works of Fol'mer, Frenkel', Stranskii, Danilov, Roginskii, and others[1-5].

It must be noted that this theory starts from the existence of ideal contact between the disappearing and the growing phases. It is completely applicable, for example, to the simplest interaction of two phases in a one-component system, that is, to the changes of state and phase transformations when drops of liquid or crystallites are formed in supersaturated vapour, crystallites or bubbles of vapour in a liquid, and so forth:

$$A_{\Phi.I} \rightarrow A_{\Phi.II}. \quad (4)$$

Here the symbol $A_{\Phi.I}$ denotes the existence of a component in a certain phase state, and $A_{\Phi.II}$ that in another phase state.

Certain general features of this theory are also correct for reactions of types (1) and (2), as is usually stressed in contemporary literature[6-9]. However, the unusualness of these processes necessitates considerable modification of the theory in analysing their mechanism. Jacobs and Tompkins[10] attempted to develop the theory applicable to this class of change.

To make more precise current views about the mechanism and kinetics of formation of a new phase in topochemical reactions of types (1) and (2), we will attempt to systematise the principal differences between the features of the reactions now being considered and those of processes (4). These differences impose certain features on the thermodynamic analysis and particular attention must be paid to them in the kinetic analysis of the changes being compared (see Table 1).

The extension of Gibbs' theory to the class of topochemical reactions now under consideration led to the conclusion that a peculiarity of these crystal chemical transformations is the existence of two crystalline phases with a boundary surface, which acts as a reaction surface. The development of the process is shown in the growth and changes of this surface.

It must also be remembered that the extension of the theory of the nucleation and growth of a new phase,

TABLE 1. Most characteristic differences between processes (1), (2), and (4).

| (4) | (1) and (2) |
|---|---|
| Reaction of two phases in a one-component system. Ideal contact is maintained between the phases. | Three phases take part in the process. Forced formation of product B is brought about during contact of phases A and D or A and C. |
| Accumulation of the product does not hinder the course of the process, which takes place at the phase separation boundary, but, on the contrary, facilitates its development. | Accumulation of the product can spatially separate phase A from the gas and retard the process. |
| The formation of heterofacial fluctuations, which are nuclei of a new phase, is connected with the movement of the particles, bringing about consolidation and rarefaction in micro-volumes. | The formation of heterofacial fluctuations, leading to the appearance of new phase B, is linked with the removal of material from the bulk of the initial phase. |
| With the same temperature throughout the whole volume of the initial phase the fluctuations are distributed in it according to statistical laws. | With the same temperature throughout the whole volume of the initial phase the distribution of the fluctuations depends on the rate at which the gaseous substance leaves them. |
| The formation of nuclei of a new phase leads to the appearance of an interfacial surface. Work must be expended in the creation of this surface. | The formation of nuclei of a new phase can, by virtue of relation (3), lead to breaking-away from the old phase from separate parts of the surface. Work is required for the deformation of the crystal lattices at the point at which the phases meet and for their breaking away, that is, work on the reproduction of another two separation surfaces: A – gas and B – gas. |
| The growth of the new phase is connected with the supply to it of material from the initial feed medium. | The disappearance of the old phase is accompanied by the accumulation of material in the two growing phases. |
| The growth of the new phase is not accompanied by breaking of its contact with the old. | The growth of the new phase can bring about its rupture from the old. |
| The newly formed, growing, solid phase is usually compact and free from porosity. | The growth of phase B is usually accompanied by the great development of porosity in its bulk. Subsequent recrystallisation and sintering can complicate the course of the process. |

loped mainly for processes (4), to reactions (1) and (2) without essential modifications to it can be considered unjustified in the light of the differences given in Table 1.

Let us consider in more detail some aspects of the mechanism and kinetics of reactions of interest to us.

## II. DIFFUSION INSIDE THE CRYSTAL LATTICE OF THE INITIAL PHASE

The essence of processes (1) and (2) is the removal of material from the crystal lattice of the old phase and its subsequent reconstruction into a new phase. Therefore there is great interest in explaining the problems of the diffusion of $CO_2$ in carbonates, of $O^{2-}$ and $S^{2-}$ ions in oxides and sulphides during their decomposition, and also of $O^{2-}$ ions in oxides during the reduction of the metals, etc.

### 1. Diffusion of $CO_2$ in the Calcite Lattice

The appearance of CaO nuclei in the depths of the $CaCO_3$ phase precedes the formation of a supersaturated solution of B in A. Its formation is linked with the departure of $CO_2$ molecules from the crystal lattice of the carbonate. Therefore the investigation of the diffusion of $CO_2$ in $CaCO_3$ is of considerable practical interest. Such an investigation[11] was made using the carbon isotope $^{13}C$. From the decrease in the concentration of "labelled" carbon in the gas phase in contact with the calcite the coefficient of self-diffusion of $CO_2$ in $CaCO_3$ at 692–848° was found. The temperature dependence:

$$D = D_0 \exp\left(-\frac{58\,000}{RT}\right),$$

was determined and the entropy of activation of the self-diffusion of $CO_2$ was calculated:

$$\Delta S^* = R \ln\left(\frac{D_0}{d^2\nu}\right) = 4.7 \text{ cal deg}^{-1} \text{ mole}^{-1},$$

where $D_0 = 4.5 \times 10^{-4}$ cm$^2$ s$^{-1}$, $d = 4.04$ Å is the distance between the carbon atoms in the calcite lattice, and $\nu = 3 \times 10^{-12}$ s$^{-1}$ is the frequency of their vibration.

But it must be noted that there is a substantial difference between the self-diffusion of $CO_2$ in the stable $CaCO_3$ lattice and diffusion under the conditions of dissociation of the carbonate. The first process can be hindered by an absence (or insignificant proportion) of $CO_2$ vacancies in the crystal lattice. In the surface layers of calcite the second process can be greatly facilitated by the disintegration of the anionic sublattice. The elimination of molecules of $CO_2$ and the formation of $O^{2-}$ ions instead of $CO_3^{2-}$ can be considered as the production of vacancies for the diffusion of $CO_2$ in the lattice of the carbonate. These vacancies can be propagated into the depth of the crystal lattice.

Hence the diffusion media for both types of migration will be different and the energy characteristic obtained ($E$ = 58 000 cal mole$^{-1}$) and the value of $\Delta S^*$ scarcely give a correct representation of the difficulty of carrying out the removal of $CO_2$ from the $CaCO_3$ lattice during the dissociation of the carbonate.

### 2. Diffusion of Oxygen in an Oxide Lattice

The removal of oxygen from the crystal lattice of the oxides is the main aim in the reduction of metals. Moreover, the part played by oxygen diffusion in such processes is still uncertain.

Many oxides of commercially important metals (Zn, Cu, Fe, Ni, etc.) are either reduction semiconductors (ZnO) or oxidation semiconductors ($Cu_2O$, FeO, NiO) in which the cations have a higher mobility than the anions. This experimental fact, together with the results from investigations of the transport numbers of ions in oxide crystals, gives basis for considering the process of scale formation often as a preferential transfer of cations in the presence of a rigid network of the oxygen (or in the more general case, anion) sublattice.

Actually, in many experiments neutral particles on the surface of copper, nickel, or iron form a scale during high-temperature oxidation, by appearing closer to the metal–oxide boundary and not the oxide–gas boundary. Experiments on the sulphiding of silver[12] and copper[13] showed the incommensurably greater mobility of the metal cations compared with the sulphur anions.

All this provided a basis for some investigators to carry too far the analogy in the mechanisms of high-temperature oxidation and reduction. For example, in an analysis of the mechanism of reduction of iron[14,15] the preferential diffusion of the cations is considered in detail and no attention is paid to the possible movement of the anions, although without a corresponding removal (departure) of oxygen atoms it is difficult to understand the formation of three-dimensional metallic nuclei, the zonality of the process, the reconstruction of the oxygen sublattice in phase transformations, and other phenomena. In this, the preferential diffusion of the cations is "confirmed" by such experimental results as could equally well be explained by two-way diffusion of the cations and anions and even by the preferential motion of the latter.

Direct reduction of iron from oxides[16] is also treated as a process in which the diffusion of oxygen does not take place. But in addition the authors had to suggest that after the filling of the last cationic vacancies in the wüstite lattice and the formation of three-dimensional metallic nuclei further reduction proceeds by diffusion of oxygen along the metal–oxide interface. The problem of how three-dimensional metallic nuclei can appear without the corresponding exit of oxygen atoms, why these atoms should "await" the complete filling of all the cationic vacancies in the wüstite, why the reductant should invariably react with the oxygen which is diffusing from the deep zones along the metal–oxide interface and not react with the oxygen atoms which are nearer and more accessible for reaction, etc. was left completely unresolved.

Such a biased treatment of the mechanism of the reduction processes was due, evidently, to the fact that until quite recently nothing was known about the diffusion of oxygen in oxides. However, many recent studies have established the diffusion of oxygen in various oxides. For example, Barzakovskii and Volkov's review[17] gave the data in Table 2.

Calculation of the diffusion coefficients for oxygen by the formula:

$$D = D_0 \exp\left(-\frac{E}{RT}\right),$$

TABLE 2. Diffusion of oxygen in oxides†.

| Oxide | Temperature range | $D_0$, $cm^2 s^{-1}$ | $E$, kcal $mole^{-1}$ | $\Delta S^*$, cal × × $mole^{-1}$ $deg^{-1}$ |
|---|---|---|---|---|
| BeO | 1600—1900 | $5.2 \cdot 10^{-7}$ | 4.29 | — |
| $Cu_2O$ | 1030—1120 | $6.5 \cdot 10^{-3}$ | 39.3 | −3.4 |
| $UO_2$ | 550— 800 | $1.2 \cdot 10^{+3}$ | 65.3 | — |
| $TiO_2$ | 860—1030 | 1.1 | 73 | +12 |
| CdO | 640— 820 | $8 \cdot 10^{6}$ | 93 | +43 |
| ZnO | 1100—1300 | $6.5 \cdot 10^{11}$ | 165 | +59 |

† $D_0$ is the pre-exponential factor in the equation for the temperature dependence of the diffusion coefficient $D$, $E$ the activation energy, and $\Delta S^*$ the entropy of activation of the process.

from the results of Table 2 suggests that at high temperatures (800–1400°) the rate of motion of the oxygen often becomes close to the similar quantity for the cations of the metals. Barzakovskii and Volkov[17] concluded that it may be necessary to take into account the mass transfer of oxygen in reactions between solid oxides.

It must be specially emphasised that these results were obtained under conditions where the oxides are stable. The usual method of studying self-diffusion of oxygen in oxides involves the observation of the isotopic exchange between the gaseous oxygen labelled with the isotope $^{18}O$ and the oxide crystal. Knowing the surface area of the powder and the fall in concentration of the isotope, the diffusion coefficient can be calculated.

The data in Table 2 are not readily comparable with one another, since the experiments for different oxides were performed in different temperature ranges. However, it is evident that the quantities $D$ and $E$ vary within very wide limits, which, finally, depend on the nature of the oxide, the presence of lattice defects (in particular, oxygen vacancies), the diffusion mechanism, and other factors.

In this connection, attention must be paid to the fact that in high-temperature reductions which take place with irreversible disordering of the oxygen sublattice, the conditions for the diffusion of oxygen from the deep layers of the crystal to its surface should be incomparably more favourable than for the stable existence of the oxides. Here the analogy with the destruction of the anionic sublattice during the dissociation of carbonates is completely relevant.

In a conductimetric investigation[18] it was concluded that during the reduction of metals by diffusion of oxygen, in the surface layers of the oxides at least, the process can be preferred to the migration of cations in a positive direction both from the thermodynamic and from the molecular-kinetic points of view.

It has been noted[19,20] that in the reduction of wüstite a dense film of iron can be formed on its surface. Examination of this film under the electron microscope showed the complete absence of pores. Moreover, the reduction of wüstite continues, although very slowly. It can proceed here only by diffusion of oxygen through the compact layer of iron. The calculated[20] activation energy for this diffusion is 53 000 ± 4000 cal per g-atom of oxygen.

Hence, when the diffusion of oxygen through a compact film of iron in the reduction of wüstite is considered, then the possibility of the movement of oxygen in oxides with breakdown of the oxygen sublattice in process (2) cannot be doubted.

Evidently the time has come to reconsider the part played by diffusion of oxygen in the reduction of iron and other metals from their crystalline oxides. The theoretical or experimental evaluation of the rates of diffusion of anions under the conditions of breakdown of the anionic sublattice would be a considerable achievement.

## III. MECHANISM OF THE FORMATION OF A NEW PHASE

### 1. Nature of a Solid Solution of B in A

It must be assumed that the production of nuclei of a new phase precedes the formation of a solid solution of component B in A. Whereas from a thermodynamic viewpoint such a solution can be considered as an excess of MO in $MCO_3$ or of M in MO and MS as compared with the stoichiometric formulae of the carbonates, oxides, and sulphides, from the viewpoint of its formation mechanism two treatments are possible.

On the one hand the formation of the solution can be considered as the introduction of metal cations and oxide anions during the dissociation of carbonates or of metal cations during the reduction and dissociation of oxides and sulphides into the crystal lattice of the initial phase.

On the other hand, the departure of $CO_2$ molecules, oxygen atoms, or sulphur atoms from the initial substance A in the processes under consideration creates an unstable transition structure in the surface layer, which can be considered to be a solid solution. It is completely clear, however, that its nature will be quite different in comparison with the solution which is obtained by contact saturation of the carbonate with oxide, or of the oxide and sulphide with the metal.

The solubility of oxides in carbonates is apparently negligible. Thus, Gel'd and coworkers[21] could not detect it, and concluded that the solubility of the components could not exceed 0.06%, that is, the accuracy of the measurements.

As regards the solubility of metals, such a definite conclusion cannot be drawn for even the lower oxides and sulphides. The oxide and sulphide phases can have an excess of the metal or the non-metal[22] and their homogeneity region can be rather broad. Metals can be dissolved in the oxide by introduction between the sites of the crystal lattice. The filling of vacancies is evidently more correctly considered as chemical reaction, and not as dissolution, because this act is connected with the redistribution of electrons in the crystal.

A feature of the reactions we are considering is that the appearance of a new phase is associated with the loss of material from the old, and therefore here the greatest interest will relate to unstable transition structures arising during processes (1) and (2) and not to solutions formed by contact saturation of phases A and B.

The instability of the transition structure is linked with the degree of departure of the system from equilibrium and from the thermodynamic standpoint can be treated as chemical supersaturation of the solid solution of B in A. The onset of this supersaturation in the surface layer, in some of, or in the whole volume will evidently depend (at a

temperature) on the rate of removal of material from the initial phase.

For example, the very rapid removal of $CO_2$ from the carbonate lattice and the replacement of $CO_3^{2-}$ anions by $O^{2-}$ can comparatively easily bring about the formation of oxide in the micro-volumes of the surface layer. On the other hand, it can be thought that the removal of some $CO_2$ molecules still does not bring about the reorganisation of the old lattice into the new and when conditions for the equilibrium redistribution of particles throughout the whole volume are created by withdrawing negligible amounts of $CO_2$, then supersaturation can be attained throughout the whole piece of carbonate. Hence the smaller the piece the easier it is to reach supersaturation throughout it (less time is required for this). From this viewpoint it is understandable why the stepwise nature of the process during the reduction of oxides can be followed more easily the smaller the dimensions of the grains being reduced and the lower the rate of conversion.

A thermodynamically necessary condition for the supersaturation is that the chemical potential of the substance in the new phase should be less than its value in the solid solution:

$$\mu_2 < \mu_1, \tag{5}$$

Esin and Gel'd[8] proposed that for the dissociation of carbonates $\mu_2$ should be considered to be the chemical potential of the pure oxide and $\mu_1$ that of the oxide in the solid solution. By analogy with this it can be assumed that in the dissociation of oxides and their reduction $\mu_2$ will be the potential of the pure metal and $\mu_1$ that of the metal dissolved in the oxide. For a thermodynamic evaluation of the supersaturation it does not matter how this difference in chemical potentials arises: by the dissociation of an oxide or its reduction. But from the standpoint of the practical realisation of the process, it is known how difficult it is to create chemical supersaturation in order to bring about dissociation, for example, of the lower oxides of copper, iron, nickel, chromium, and other metals (at least, at the temperatures of ordinary pyrometallurgical processes), and how it is reached comparatively easily in the high-temperature reduction of these metals.

The magnitude of the chemical supersaturation expresses the probability of formation of a new phase, and with the aid of the latter, the rate of the process, thus connecting in this way a thermodynamic quantity with a kinetic characteristic.

A feature of the transformations being considered is that the supersaturation of the solid solution is connected in a definite way with the extent of the departure from equilibrium of the system as a whole. The way of writing:

$$\Delta G = \mu_2 - \mu_1 \tag{6}$$

ignores the thermodynamic properties of the gas which actively participates in the process of establishing the new condensed phase. Therefore it is evidently more correct to take for the characteristic of the method of reaching supersaturation in the "solution" the probability of the formation of nuclei, not the difference (6) but the magnitude of $\Delta G_i$ based on the occurrence of reactions (1) and (2):

$$\Delta G_1 = \mu_D + \mu_B - \mu_A \tag{7}$$

or

$$\Delta G_2 = \mu_D + \mu_B - \mu_C - \mu_A. \tag{8}$$

In Eqn. (6) $\Delta G$ is the change in free energy of the system due to the appearance of the new solid phase B, and $\Delta G_1$ and $\Delta G_2$ are the changes in potential of the system brought about by the course of reactions (1) and (2); $\mu_i$ are the chemical potentials of each of the substances taking part in the reaction.

When D is absent from system (1), then $\mu = \infty$, so that:

$$\mu_D = \mu_D^0 + RT \ln P_D, \tag{9}$$

where $P_D$ is the pressure of gas D in the system and $\Delta G_1 = -\infty$. The thermodynamic probability of the formation of phase B in this system should be very great.

From these relations, in a comparative investigation of the rates of oxidation of iron and of its reduction from oxides[23] the probability of formation of nuclei of a new phase was linked with the quantity $\Delta G_2$.

## 2. Heterofacial Fluctuations

Variations in density exist in carbonates, oxides, and sulphides, as in all other thermodynamic systems. However, the heterofacial fluctuations which can become the stable nuclei of new phase B also arise as the result of a chemical process — the essential difference in the mechanism of formation of a new phase in changes (1) and (2) as compared with processes of type (4).

Thus, in the dissociation of carbonates the chemical act of detachment of $CO_2$ from the complex anion $CO_3^{2-}$ and also the diffusion of $CO_2$ lead to the replacement of the $CO_3^{2-}$ anions by the monatomic $O^{2-}$. This destroys the symmetry of the force fields and distorts the carbonate crystal lattice, creating an unstable transition structure, within which the formation of heterofacial fluctuations is possible — the nuclei of the new phase MO.

In the dissociation or reduction of oxides or sulphides the chemical act is the transfer of electrons to the metal cations, which, together with the departure of oxygen or sulphur from the crystal lattice, also leads to the appearance of a transition structure, a "solid solution".

When the oxides or sulphides have cationic vacancies, then during the course of the reaction it is possible for monatomic particles of metal to migrate to the unfilled lattice sites[24]. But when the rate of production of anionic vacancies is so great that the rate of diffusion of oxygen or sulphur surpasses the intensity of movement of metal in the bulk of the oxide or sulphide, which is evidently so in real technological processes, then the "solution" will be none other than unfilled anionic places in the lattice of phase A. Its supersaturation provokes the appearance of stable heterofacial fluctuations which can become the nuclei of the new phase.

The instability of the transition structures is also connected with the replacement of the pair $M^{2+}-CO_3^{2-}$ by $M^{2+}-O^{2-}$ or $M^{2+}-O^{2-}$ by M–M, which are characterised by a lesser distance between the particles and a tendency to approach one another.

From this position it is easy to explain the appearance of three-dimensional nuclei of product B and also the appearance of zonality during the reduction of an oxide. Rostovtsev and Rudenko[25] discussed the problem of whether atomised iron is present at the interfacial surface. Each iron ion is in an environment of oxygen anions. In the defect sites of the oxide surface there are evidently almost

"gaseous" metal atoms, which can easily be reduced to the metallic state. But such atoms can hardly become stable nuclei of the new phase.

A heterofacial fluctuation can appear in any part of the volume of phase A, but its appearance in the surface layer is the most probable. When the process is proceeding intensively the fluctuations arising on the surface do not extend through the whole volume of the initial phase; their "concentration" in the surface layer becomes high. Under such conditions the coagulation (merging) of small fluctuations into coarser and more stable ones is even possible. The formation of nuclei of a new phase on the surface, but not in the volume, becomes predominant.

It is assumed that the processes of dissociation and reduction start from active centres, which are the most distorted sites of the crystal lattice, surface defects of the crystals: here the bond between particles can be weakened and the initial act of removal of oxygen or carbon dioxide is more probable [26]. In this connection it should be noted that the origination of heterofacial fluctuations (the three-dimensional nuclei of a new phase) is not only connected with the removal of individual oxygen atoms of oxygen, sulphur, or molecules of carbon dioxide from the crystal surface, but also with the probability of their departure from the bulk of the external layer of phase A.

From the diagram (Fig. 1) it is easy to see that this probability is quite dissimilar for particles situated on the protuberances and in the depressions. Points *a* and *b* are equally removed from the crystal surface, but whereas the first has more than one shortest path to the surface, the second has only one. Therefore the probability of fluctuations arising at the vertices of a cube will be greater than on an edge; at the latter, greater than around a face, and at a face greater than around the corner of a depression.

If it is assumed that the crystal surface is ideal and does not have defect sites, then again the probability of the occurrence of the elementary act of removal of a particle at its individual points will be unequal, because of the different energetic states of the ions. There will always be individual particles which are energetically more prepared for the completion of the elementary chemical act than the others.

## 3. The Formation of Nuclei of a New Phase

In phase transformations (4) at least one of the phases is mobile and this ensures ideal contact between the phases. When in a one-component system there is interaction between two solid phases with only a slight difference in specific volumes, then contact between them can also be very enduring and stable.

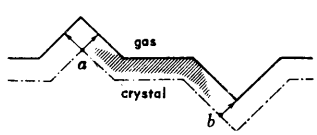



Fig. 1. Mechanism of loss of material from defect places of a crystal surface.

Relation (3) is responsible for the appearance of specific features in the mechanism of formation of nuclei of a new phase. It is clear that in processes (1) and (2) the contact between solid phases A and B can be very imperfect and in individual parts even completely destroyed. The existence of submicroscopic porosity in the products has also received direct confirmation [19,27].

Since the crystallites of the new phase should exhibit their intrinsic properties and have corresponding lattice parameters, its formation as a result of the operation of inequality (3) should be accompanied by detachment from the matrix medium A, if not along the whole interfacial surface, then at least partly. The formation, for example, of nuclei of calcium oxide in calcite should lead to the appearance in their vicinity of a "free" volume, approaching ~ 117% of the volume of the nucleus itself.

This circumstance should be reflected even in the initial equation for the change in free energy for formation of heterofacial fluctuations:

$$\Delta G = (\mu_2 - \mu_1)n + \alpha\sigma n^{2/3}, \qquad (10)$$

where the first term reflects the change in $G$ due to the difference in the chemical potential of the particles in the new (2) and old (1) states, and the second term the work in the creation of the interfacial surface A–B.

Recently it was even noted that the quantity $\sigma$ should not be treated as interfacial tension for changes (1) and (2) [10,23].

The directed action of the atomic forces at the contact surface of the two crystal lattices or the internal stresses should cause corresponding deformations or changes in the lattice parameters, which requires a definite amount of work. This was studied in a review [10] by Jacobs and Tompkins [10], where instead of $\sigma$, the quantity $\gamma$ is introduced, the energy of the stress associated with unit surface of separation:

$$\Delta G = \Delta G_i n + \alpha\gamma n^{2/3}. \qquad (11)$$

It is not difficult to see that the nature of processes (1) and (2) is not reflected completely here either, since relation (3) is not obeyed.

For reactions of type (1) and (2) the second term in Eqns. (10) or (11) should also take into account the work of breaking away of the new phase from the old, which can be done by the introduction of a third term:

$$\Delta G = \Delta G_i n + x\alpha\gamma n^{2/3} + y\alpha\varepsilon n^{2/3}, \qquad (12)$$

where $\alpha$ is a numerical factor depending on the geometrical form of the fluctuations which arise; $\gamma$ the energy of the stress, $\epsilon$ the work of adhesion (if the nuclei break away from the initial phase) or cohesion (if the nucleus itself ruptures), $x$ the fraction of interfacial surface A–B, $y$ the fraction of interfacial surface A–gas or B–gas, and $n$ the number of particles.

Evidently $x + y = 1$. But it must be remembered that the areas of the A–gas and B–gas surfaces for nuclei can be somewhat different by virtue of ratio (3).

Apparently instances are possible when either $x$ or $y$ can be neglected and the more general Eqn. (12) takes the form of the partial equations (10) and (11).

$\Delta G_i$ can be determined by Eqns. (7) and (8). It must then be remembered that in Eqn. (12) it relates to a single elementary particle; in the formation of a metallic nucleus, to one atom of the metal; in the formation of oxide from carbonate, to one pair of ions $M^{2+}$–$O^{2-}$.

## IV. DEVELOPMENT OF THE PROCESS AND PECULIARITIES OF ITS MECHANISM AND KINETICS

### 1. Role of the Gaseous Phase

In reactions (1) and (2) the new phase can appear only as a result of the interaction of the initial phase and the gas. Therefore the process always starts at the A–D or A–C boundary. The appearance of reaction product B complicates the course of the process, since it separates the reagents spatially.

This is well evident from the following examples. Almost all the metals (with the exception of palladium, iridium, platinum, and gold) are unstable under ordinary atmospheric conditions and should be changed into the ionic state[28]. But it is well known that most of them do not oxidise under these conditions, since the very thin oxide film formed separates the metal from the oxygen of the air. According to current views[29] the time for the formation of the film on iron in an atmosphere of air is 0.05 s. Often the reaction of carbonation also ceases almost completely because of the formation of a compact film of carbonate on the crystalline oxide.

These two examples relate to the reverse course of reactions (1) and (2), in which a relation opposite to inequality (3) holds. The direct course of these processes is usually aided by the new phase being very porous. This leads to the conclusion[19,30] that the formation of the product does not lead to the breaking of the A–gas contact between the reagents. But in the very investigations, on the basis of which these conclusions were made, it was observed that when a dense and pore-free product is obtained the process is sharply retarded. It is still possible only owing to the diffusion of elementary particles through the crystal lattice of the reaction product. In this the operation of the chemical reaction no longer takes place at the (initial phase)–gas boundary, but at the (new phase)–gas boundary or the surface of separation of the solid phases.

Thus in the oxidation of a metal the initial reaction proceeds owing to its contact with the oxidant gas, and then (after the formation of a film) is continued either owing to the movement of cations to the oxide surface, where they react with oxygen, or by diffusion of oxygen through the oxide layer to the metal surface.

In the reduction of oxides with the formation on them of a compact film of metal, the place of that reaction also moves from the oxide–gas-reductant boundary to the metal–gas separation surface, to which oxygen diffuses, there reacting with the reductant[19,20].

Hence the chemical reaction and the phase transformation can be spatially separated. This shows that the mechanism of changes (1) and (2) is more complicated than that for transformations (4).

Consequently, in these reactions the formation of products which block the surface of reagent A can sharply retard the course of the process. On the other hand, the breakdown of this blockade owing, for example, to cracking of the scale during the high-temperature oxidation of metals, or the formation of pores and cracks in the product during the dissociation of carbonates and the reduction of oxides can greatly accelerate the process, both as a result of the renewal of the (phase A)–gas contact, and also as a result of the great shortening of the diffusion paths of the elementary particles.

Note that in many investigations the rate of reactions (1) and (2) are usually considerably greater than the rate of the back reactions, when they relate to the same physical and geometrical conditions of the experiment. For example conductimetric investigation of the rates of oxidation and reduction of copper and iron wires[18] showed that under the same conditions reduction requires ten times less time than oxidation. The dissociation of carbonate is incomparably more rapid and more complete than carbonation[31].

### 2. Rate of Formation of Nuclei and Their Growth

The thermodynamic stability of the heterofacial fluctuations — the nuclei of the new phase — is determined by Eqn. (12), from which it is evident that even when the first term is negative the positive values of the last two terms can affect the absolute magnitude more than the first term, and the fluctuations then become unstable.

Since for a given degree of departure of the system from equilibrium (or for a definite chemical supersaturation) the first term in Eqn. (12) grows more rapidly than the sum of the second and third terms with increase in the number of particles $n$, $\Delta G$, as a function of $n$, has a maximum. The value of $\Delta G_{max}$ corresponds to that critical value of $n$ at which the growth of the nucleus can occur spontaneously, because it is accompanied by a fall in $\Delta G$.

$$\frac{\partial(\Delta G)}{\partial n}=\Delta G_i+\frac{2}{3}\varkappa\alpha\gamma n^{-\frac{1}{3}}+\frac{2}{3}y\alpha\varepsilon n^{-\frac{1}{3}}. \qquad (13)$$

Equating this derivative to zero, we find $n_{crit}$:

$$n_{crit}=\frac{8}{27}\alpha^3\frac{(x\gamma+y\varepsilon)^3}{(-\Delta G_i)^3}. \qquad (14)$$

An analysis of this equation shows that not only the energy of deformation of the crystal lattice, but also the work of formation of the primary submicroscopic particles should affect the value of $n$. From Eqn. (14) it follows that the necessary condition for the formation of critical nuclei is the inequality:

$$\Delta G_i<0, \qquad (15)$$

since if the reverse of (15) holds we obtain $n_{crit}<0$, which has no physical significance. For reactions (1) and (2) it is very important to emphasise that when, during its formation, the crystallite of the new phase is separated from the initial phase and the possibility of its further growth is excluded, then it can be thermodynamically stable only under the condition $\Delta G<0$. Note that if the nuclei in reactions (1) and (2) cannot grow at their points of detachment from phase A by the addition of elementary particles, the possibility of their growth by mutual cohesion is obviously not excluded (especially when there is great chemical supersaturation in the system).

The probability ($p$) of the formation of the nuclei depends not only on $\Delta G$, but also on the mobility of the atoms, since the formation of the new phase requires the reconstruction of the crystal lattice, which is impossible without corresponding movement of the particles. Starting from this consideration, $p$ is determined by the relation:

$$p=C\exp\left(-\frac{U+\Delta G}{KT}\right), \qquad (16)$$

and the rate of formation of nuclei ($v$):

$$v=A\exp\left(-\frac{U+\Delta G}{KT}\right), \qquad (17)$$

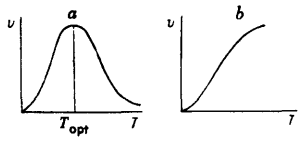



Fig. 2. Rate of formation of three-dimensional nuclei ($v$) as a function of temperature ($T$): $a$) for crystallisation from a melt; $b$) for the dissociation of carbonates, oxides, and sulphides.

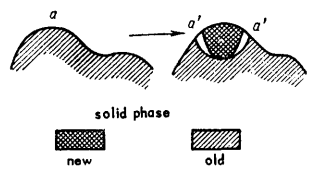



Fig. 3. Scheme for the reproduction of "defect" places — active centres of reaction.

where the energy factor $U$ is identified with the activation energy of diffusion, $A$ and $C$ are proportionality coefficients, and $K$ is Boltzmann's constant.

During crystallisation from the melt, $\Delta G$ increases with temperature but $U$ falls. There is therefore a temperature at which the rate of formation of the nuclei will be maximal (Fig. 2$a$).

For dissociations (1), there may not be an optimal temperature. At constant pressure, increase in $T$ should decrease both $\Delta G$ and $U$. Therefore the rate of formation of the nuclei will be an increasing function of temperature (Fig. 2$b$). It is necessary to mention this because in recent monographs[7,8], in discussing the above mechanism and kinetics of the dissociation of carbonates in terms of the theory of the formation and growth of a new phase and in fixing the position of the optimal temperature on the $v-T$ curve, for some reason it was not observed that there could not be one for the processes considered.

As regards reduction processes, there is evidently always a decrease in $U$ and rise in temperature affects $\Delta G$ differently. For example, in the reduction of magnetite and wüstite to iron by hydrogen, $\Delta G$, as well as $U$, is a decreasing function of temperature and therefore extremal values cannot be expected on the $v-T$ curve. But in the reduction of the same compounds with carbon monoxide there is one, for $\Delta G$ is an increasing function of temperature.

In real technological processes changes (1) and (2) are carried out at great degrees of chemical supersaturation and high rates. Under such conditions the rate of nucleation of the new phase is extremely high and the conditions for their growth can appear very unfavourable. The following features of the reactions being considered hinder the growth of the nuclei.

1. Whereas in processes (4) the supply of material is effected comparatively readily, in changes (1) and (2) the growth of the nuclei of the new phase is complicated by the slowness of the diffusion of the elementary particles in the crystal lattice.

2. The formation of a crystallite of the new phase should be accompanied — if not by complete — then at least by partial detachment of it from the initial substance, because of relation (3) (see, for example, Fig. 3). The gaps formed in the neighbourhood of the crystallite will be insurmountable obstacles for the diffusion of particles to the surface of the nucleus.

3. If the attachment of the nucleus of the new phase to the old is not coherent but has a distinct boundary, then its motion should bring about movement of the nucleus, since $v_B < v_A$. But with the condition of intensive formation of nuclei, their free movement is excluded (not for a gas and not for a liquid). The crystallites press one another and even their insignificant formation at the interfacial boundary should lead to fracture of the phase.

Obviously the growth of the crystallites is strongly connected with the processes of coalescence, sintering, and recrystallisation, which will be the more successful and occur at lower temperatures the smaller, and consequently the more active and more mobile the nuclei themselves; to a lesser extent the growth occurs by the attachment of elementary particles. This obviously also explains the possibility of obtaining pyrophoric metals in the low-temperature reduction of the oxides[30].

What has been stated agrees well with the ease of obtaining very finely dispersed and porous products B during reactions (1) and (2), which is observable in practice.

It is worth noting that very few results of investigations of the physical and chemical properties of the products of reactions of type (1) and (2) (for example, properties such as density, electrical conductivity, mechanical strength, adsorptivity, chemical activity, etc.) have been published. Such investigations are extremely desirable since they can give additional information about the mechanism of the process.

## 3. Pore Formation

In the mechanism of the changes which we are analysing, a special place is occupied by the formation of pores and their part in the development of the reaction. The origination of pores can often be considered to be the same result of a process as the formation of a product. Therefore the size of the relative porosity (the volume of pores compared with the volume of the lump of carbonate, oxide, or sulphide) can even serve as a measure of the completion of the process.

In several investigations, for example, that of Edström[30], it was noted that the dimensions of lump specimens either did not change at all or changed insignificantly during dissociation and reduction, although the difference in the volumes of phase A and B can be very considerable. If therefore the change in dimensions of single-crystal or polycrystalline specimens during the conversion be neglected, then it is not difficult to calculate the limiting value of the overall porosity ($\pi_p$, %) corresponding to complete conversion of the old phase into the new.

For example: $CaCO_3 \rightarrow CaO + CO_2 + \text{pores}$

$$\pi_p = \left(1 - \frac{2.8 \times 56}{100 \times 3.4}\right) \times 100 = 54\%,$$

where 100 and 56 are the molecular weights of $CaCO_3$ and CaO respectively, and 2.8 and 3.4 their densities in g cm$^{-3}$.

Similarly, it is possible to calculate that the reduction of $Fe_3O_4$ to FeO requires the appearance in the product of

a relative porosity of ~15%: $Fe_3O_4$ to Fe ~52%; FeO to Fe ~40%.

Then the ratio of porosity $\pi$ corresponding to a definite stage in the process, to its limiting value $\pi_p$ provides a criterion of the degree of completion of process A:

$$(\pi/\pi_p) \times 100 = A\%. \quad (18)$$

The difference between the value thus found for A and the real value is usually due to sintering or recrystallisation.

It has often[23,32-34] been observed that the sintering of a layer of products can even bring about some decrease in the rate of the process with rise in temperature, which explains why obstacles to diffusion arise with densification of the layer. In this connection, there is great interest in investigating not only the overall, but also the differential, porosity and also the true surface of the reagents.

Tatievskaya and Chufarov[27] found that from 65 to 90% of the pores formed as a result of the reduction of haematite and magnetite at temperatures up to 500° are very fine capillaries with a radius not exceeding $50 \times 10^{-7}$ cm. An increase in temperature to 800° leads to the almost complete disappearance of fine pores with a radius less than $200 \times 10^{-7}$ cm.

In a later investigation[19] of the reduction of wüstite at temperatures between 600 and 870° the fraction of pores with radii up to $1.3 \times 10^{-5}$ cm varied accordingly from 42.8 to 56.3%. It was found that the relative surface of the products decreased from 23 540 to 13 910 $cm^2\ cm^{-3}$.

These experimental results suggest that submicropores appear in the products of reactions (1) and (2) during the formation of the crystallites of the new phase as a consequence of the inequality (3).

The formation of pores leads to the reestablishment of the contact between the initial solid and gaseous phases, considerably facilitating the course of reactions (1) and (2) in comparison with the back reactions. In the latter the products should be compact and pore-free, since its volume is greater than the volume of the solid substance entering into the reaction. True, in the processes which are the reverse of the reactions which we are analysing pores can be formed in the internal layers of the product (for example, in the high-temperature oxidation of metals) but for another reason — due to the Kirkendall effect[35].

Hence the change from the oxidation of metals to their reduction significantly changes the mechanism of the process: the transport of the reagents in oxidative reactions is realised almost exclusively by mass transfer of them through the crystal lattice of the product, but in reductions, by motion along the micropores, that is, by Knudsen diffusion.

## 4. "Autocatalysis"

The following feature is characteristic for changes (1) and (2): there is a maximum on many rate–time graphs. This phenomenon is termed autocatalysis, since as the reaction develops it accelerates itself. The explanation is that the main place at which the reactions proceed is the surface separating phases A and B. The interfacial boundary grows during the process, but since the reaction is heterogeneous and its rate is proportional to the surface, this rate must also increase and reach a maximal value.

The many investigations of Chufarov, of Rostovtsev, and others[36-39] provide an experimental basis for the autocatalytic theory applicable to the processes we are considering.

Chufarov developed the adsorption-autocatalytic theory for the reduction of a metal; this theory has been widely recognised and extended. It is the leading theory in the contemporary educational literature on the theory of metallurgical processes.

Many papers have considered in detail the adsorption nature of reduction processes[40-42].

However, it must be noted that some aspects of the adsorption-autocatalytic theory are not satisfactory. Thus in Lyuban's monograph[43] it is stated that as the temperature is raised the role of adsorption in the reduction processes must necessarily be diminished. But here it must be remembered that chemical adsorption of gases can occur at comparatively high temperatures. Thus, oxygen is adsorbed on graphite even at 1200°.

The adsorption side of the theory was criticised in Manchinskii and Shkodin's review[44], where it was shown that in many experiments which provide an experimental basis for the theory and from which quite important conclusions were drawn about the nature and mechanism of the reactions being studied, the use of a vacuum could change the process in the diffusion, but not in the kinetic, region, notwithstanding the opinions of their authors.

It is noted that from the standpoint of the adsorption theory, in criticising the baseless analogies between equilibrium and kinetic characteristics in the "two-stage" hypothesis on the mechanism of the reduction of metals, they themselves tolerate a similar error, by explaining the difference in the rates of reaction of metals with hydrogen and carbon monoxide in terms of the equilibrium values of adsorption of these gases. These values are extrapolated into the region of high temperatures without sufficient reason. Furthermore, adsorption relates not to unit volume of the adsorbent but to its unit surface and the true surface of the solid phases in the experiments was not estimated. The authors unfortunately did not discuss the question of how the adsorption in real processes departs from its equilibrium values.

The "autocatalytic" mechanism for the processes being analysed also needs considerable refinement.

It is now thought[7-9] that, after the formation of the nuclei of the new phase, reactions (1) and (2) are localised on the surface of separation A–B, that is, in those places where their operation is complicated by the above three circumstances. This starts from the fact that the process of building up a new phase is easier (from the energetic point of view) than its initial formation.

Here, evidently, the difficulties of the reactions proceeding on the surface of separation between two solid phases are partly understated and the difficulties of formation of three-dimensional nuclei (which cannot be so great at high chemical supersaturations) are exaggerated to a certain extent.

As a sharp separation surface between the solid phases is necessary for catalysis, first of all it is necessary to settle the question as to whether such a surface is always present in the changes being studied.

Starting from the analysis given above of the nature of the "solid solution" it is expected that there can also be

continuous — coherent change between A and B. It is interesting in this connection to note that some authors confirm the accelerating action of the reaction product[45,46] whereas others do not[47-49].

Furthermore, if reaction (3) is obeyed, then both the initiation and the growth of the new phase can lead to the disappearance of the A–B surface of separation and to the production of A–D and A–C contacts. Then the main place for the reaction to take place can become the surface of separation of the initial solid phase from the gas. But then the explanation of the maximum on the atuocatalytic curves in terms of the growth of the A–B interfacial surface does not seem very convincing.

With the exception, for example, of such processes as the formation of a condensed phase from saturated vapour, of a crystallite from a melt, etc., the mechanism of which can prove to be quite different from that in reactions (1) and (2), where three phases interact, the genesis of an interfacial surface, which brings about the separation of the reagents, may not only accelerate but also complicate and retard the change. The essence of the latter is that loss of material from initial reagent A is hindered by the appearance of the product and boundaries separating the solid phases.

Hence the phenomenon of "autocatalysis" can be explained by the change in the A–B interfacial surface only when good contact is maintained between the phases which are interacting and there is a distinct separation surface between them.

In accordance with what has been stated other possible reasons for the appearance of a maximum on the rate–time curves must be considered.

1. When as a result of inequality (3) there is detachment of the new phase from the old, then this can bring about extensive renewal of an A–gas separation surface. This has a limit. As reagent A is consumed a moment is reached after which the occurrence of the reaction is accompanied by a decrease in this surface.

At high degrees of chemical supersaturation and almost continuous covering of phase A by the nuclei of phase B the surface of contact between the initial substance and the gas very rapidly reaches a maximal value and subsequently can only decrease, which agrees well with experiment.

2. The nuclei of the new phase are formed mainly in defect sites on the surface of the crystallites. Even partial rupture of a crystallite of B from the initial substance A signifies renewal of the defect sites, which can also accelerate the process. This can be represented, for example, by the scheme shown in Fig. 3. Here it is evident that instead of one active centre $a$, the sharp edge $a'$–$a'$ of a crater is formed and on this there will be many defect sites.

The appearance of the descending branch of the autocatalytic curve is due not only to the decrease in the reaction surface and the number of defects but also the growth in the thickness of the layer of product, which hinders the supply or removal of gaseous reagents and the heat exchange.

Hence the advances in general and physical chemistry in the investigation of the processes analysed in the present review make it possible to build up a mechanism for them from new points of view. These advances also enable us to hope that in the near future essential modifications will be made to the theory of nucleation and growth of a new phase in topochemical changes of the type considered here.

We think that the following are the most interesting features of the mechanism and kinetics of these reactions.

1. Processes (1) and (2) are complex heterogeneous interactions which include at least six stages: (a) the chemical reaction itself; (b) reconstruction of the crystal lattice of the initial phase A into that of the new phase B; (c) transport of the gaseous reagents and products between the reaction surface and the centre of the gas stream; (d) diffusion of the gases into the pores of the initial crystalline phase; (e) the diffusion of gases into the pores (capillaries) of the solid reaction products; and (f) the diffusion of particles (atoms, ions, molecules) in the crystal lattices of the solid phases.

Each of these stages can be rate-limiting — it depends on the particular conditions under which the process is carried out.

2. The formation of the solid product B leads to spatial separation of the reagents and to difficulties in carrying out the process.

3. The difference (3) between the volumes of the solid phases originating and disappearing during the course of the interaction leads to the development of porosity, to the spatial drawing together of the reagents, and even to renewal of their contact, which in turn facilitates the course of the reaction, in distinction, for example, from the back reaction.

4. The interaction of these two tendencies (those mentioned in paragraphs 2 and 3) bring about the peculiar features of the kinetics of the processes analysed here, sometimes causing their acceleration and sometimes their retardation.

The reaction rate at a given temperature and degree of chemical supersaturation can be affected by: (a) the topography of the surfaces of the solid phases and the renewal of defect places; (b) the disordering of the crystal lattices and the formation of transition structures during the transformation; (c) the formation of electrical fields and the possibility of their penetration in connection with the development of porosity in the depth of the crystal of the solid phase; (d) the sintering (recrystallisation) of the reaction products and the hindering (or facilitation) of capillary diffusion of the gaseous reagents, and also the supply or removal of heat necessary for the course of the reaction.

5. Many experimental results show that the solid product of reactions of the type considered are usually obtained finely disperse with a strongly developed surface and consequently high chemical activity. The production of coarsely crystalline and single-crystal products is greatly hindered by the operation of inequality (3). Crystal growth is evidently mainly brought about by their sintering and to a lesser extent by the addition of elementary particles.

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# QUANTITATIVE ASPECTS OF GAS-PHASE CHEMICAL KINETICS

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Chemical kinetics has long been, by its very nature, a quantitative science, concerned mainly with measuring the rates of chemical reactions. However, measurements of the reaction rates under a given set of conditions (temperature and pressure, initial composition, presence or absence of an inert diluent) give no indication at all of the rate of the same reaction under arbitrarily prescribed conditions. Yet the main value of kinetic investigations lies, both from the theoretical and especially from the practical point of view, in the ability to predict the rate of a given chemical reaction over a wide range of different conditions. A knowledge of the reaction mechanism and of the rate constants of (at least) all the main elementary processes involved is an invariable prerequisite.

At present, the mechanism of the oxidation (combustion) of hydrogen, and of reaction in hydrogen–halogen systems, among those of complex gas-phase reactions, have been studied in some detail, as has the mechanism of the oxidation (combustion) of carbon monoxide (but far from exhaustively); the mechanism of chemical changes in the nitrogen–oxygen system has been examined in broad outline; and individual steps in the oxidation of hydrocarbons and in various other complex reactions have been elucidated. Studies of the mechanism of a variety of chemical reactions, vigorously pursued over a wide front by physical chemists of many countries, are steadily adding to the number of reactions whose mechanism is understood. However, we are still at a relatively early stage, and a large number of reaction mechanisms (including those of technically important reactions) still remain to be investigated and made more precise.

In spite of the many studies devoted to measurements of the rate constants of elementary processes, and in spite of the very large number of kinetic constants which have now been measured, our existing fund of constants is far from adequate for a prediction of the rates of chemical reactions under prescribed conditions. Even in the rare instances where the reaction mechanism is known, and the rate constants of all the main elementary processes have been measured, the precision of the constants is often found to be inadequate. This is particularly true when it becomes necessary to extrapolate to high temperatures the values of these constants measured at relatively low temperatures (a problem which present-day practice often puts to chemical kineticists).

Before discussing the present state of the problem of the rate constants of elementary chemical processes, we shall review briefly some modern experimental methods of measurement.

The experimental methods used to measure rate constants of elementary chemical processes can be divided into two groups: in the first, the constants are measured in the course of the reaction itself, whilst in the second group a single process (often the primary process for the particular experimental conditions) is artificially isolated from the many concomitant elementary processes. The second group of methods is often used to measure the rate constants of processes in which atoms and free radicals interact with molecules or with each other, the atoms and radicals being generated thermally, photochemically, or electrically. Generation can be effected either in the reaction zone or elsewhere. Thus, the photochemical generation of active reaction centres is most frequently carried out in the reaction vessel, whereas when the active centres are generated electrically they appear in a region of electrical discharge, and they are led to the reactor, through a jet, by the flowing gas.

The method of crossed molecular beams is ideal for studying a single, isolated elementary process, but its application has so far been severely limited by the difficulty of measuring the reaction rates.

Among the first group of methods should be listed the shock tube method and the related method of adiabatic compression. The problem of measuring the dissociation constants of diatomic molecules, when the progress of the reaction is usually monitored from the change in concentration of the experimental gas (e.g. by absorption spectroscopy), is solved most easily by the shock tube method. The main difficulty, arising from insufficient accuracy in the measurements, is encountered in the analytical presentation of the measured rate constant. In using the expression from classical collision theory for the dissociation rate constant[1]

$$k_d = c\sqrt{T}\left(\frac{D}{RT}\right)^n e^{-D/RT} \qquad (1)$$

(where $c$ is a constant factor, $D$ the dissociation energy, and $n$ the number of internal degrees of freedom involved in activation of the dissociating molecule), a value of $n$ is usually chosen such that the experimentally observed temperature variation of the constant $k_d$ is described as accurately as possible by formula (1). The extent to which such choice can vary (as a direct consequence of the low precision of the measurements) can be assessed from Table 1.

One important result from the shock tube method for measuring $k_d$ has been to verify the correctness of the expression

$$K = \frac{k_d}{k_r}, \qquad (2)$$

where $K$ is the equilibrium constant and $k_r$ the rate constant for recombination of the atoms (the reverse of the molecular dissociation process).

Measurements of the dissociation rate constants of polyatomic molecules are usually complicated by the great variety of secondary processes which follow the primary process. Thus, all stages of cracking, as far as carbon, have been demonstrated in the thermal decomposition of methane:

$$CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow C.$$

However, the initial stage of the reaction can be isolated by restricting the reaction time. In this way, formulae for the dissociation rate constant in which the dissociation energy and the preexponential factor have closely similar values have been reported in three independent studies[8-10] of the decomposition of methane.

To interpret the experimental results from this type of work correctly, it is essential to ascertain correctly whether the primary process involves dissociation of the methane molecules by the mechanism $CH_4 \rightarrow CH_3 + H$ or by the mechanism $CH_4 \rightarrow CH_2 + H_2$, and whether this process follows first-order or second-order kinetics.

The first of these two questions can now be said to have been resolved in favour of the process $CH_4 \rightarrow CH_3 + H$. A strong argument in its favour was the identity of the activation energy measured for the primary process with the dissociation energy of the $H_3C-H$ bond, and also the fact that $CH_3$ radicals have been detected, by the Paneth mirror technique [by the formation of $(CH_3)_2Te_2$] in the gas stream issuing from the region of methane cracking, whilst no $CH_2$ radicals were detected (absence of $CH_2Te$).[11]

The problem of the order of reaction has been analysed in a previous paper[10], which showed that the process $CH_4 \rightarrow CH_3 + H$ is a first-order reaction (at least, under the experimental conditions of the adiabatic compression method[12]). Thus, the statistical theory of unimolecular decomposition[13] gives for the rate constant of the second-order process $CH_4 + Ar = CH_3 + H + Ar$ the formula

$$k_{d,2} = 10^{21} e^{-E/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},$$

correct to an order of magnitude at temperatures below 1860°K. Furthermore, the same theory shows that decomposition will occur by a first-order law if

$$k_{d,2}[Ar] > k_{d,1}, \qquad (3)$$

where $k_{d,1}$ is the first-order dissociation constant, and [Ar] the concentration of argon. (The reactions occur in methane diluted with 20–100 times its volume of argon.) Substituting in this inequality the formula obtained[10] for $k_{d,1}$

$$k_{d,1} = 10^{15} e^{-E/RT} \text{ s}^{-1},$$

and [Ar] = $10^{-3}$ mole cm$^{-3}$ (degree of adiabatic compression = 20) we obtain $10^{21} \times 10^{-3} = 10^{18} \gg 10^{15}$, showing that the condition for unimolecular decomposition by the first-order law is satisfied.

Studies of the thermal decomposition of polyatomic molecules in shock tubes sometimes lead to an Arrhenius formula for the decomposition rate constant in which the activation energy $E$ is considerably lower than the dissociation energy. Thus, the following formulae have been obtained[14-17] for the rate constant of the thermal dissociation of $CO_2$:

$$k_d = 3 \times 10^{11} \sqrt{T}\, e^{-86\,000/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}, \quad M = Ar, \quad T = 2500\text{–}3000^\circ K,^{14}$$

$$k_d = 1.5 \times 10^{14} e^{-87\,000/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}, \quad M = CO_2, \quad T = 3000\text{–}5500^\circ K,^{15,16}$$

$$k_d = 2.9 \times 10^{11} \sqrt{T}\, e^{-74\,700/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}, \quad M = Ar, \quad T = 3500\text{–}6000^\circ K,^{17}$$

$$k_d = 2.5 \times 10^{11} \sqrt{T}\, e^{-74\,500/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}, \quad M = N_2, \quad T = 3500\text{–}6000^\circ K,^{17}$$

whereas the dissociation energy of $CO_2$ into CO and O is $D$ = 125.75 kcal mole$^{-1}$. The $k_d$ constants measured in this work can also be represented by formulae of the type of Eqn. (1):

$$k_d = 1.2 \times 10^2 \sqrt{T} \left(\frac{D}{RT}\right)^{7.11} e^{-D/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},^{14}$$

$$k_d = 3 \times 10^7 \sqrt{T} \left(\frac{D}{RT}\right)^{6} e^{-D/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},^{15,16}$$

$$k_d = 5.8 \times 10^{10} \sqrt{T} \left(\frac{D}{RT}\right)^{4.56} e^{-D/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},^{17}$$

$$k_d = 2.0 \times 10^{10} \sqrt{T} \left(\frac{D}{RT}\right)^{4.72} e^{-D/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}.^{17}$$

TABLE 1. Temperature dependence of the preexponential factor in the expression for the rate constant of the dissociation of the $O_2$ molecule ($O_2 + O_2 = 2O + O_2$), as reported by various workers ($D$ = 118 000 cal mole$^{-1}$).

| $k_d e^{D/RT}$, cm$^3$ mole$^{-1}$ s$^{-1}$ | $T$, °K | Ref. |
|---|---|---|
| $7.4 \cdot 10^{11} \sqrt{T} (D/RT)^{1.5 \pm 0.2}$ | 6000—7000 | 2 |
| $2.25 \cdot 10^{12} \sqrt{T} (D/RT)^{1.5}$ | 3000—8000 | 3 |
| $5.5 \cdot 10^{11} \sqrt{T} (D/RT)^{3}$ | 2800—3900 | 2, 4 |
| $5.4 \cdot 10^{10} \sqrt{T} (D/RT)^{3}$ | 3000—5000 | 5 |
| $5.1 \cdot 10^{10} \sqrt{T} (D/RT)^{3}$ | 4000—7000 | 6 |
| $4.6 \cdot 10^{9} \sqrt{T} (D/RT)^{4}$ | 2600—7000 | 7 |

Since the exponent of the term $D/RT$ cannot exceed 5 when M = Ar, and therefore the number 7.11 has no physical significance, Brabbs et al.[14] assumed that the thermal dissociation of carbon dioxide occurs in the two steps

$$CO_2(^1\Sigma) + Ar = CO_2^*(^3\Pi) + Ar,$$
$$CO_2^*(^3\Pi) \rightarrow CO + O,$$

of which the first is rate-determining†. These authors[14] interpret the glow (characteristic of the CO flame) which is observed during the thermal dissociation as evidence for the participation of electronically excited $CO_2^*$ molecules. They base one of their two methods for measuring the rate constant of the dissociation of $CO_2$ on measurements of the intensity of this glow.

According to Davies[17], however, the glow is a secondary process, associated with the recombination of CO + O leading to the formation of electronically excited $CO_2^*$ ($^3\Pi$) molecules; while the dissociation of $CO_2$ occurs in a single step, $CO_2 + M = CO + O + M$ (in Davies' formulae $n < 5$).

To establish the true mechanism of the thermal dissociation of $CO_2$ it is very important to determine the difference in energy between the $^3\Pi$ and $^1\Sigma$ levels, which is not known at present. It is interesting to note that in the thermal dissociation of carbon disulphide, for which the activation energy $E$ is also smaller than the energy required to break the SC–S bond, but for which the excitation energy of the $^3\Pi$ level is known from spectroscopic data, the value of $E$ agrees[18] with the energy difference between the $^3\Pi$ and $^1\Sigma$ levels. This is convincing evidence in favour of the two-stage mechanism for the reaction.

Two-stage thermal decomposition has been established also in the case of $SO_2$, for which the activation energy calculated from the formula

$$k_d = 10^9 \sqrt{T} \left(\frac{E}{RT}\right)^3 e^{-E/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},$$

coincides with the excitation energy of the triplet state[19] of the $SO_2$ molecule. The dissociation process in this case occurs according to the scheme

$$SO_2 + M = SO_2^* + M - 73.6 \text{ kcal mole}^{-1},$$
$$SO_2^* + SO_2 = SO_3 + SO + 25.6 \text{ kcal mole}^{-1},$$

where M denotes any species.

The thermal ionisation of the inert gases has also been shown to be a two-stage process. Thus, the ionisation of xenon in a shock tube proceeds according to the scheme[20,21]

$$Xe + M = Xe^* + M,$$
$$Xe^* + M = Xe^+ + e^- + M.$$

Whereas measurements of the rate of decomposition of saturated molecules, needed in order to determine rate constants, present no special difficulties, measurements of the rates of reactions involving atoms and free radicals, formed in the reaction itself or generated externally, present a much more difficult problem. To determine the rate constants in these cases, the concentration of active centres taking part in the reaction must be measured, or else the rate constant of another reaction involving the same active species must be known.

† The second stage can be written

either $CO_2^*(^3\Pi) + Ar = CO + O + Ar$ or $CO_2^*(^3\Pi) + CO_2 = 2CO + O_2$.

Without attempting to list existing methods of measuring concentrations of atoms and free radicals, we shall only state that the electron spin resonance (e.s.r.) method, recently included among these methods on account of its potentialities, now appears to be the most effective and the most promising. Kinetic investigations of reactions involving H and O atoms, halogen atoms, and OH radicals have already been successfully carried out with the help of the e.s.r. method.

An example of this is the recent work of Panfilov[22], who has measured the rate constants of twelve reactions of the type $H + RH = H_2 + R$, as well as of the reaction $H + O_2 = OH + O$ in low-pressure oxyhydrogen flames (500–600°C, 3–6 mmHg) containing small quantities of the compound RH, the concentrations of H atoms being measured by e.s.r. spectroscopy.

The measurement of the rate constant of one reaction from the known rate constant of another reaction usually relies on the change in the combustion limits[23–30]. The basis of this method can be understood by considering the hydrogen–oxygen flame. With fairly rich hydrogen–oxygen mixtures (the lower combustion limit is set by the removal of H atoms at the walls), if a small amount of a substance M with which H atoms can react is present in the gas mixture, the displacement (in pressure) of the lower limit $\Delta p_1$ can be expressed by the formula

$$\frac{\Delta p_1}{p_1^0} = \frac{k[M]}{k_0}, \quad (4)$$

where $p_1^0$ is the pressure at the lower limit in the absence of the additive, $k$ the rate constant of the reaction between H atoms and the substance M (for example, the rate constant of the reaction $H + RH = H_2 + R$, if M = RH), and $k_0$ the rate constant for the heterogeneous removal of H atoms.

Nalbandyan and his coworkers[31] have tried, by appropriate treatment of the walls of the reaction vessel, to induce the reaction to occur in the diffusion region, where the constant $k_0$ can be calculated very accurately in terms of the diffusion coefficient. Thus, from a knowledge of $k_0$ combined with measurements of the relative displacement of the lower combustion limit $\Delta p_1/p_1^0$ at various values of [M], they calculated the constant $k$ as the slope of the linear plot of Eqn. (4). A common drawback of the method of limit displacement is the fact that the temperature range over which reliable results are obtained is relatively narrow.

The method of "competing reactions", extensively used by Steacie, and also by Trotman-Dickenson, Noyes, and others to study the reactivity of methyl radicals, also relies on measuring the rate constant of one reaction in terms of the rate constant of another reaction.

In the simplest case, when only one substance (e.g. acetone) is present in the system initially, thermal or photochemical decomposition generates $CH_3$ radicals, which proceed to recombine or to react with acetone molecules, splitting off an H atom. The kinetic equations for this system lead to the relationship

$$\frac{R_{CH_4}}{\sqrt{R_{C_2H_6}}} = \frac{k[CH_3COCH_3]}{\sqrt{k_r}}, \quad (5)$$

where $R_{CH_4}$ and $R_{C_2H_6}$ are the rates of formation of methane and ethane respectively, $k$ is the rate constant of the reaction $CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3$, and $k_r$ is the recombination constant of methyl radicals. Thus, formula (5) allows the rate constant $k$ to be calculated from measurements of $R_{CH_4}$ and $R_{C_2H_6}$ if the constant $k_r$ is known.

At this stage, we must make the following observation. The constant $k_r$ is often assumed to be independent both of temperature and of pressure. Thus, for example, Trotman-Dickenson and Steacie adopt a value of $7 \times 10^{13}$ cm$^3$ mole$^{-1}$ s$^{-1}$ for the constant $k_r$ in their paper[32] on the reactions of the methyl radical with acetone and with hydrocarbons; Brinton[33] takes $k_r$ to be $4.5 \times 10^{13}$ cm$^3$ mole$^{-1}$ s$^{-1}$ in his work on the reactions of the $CH_3$ radical with various imines; Gray and Thynne[34] studied reactions of the type $CH_3 + CH_3NH_2 = CH_4 + CH_3NH$ or $CH_4 + CH_2NH_2$, and adopted the value $k_r = 2.2 \times 10^{13}$ cm$^3$ mole$^{-1}$ s$^{-1}$; and so on. All these workers calculate the value of $k_r$ from data obtained in Kistiakowsky's laboratory[35,36], or from the same data, corrected by refinements of the theory of the sector method[37]. Yet it was shown[38] in Kistiakowsky's own laboratory that at low pressures of acetone vapour the constant $k_r$ varies with pressure (in the temperature range 180–240°C) approximately as

$$k_r = \frac{k_{r,2}}{1 + \frac{3.6}{p}}, \qquad (6)$$

where $p$ is the pressure of acetone vapour in mmHg. Lossing and his coworkers have demonstrated[39,40] a dependence of $k_r$ upon helium pressure. By comparing the results of these workers with those already mentioned we conclude that helium is approximately one-fifteenth as effective as acetone in the role of the species M in the reaction

$$CH_3 + CH_3 + M = C_2H_6 + M.$$

Lossing and his coworkers also reported a temperature dependence of the third-order recombination constant (in the range 434–1087°K). When interpreted by means of an Arrhenius expression, these results lead to an activation energy of $E = -1.5 \pm 0.5$ kcal mole$^{-1}$; when substituted in a power law ($\propto T^{-n}$) they give $n = 1.0$–$1.5$. On analysing all available data on the recombination constant of methyl radicals, we conclude that the second-order (high-pressure) recombination constant should be expressed by the formula

$$k_{r,2} = 1.1 \times 10^{12} \sqrt{T} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},$$

and the third-order (low-pressure) recombination constant should be expressed by the formula

$$k_{r,3} = 4.3 \times 10^{19} e^{(1500 \pm 500)/RT} \text{ cm}^6 \text{ mole}^{-2} \text{ s}^{-1}$$

for $M = CH_3COCH_3$, and by

$$k_{r,3} = 2.9 \times 10^{18} e^{(1500 \pm 500)/RT} \text{ cm}^6 \text{ mole}^{-2} \text{ s}^{-1}$$

for M = He. The identical temperature dependence of the constant $k_{r,3}$ when $M = CH_3COCH_3$ and when M = He is based on the assumption[39,40] that it is mainly due to the increase in probability of dissociation of the complex $[CH_3 \cdot CH_3]^*$ with increase in temperature.

Thus, it is evident that rate constants calculated in terms of the recombination rate constant of methyl radicals on the assumption that the latter is independent of both temperature and pressure stand in need of revision.

We shall discuss next the method of measuring rate constants in which active species are produced in an electrical discharge and are led by the gas stream into the reaction vessel, where they interact with various substances. This method was used in Steacie's early work, and also by Avramenko, Kaufman, Schiff, and others. Its most extensive application is found in the work of Avramenko[41].

In the simplest case, when the discharge produces active particles of a single kind (atoms of A), which react with the added molecules of M by a single path to give the reaction product P, the kinetic equations can be written

$$-\frac{d[A]}{dt} = (k_0 + k[M])\ [A],$$

$$\frac{d[P]}{dt} = k[M]\ [A],$$

where $k$ is the rate constant of the reaction $A + M \rightarrow P$ and $k_0$ the rate constant for the disappearance of A atoms. If the atoms are removed by a first-order process (e.g. by adsorption on the walls), $k_0$ is independent of the concentration of A atoms. In this case, assuming negligible consumption of the substance M and replacing [M] by the initial concentration $[M]_0$, and making the further assumption that the gas stream emerging from the reaction vessel contains practically no A atoms, the above kinetic equations can be solved to give

$$\frac{1}{[P]} = \frac{1}{[A]_0} + \frac{k_0}{k[M]_0[A]_0}. \qquad (7)$$

If the reciprocal of the measured concentration of reaction product is plotted (vertically) against the reciprocal of the initial concentration of M for various values of $[M]_0$ (with $[M]_0 - [M] \ll [M]_0$, and $[A]_0$ constant), Eqn. (7) leads to a linear plot whose parameters yield the ratio of the constants $k/k_0$.

Avramenko obtained the constant $k_0$ from measurements of the relative concentrations of A at different points in the reaction vessel. This, in conjunction with the ratio of $k/k_0$ obtained from the linear plot of Eqn. (7), allows the constant $k$ to be calculated.

However, this simple method demands great care to ensure that the underlying assumptions are satisfied. Thus, when the rate constant of a homogeneous process is being measured, it must be quite certain that A and M do not interact on the walls of the reaction vessel. Nevertheless, the relatively low pressures normally used in the experiments by the electrical discharge method greatly increase the probability of heterogeneous reaction. Furthermore, we must know that the constant $k_0$ is unaffected by the presence or absence of the substance M. Since at low pressures and low concentrations the active particles are usually lost at the walls, on which they become adsorbed, there is likely to be an effect of impurities on the adsorption properties of the walls. It is also necessary to check that the value of $[A]_0$ remains constant at different values of $[M]_0$. Further complications are introduced by the possibility of reactions between A and M by two or more paths, when formula (7) is replaced by

$$\frac{1}{\Sigma[P_i]} = \frac{1}{[A]_0} + \frac{k_0}{\Sigma k_i [M]_0[A]_0}, \qquad (7')$$

or, if the yield of only one of the products ($P_1$) is monitored, by the formula

$$\frac{1}{[P_1]} = \frac{\Sigma k_i}{k_1}\frac{1}{[A]_0} + \frac{k_0}{k_1[M]_0[A]_0}. \qquad (7'')$$

It is easy to see that formula (7′) allows only the sum of the rate constants $\Sigma k_i$ for the interaction of A and M to be determined. From formula (7″), on the other hand, we can obtain the rate constant of a single process $k_1$ if the initial concentration of A particles is measured independently.

We have assumed that the reaction products whose concentration is measured during the experiment are obtained by direct interaction between A and M. However, the primary products of an interaction of this type are often certain intermediates, which undergo further transformation to give the products whose yield is taken as a measure of the rate of interaction of A and M by a particular path. Thus, for example, when we measure the rate constant of the reaction $O + H_2 = OH + H$ from the yield of water, we must be absolutely certain that the rate of this reaction and the rate of formation of water are either identical or interrelated in a specific (and known) way.

It follows from what has been said that the rate constants of elementary chemical reactions measured by the electrical discharge method can be considered reliable only if all possible factors affecting the course of the reaction have been carefully weighed and evaluated.

We will now turn to the photochemical method of producing atoms and free radicals, whose rates of interaction with various substances it is desired to measure. This method has been used extensively by Steacie, Noyes, Cvetanović, Nalbandyan, and others. One of its advantages over the electrical discharge method is the fact that chemical reactions can be studied at relatively high pressures, when heterogeneous processes may be ignored.

However, the photochemical method also presents one very important disadvantage, which compels us to regard with the greatest caution the rate constants measured by this method. This drawback arises from the possibility of producing "hot particles", whose reactivity is higher than that of similar particles having an equilibrium (or close to equilibrium) energy distribution.

The possibility of obtaining hot particles in photochemical reactions, and their role in the reaction, were pointed out[42] as early as 1934 (although the concept of "hot particles" came later). In that investigation, the proportion of hydrogen iodide which was oxidised was measured by irradiating a mixture of $HI + O_2$ in Uviol ($\lambda > 2800$ Å) and quartz ($\lambda > 2000$ Å) vessels near room temperature. Since in the first case the maximum energy of the H atoms produced by the primary process $HI + h\nu = H + I^*$ did not exceed 10 kcal mole$^{-1}$, whilst in the second case it reached 20 kcal mole$^{-1}$ ($\lambda = 2537$ Å) or more, the approximate doubling of the amount of HI oxidised, observed when the Uviol vessel was replaced by a quartz vessel, was ascribed to the high reactivity of the intermediate $HO_2$ radical, formed by the reaction between a fast ("hot") H atom and an $O_2$ molecule. An alternative explanation was also put forward: in the presence of fast H atoms, a different intermediate process becomes possible, namely $H + O_2 = OH + O - 16.7$ kcal mole$^{-1}$, and this can lead to an increase in the fraction of HI which is oxidised.

The formation of hot H atoms in the photolysis of HI has recently been confirmed by Dzantiev et al.[43], who studied the photochemical reaction in mixtures of HI and ethylene at temperatures between 0° and 250°C. They showed that the main product of this reaction is ethane, and that its yield is independent of temperature over the experimental temperature range (curve *a*, Fig. 1), is practically unaffected by dilution with argon (curve *a*, Fig. 2), and decreases sharply when the mixture is diluted with helium (curve *b*, Fig. 2). The mixture diluted with helium showed a variation in yield of ethane of the Arrhenius type (curve *b*, Fig. 1), corresponding to an effective activation energy of 3.5 kcal mole$^{-1}$.

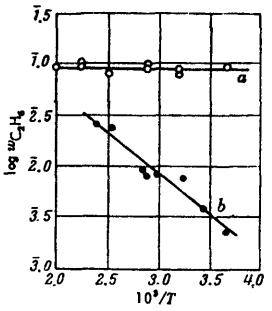



Fig. 1. Variation of the rate of formation of ethane (cm$^3$ min$^{-1}$) with temperature: *a*) $HI : C_2H_4 = 9 : 1$; *b*) $HI : C_2H_4 : He = 9 : 1 : 40$.

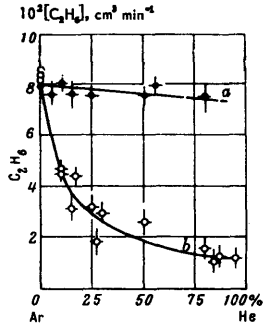



Fig. 2. Variation of the yield of ethane on dilution with: *a*) argon; *b*) helium.

These results were interpreted by postulating that the hot H atoms, which are mainly consumed by the reaction $H + HI = H_2 + I$, can react also with ethylene to some extent, forming "hot" $C_2H_5^*$ radicals which then react with HI according to the scheme $C_2H_5^* + HI = C_2H_6 + I$. Dilution with helium brings about thermal equilibration of the hot H atoms, as evidenced by the lower yield of $C_2H_6$ and by the appearance of a temperature dependence of the reaction rate.

Whereas in this work the hot $C_2H_5$ radicals are formed through the agency of the primary hot H atoms, many instances are known of the formation of hot radicals in the primary photochemical act. We shall mention only one example[44], which showed that the photolysis of azomethane $CH_3NNCH_3$ produces a certain proportion of hot $CH_3^*$ radicals. Until they have reach thermal equilibrium, these radicals can easily abstract H atoms from hydrocarbon molecules at room temperature. As in the work on the oxidation of hydrogen iodide, the activity of the $CH_3$ radicals was found to decrease with increase in wavelength (since the relative yield of methane decreases).

The problem of hot particles, and in particular of the particles formed during photolysis, cannot as yet be considered fully solved. However, in view of the above and other similar observations, it is evident that great caution must be exercised in the quantitative interpretation of kinetic results obtained under conditions admitting the formation of hot particles and their participation in the reaction.

The conclusion to be drawn from this discussion of the methods for measuring the rate constants of chemical processes is that each method has some unsatisfactory features, and that a critical approach is imperative in dealing with quantitative data based on these methods. The lack of a duly critical attitude, particularly on the part of the authors themselves (who do not always attach due weight to the errors in their measurements), is often responsible for the large discrepancies found between the quantitative results obtained by different authors using different or even the same methods.

The results given above (Table 1) for the rate constant of the dissociation of oxygen serve to illustrate the large errors involved in measurements of this type. Further simple examples are given below.

Table 2 lists the rate constants for the reaction $H + O_2 + H_2 = HO_2 + H_2$ reported by various workers. It can be seen that the extreme values differ by a factor of $10^4$.

The values of the constant $k_r$ obtained by different workers from measurements of the second combustion limit of hydrogen in the neighbourhood of 800°K do not differ by more than a factor of 2, averaging[48,53] about $10^{16}$ cm$^6$ mole$^{-2}$ s$^{-1}$. Since the temperature dependence of the recombination constant is usually expressed by a formula of the type

$$k_r = aT^{-n}, \qquad (8)$$

where $1 \leqslant n \leqslant 2$, extrapolation to 300°K gives $k_r = 2.6 \times 10^{16}$ for $n = 1$ and $k_r = 7.0 \times 10^{16}$ for $n = 2$. Comparing these values with those set out in Table 2 we conclude that the only admissible value is[48] $4 \times 10^{16}$. Of all the data given in Table 2, this can be considered the most reliable.

Table 3 gives data for the reaction $H + CH_4 = H_2 + CH_3$. With one exception, the activation energy and the preexponential term increase with temperature. We may conclude that the large scatter of the rate formulae obtained by different authors is due essentially to a large error in the measurement of the temperature variation of the constant $k$. The correctness of this conclusion is confirmed by the almost identical values given by three of the five formulae at a constant temperature (800°K). We may therefore adopt as the most reliable formula for the constant

$$k = 10^{13.17} \exp(-11\,200/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1},$$

obtained as the geometric mean of the three formulae.

TABLE 2. Rate constant of the reaction $H + O_2 + H_2 = HO_2 + H_2$ at room temperature.

| $k_r$, cm$^6$ mole$^{-2}$ s$^{-1}$ | Method | Ref. |
|---|---|---|
| $6.9 \times 10^{15}$ | electrical discharge; concn. of H determined from ortho–para conversion | 45 |
| $3.3 \times 10^{14}$ | photochemical oxidation of HI | 46 |
| $4.3 \times 10^{14}$ | electrical discharge; rate of formation of $HO_2$ determined from yield of $H_2O_2$ | 47 |
| $4.0 \times 10^{16}$ | electrical discharge; concn. of H determined from HNO glow | 48 |
| $1.8 \times 10^{17}$ | Hg photosensitisation of $H_2 + O_2$ reaction | 49 |
| $2.9 \times 10^{17}$ | electrical discharge; products estimated mass-spectroscopically | 50, 51 |
| $6.1 \times 10^{17}$ | Hg photosensitisation of $H_2 + O_2$ reaction | 52 |

TABLE 3. Rate constant of the reaction $H + CH_4 = H_2 + CH_3$.

| $k$, cm$^3$ mole$^{-1}$ s$^{-1}$ | $T$, °K | $k$(800°K) | Ref. |
|---|---|---|---|
| $10^{10.0} \exp(-4500/RT)$ | 372–436 | $10^{8.77}$ | 54 |
| $10^{12.5} \exp(-9000/RT)$ | 403–503 | $10^{10.03}$ | 55 |
| $10^{13.925} \exp(-14\,100/RT)$ | 773–873 | $10^{10.06}$ | 22 |
| $10^{13.08 \pm 0.35} \exp(-10\,600 \pm 1000/RT)$ | 843–933 | $10^{10.18}$ | 56,57 |
| $10^{14.3} \exp(-11\,500 \pm 1500/RT)$ | 1100–1900 | $10^{11.15}$ | 58 |

The formulae obtained by different authors for the reaction $OH + HCHO = H_2O + HCO$ show even greater scatter, as can be seen in Table 4. Measurements obtained in Refs. 59–61 are described accurate to a factor of 3 by the formula

$$k = 10^{12} \exp(-6300/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$$

(see Fig. 3).

The formulae obtained by different authors for the reaction $OH + H_2 = H_2O + H$ are presented in Table 5. We see that there is close agreement between the first three formulae, obtained by different methods, whereas in the last three formulae the activation energy differs considerably. This is due to the difference between the measured value[65] of the rate constant at 310°K — $(4.3 \pm 1.0) \times 10^9$ cm$^3$ × × mole$^{-1}$ s$^{-1}$ — and the values extrapolated to that temperature by means of the first three formulae of Table 5, amounting to 2–3 orders of magnitude.

It is interesting to note that a value of 5 kcal mole$^{-1}$ has been obtained[68] for the difference $E_{OH+H_2} - E_{OH+CO}$. Hence, with $E_{OH+H_2} = 10$ kcal mole$^{-1}$ we find that $E_{OH+CO} = 5$ kcal mole$^{-1}$, a value consistent with measurements by various authors (ranging from 3.4 to 10.3 kcal mole$^{-1}$), whereas if $E_{OH+H_2} = 5.9$ kcal mole$^{-1}$ we obtain ~1 kcal × × mole$^{-1}$ for the activation energy of the process $OH + CO = CO_2 + H$. Further experimental work is needed to solve the problem of the true activation energies of the reactions $OH + H_2 = H_2O + H$ and $OH + CO = CO_2 + H$.

TABLE 4. Rate constant of the reaction $OH + CH_2O = H_2O + HCO$.

| $k$, cm$^3$ mole$^{-1}$ s$^{-1}$ | $T$, °K | Ref. |
|---|---|---|
| $1.2 \cdot 10^{13} \exp(-900/RT)$ | 346–489 | 59 |
| $5.1 \cdot 10^{14} \exp(-3650/RT)$ | 798–923 | 60 |
| $5 \cdot 10^{13} \exp(-13\,000/RT)$ | 1250–1400 | 61 |

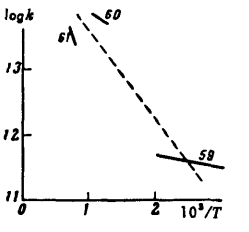



Fig. 3. Rate constant of the reaction $OH + CH_2O = H_2O + HCO$ according to different workers.

TABLE 5. Rate constant of the reaction OH + + $H_2$ = $H_2O$ + H.

| $k$, $cm^3$ $mole^{-1}$ $s^{-1}$ | $T$, °K | Ref. |
|---|---|---|
| $2.3 \cdot 10^{14} \exp(-1100/RT)$ | 900—1400 | 62 |
| $1.4 \cdot 10^{14} \exp(-10\,400/RT)$ | 380—490 | 63 |
| $2.5 \cdot 10^{14} \exp(-10\,000/RT)$ | 1660—1850 | 64 |
| $10^{13.9 \pm 0.7} \exp(-5900 \pm 1000/RT)$ | 310 and 1500 | 65 |
| $10^{13.48} \exp(-5500 \pm 600/RT)$ | 310 and 915 | 66 |
| $10^{13.6} \exp(-5700/RT)$ | 1500—2600 | 67 |

From these examples, to which many more could be added, it is evident that the present situation regarding the problem of the rate constants of elementary chemical reactions is unsatisfactory. This introduces great difficulties in the practical application of kinetic data.

In view of the difficulties in every experimental method of measuring the rate constants of chemical reactions, various theoretical or semi-theoretical indirect methods are often used with success. The statistical method for calculating second-order rate constants for the thermal dissociation of molecules must be mentioned first (see Ref. 13, p. 25). The method relies on the formula

$$k_d = Z g_s(E_0) \exp(-E_0/RT)/F(s-1), \quad (9)$$

where $Z$ is the collision factor of the kinetic theory of gases ($Z \simeq 10^{14}$ $cm^3$ $mole^{-1}$ $s^{-1}$),

$$g_s(E_0) = \left(\frac{E_0 + E_z}{h\bar{\omega}}\right)^{s-1} \frac{1}{(s-1)!},$$

$E_0$ is the dissociation energy, $E_z = \frac{1}{2}\Sigma h\omega_i$ is the zero-point vibrational energy, $\bar{\omega}$ is the mean vibration frequency, defined as

$$\bar{\omega} = \left(\prod_i \omega_i\right)^{1/s},$$

$s$ is the total number of vibrational degrees of freedom, and $F(s-1)$ is the vibrational partition function. The $k_d$ constants calculated from formula (9) agree with experiment to within an order of magnitude [69].

We have shown above (p. 894), using the thermal decomposition of methane as an example, that the order of a reaction can be ascertained from approximate calculations of the rate constant. The recombination constant of H + $O_2$ provides another example of this. Direct measurements of this constant at room temperature gave widely divergent values (see Table 2): we can calculate it through the dissociation constant and the equilibrium constant $K$ from the formula

$$k_r = \frac{k_d}{K}. \quad (2')$$

If we calculate the constant $k_d$ for 800°K and 300°K from formula (9) and adopt tabulated values [70] for the $H + O_2 \rightleftharpoons HO_2$ equilibrium constant at these temperatures, we obtain $k_r = 9 \times 10^{15}$ and $1.5 \times 10^{16}$ $cm^6$ $mole^{-2}$ $s^{-1}$ for the respective temperatures. Since it is assumed, in evaluating the number of vibrational degrees of freedom $s$, that the particle M is an atom, we can obtain values of the constant $k_r$ for M = $H_2$ by multiplying the above values by 5, it having been shown [71] that the relative efficiencies of $H_2$ and Ar in the reaction H + $O_2$ + M = $HO_2$ + M at 800°K are in the ratio 5 : 1. This gives $k_r = 4.5 \times 10^{16}$ (800°K) and $k_r = 7.5 \times 10^{16}$ (300°K). These values are only slightly higher than the experimental value of $k_r$ reported above (p. 898) for 800°K and the value measured [48] at 300°K. We should note that the two experimental values of $k_r$ differ by a factor of 4. Since the ratio of the temperatures (800° and 300°K) is 2.7, we may tentatively conclude that $k_r \propto 1/T^{3/2}$.

We shall discuss one more example. Szwarc [72] measured the rate constant for the unimolecular decomposition of hydrazine, and interpreted it as a first-order constant:

$$k_d = 4 \times 10^{12} \exp(-60\,000/RT)\ s^{-1}.$$

However, Gilbert [73] has since shown that the decomposition of $N_2H_4$ under Szwarc's experimental conditions should obey a second-order law, and he has reinterpreted Szwarc's data to give the following formula for the second-order dissociation constant

$$k_d \simeq 10^{19} \exp(-60\,000/RT)\ cm^3\ mole^{-1}\ s^{-1}.$$

Since this formula agrees exactly with that calculated by Nikitin and Sokolov [69], Gilbert's views appear to be correct.

It is important to note that the theoretical formula (9) for the constant $k_d$ implies that the temperature dependence of the preexponential factor in $k_d$ is different at low and at high temperatures respectively. In the low-temperature region ($T < h\omega/k$, where $\omega$ is the lowest vibrational frequency of the dissociating molecule) the vibrational partition function $F(s)$ is practically unity, and the temperature dependence of the preexponential factor $A$ becomes indistinguishable from that of the collision factor $Z$ of the kinetic theory of gases: i.e. $A \propto \sqrt{T}$. In the limit at fairly high temperatures, however, when $F(s)$ is expressed as $\prod_i (kT/h\omega_i)$, the temperature dependence of the preexponential factor takes the form

$$A \sim T^{1.5s-s}. \quad (10)$$

It follows that it is impossible, in principle, to express the dissociation rate constant $k_d$ by a formula of the type

$$k_d = A \exp(-E_0/RT), \quad (11)$$

in which the preexponential factor $A$ is either constant or of the form $A = A_0 T^{-n}$ ($n$ remaining constant over a wide range of temperatures). Another important test of the correctness of the interpretation of experimental kinetic results could be to calculate the preexponential factor in the expression for the bimolecular rate constant from the activated complex theory. Unfortunately, however, this method still lacks adequate theoretical development, and has been used in relatively few instances (see, for example, Refs. 53 and 74–78).

Application of the Polanyi–Semenov rule can also be of some value when testing the results of direct measurements. With a few exceptions, the linear relation

$$E = a - bQ \quad (12)$$

between the activation energy $E$ and the heat of reaction $Q$ is approximately obeyed in series of chemical reactions of similar type. Fig. 4 shows the variation of $E$ with $Q$ for the reactions H + RH = $H_2$ + R (curve $a$) and O + RH = OH + + R (curve $b$), where R = $CH_3$, $NH_2$, OH, and F. It is evident that the Polanyi–Semenov rule can be applied satisfactorily to both types of reaction within the limits of experimental error‡.

‡ In this plot the average of all measured values of $E$ has been taken, and the mean deviation calculated accordingly. The error in the values of $Q$ is determined by the inaccuracy of the corresponding thermochemical data.

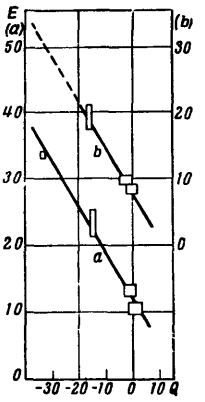



Fig. 4. Test of the Polanyi-Semenov rule for the reactions:
*a*) H + RH = $H_2$ + R;
*b*) O + RH = OH + R (R = $CH_3$, $NH_2$, OH, F).

The unsatisfactory state of our understanding of kinetic constants, which has been stressed in this review, exists also, to a greater or lesser degree, in other fields of science. In view of the vast and annually growing store of experimentally determined constants, presented with an almost complete lack of critical assessment, we are faced with an urgent need to rationalise the whole problem.

At the moment, the necessary measures are being taken (or planned) in many countries. Committees and organisations responsible for the compilation of tested and critically assessed quantitative data are being set up. In the Soviet Union, this is the responsibility of the State Committee for Standards, Measures, and Measuring Apparatus, which has begun to plan and develop efforts to produce and keep up to date exhaustive compilations of the best, most reliable, critically selected data in various fields.

As far as is known, in the USA the selection of reliable data has been undertaken by the National Bureau of Standards. The programme known as the National Standard Reference Data System [NSRDS], described in a paper by E. L. Brady of the Bureau of Standards, may be mentioned in this context.

It is obvious, however, that the critical evaluation and selection of the most reliable data should be organised on an international basis. To this end, the International Council of Scientific Unions (ICSU), acting on a report by the foreign secretary of the National Academy of Sciences of the USA, Dr. Harrison Brown, established in June 1965 a special group including representatives from many countries, charged with studying the problem of international cooperation in the preparation of international critical tables. This group will report its findings to the next session of the Executive Committee of the ICSU.


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# METAL SELENOCYANATES AND THEIR PROPERTIES

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## I. INTRODUCTION

Selenocyanates find practical use as sensitisers in photographic emulsions and for the preparation of organic derivatives of selenium. The use of selenocyanates is very promising for the production of metal selenides, which are of great value in electronics. It may also be assumed that the selenocyanates will find use in analytical chemistry, especially in various titrations in non-aqueous solutions and also in the separation of selenium and tellurium with the object of obtaining these elements in a high state of purity.

Investigation of the selenocyanates is also of great theoretical significance in connection with the more profound elucidation of the chemical individuality of selenium. Nevertheless, there are no reviews on the selenocyanates. Only the dissociation constants of silver, mercury, and cadmium selenocyanates are given in a handbook[1]. Even the book by Williams[2] on cyanogen and its compounds with various elements gives only general information about a few metal selenocyanates.

The present paper is the first attempt to systematise published information on the selenocyanates.

## II. SELENOCYANOGEN AND ITS PROPERTIES

Selenocyanogen has been prepared by a method similar to that used for the preparation of thiocyanogen[3], an ethereal solution of iodine being allowed to act on silver selenocyanate[4]:

$$2AgSeCN + I_2 = 2AgI + (SeCN)_2.$$

Selenocyanogen is a yellow powder soluble in light petroleum, chloroform, and carbon tetrachloride. It decomposes when dissolved in water. In the solid state it keeps well under a vacuum. Its structure may be represented as two isomers N≡C–Se–Se–C≡N and Se=C=N–N=C=Se.

By analogy with thiocyanogen, selenocyanogen can combine with metals and also form compounds with some non-metals. For example, a compound with selenium is known; this consists of an unbranched chain with three atoms of bivalent selenium in the middle and CN groups at the ends. The distances between the atoms in $Se(SeCN)_2$ have been found[15] to be Se–Se (2.33 Å), Se–C (1.83 Å), and C–N (1.05 Å). The Se–Se–Se valence angle is 101°.

Caesium trisselenocyanate $Cs(SeCN)_3$, which may be regarded as a polyhalide type of compound, has been obtained by the action of an ethereal solution of selenocyanogen on an alcoholic solution of caesium selenocyanate. Caesium trisselenocyanate consists of reddish brown monoclinic prisms stable in air; it is soluble in alcohol but is decomposed by water[6]. It has been shown that the compounds $KNCSeI_2$, $K(NCSe)_2I$, and $K(NCSe)_3$ are formed in the potentiometric titration of KNCSe with iodine solution.

Selenocyanic acid HNCSe was obtained by Crookes by the action of hydrogen sulphide on $Pb(SeCN)_2$ suspended in water[7]:

$$Pb(SeCN)_2 + H_2S = PbS + 2HNCSe.$$

HNCSe is known only in solution. It dissolves iron and zinc with liberation of hydrogen and displaces carbon dioxide from carbonates.

## III. ANALYTICAL CHEMISTRY OF THE $SeCN^-$ ION

The quantitative analysis of selenocyanate solutions may be carried out by the usual argentometric titration with diphenylcarbazone[8], and also by potentiometric titration of the appropriate solutions with silver nitrate[19] or mercury perchlorate[10].

In the analysis of small quantities of selenocyanates, good results may be obtained by argentometric determination of the selenium[11]. The selenocyanate ion is converted to selenite by the action of nitric acid; an excess of silver nitrate and crystalline hydrazinium sulphate are added to the acid solution. Part of the silver is converted into silver selenide. The excess of silver nitrate is titrated against ammonium thiocyanate.

The concentration of selenocyanates soluble, or even slightly soluble in water, may be conveniently determined as selenium. The selenocyanates are decomposed with hydrochloric acid:

$$KNCSe + HCl = KCl + HCN + Se.$$

The selenium that separates is filtered off, dried at 100–110°, and weighed. This method gives good results in the analysis of salts in which the selenocyanate ion is not strongly bound. Apart from selenocyanates of the alkali and alkaline-earth metals, the salts of cadmium, cobalt, nickel, and even lead may be analysed by the method. The selenocyanates of silver, mercury, copper, and platinum are not completely decomposed by hydrochloric acid, part of the selenium appearing to be precipitated as selenide.

In recent years highly sensitive methods for the determination of selenium with the use of organic reagents have been developed[12–14]. These methods have been reviewed by Ryabchikov and Nazarenko[15]. The reagents may also be used in the analysis of selenocyanates.

## IV. SIMPLE SELENOCYANATES AND THEIR PROPERTIES

The most studied compound of this series is potassium selenocyanate, first obtained by the fusion of selenium with potassium hexacyanoferrate(II).[16] It may be assumed that this reaction proceeds in the same way as the reaction of sulphur with potassium hexacyanoferrate(II):

$$6Se + 2K_4Fe(CN)_6 = 6KNCSe + FeK_2Fe(CN)_6.$$

White crystals of KNCSe are obtained when the melt is extracted. Since the selenocyanate ion is easily decomposed in the presence of water, absolute alcohol has replaced water in the extraction[7].

Later, methods for the preparation of KNCSe were proposed in which selenium was dissolved in a concentrated aqueous solution of KCN[4,17] or fused with potassium cyanide[18], the melt being subsequently extracted with water[19].

A very pure product was also obtained by boiling a suspension of selenium and potassium cyanide in absolute alcohol[20]. However, because of the interaction of the selenocyanate ion with alcohols and the formation of volatile evil-smelling alkyl selenides, this method is also inconvenient. A very unpleasant odour is also noticed in the extraction with alcohol of the product obtained by sintering selenium with potassium cyanide or potassium hexacyanoferrate(II). It is therefore more convenient to use acetone in the extraction[21]. A perfectly pure preparation of KNCSe was obtained by the reaction of selenium with potassium cyanide in liquid ammonia[22].

There are reports in the literature on the preparation of sodium selenocyanate by boiling red selenium with sodium cyanide in absolute alcohol[20]. Sodium selenocyanate may be obtained in good yield also by fusing selenium with sodium cyanide[21]. The density of sodium selenocyanate is 2.490 and that of potassium selenocyanate 2.347 g $cm^{-3}$.[20]

Caesium selenocyanate is also mentioned in the literature[6], but nothing is said about the properties of this salt. Ammonium selenocyanate was first obtained by Crookes by neutralising HNCSe with ammonia[7]. Later this salt was prepared by double decomposition between $(NH_4)_2SO_4$ and KNCSe in absolute alcohol[23], and its very poor stability noted.

Recently a communication was published on hydrazinium selenocyanate[24]. The tendency of this salt to isomerise was noted:

$$N_2H_5NCSe \rightleftharpoons H_2N–CSe–NH–NH_2.$$

Equilibrium in this reaction is rapidly reached in the presence of acetone and corresponds to 35% conversion of hydrazinium selenocyanate into the semicarbazide.

The selenocyanates of the alkaline-earth metals were first described by Crookes[7]. Since the salts he obtained were only analysed qualitatively, some caution must be used in dealing with his results. This refers particularly to the simple formulae for the salts put forward by Crookes. All the salts of the alkaline-earth metals and magnesium were obtained by the action of selenocyanic acid on the corresponding carbonates, with subsequent evaporation of the solutions over sulphuric acid in a vacuum desiccator.

As far as the properties of this group of compounds are concerned, there is more or less complete information in the literature on potassium selenocyanate. This is a colourless compound crystallising in the form of white acicular crystals, which deliquesce in air and are readily decomposed by acid vapours. When heated in a sealed vessel, potassium selenocyanate melts without decomposition; when heated in air, it decomposes at 100°. It dissolves readily in water, producing an appreciable reduction in temperature. The aqueous solution is alkaline; when the pH of the solution is reduced to 5, the salt begins to decompose.

Potassium selenocyanate behaves differently in the presence of foreign ions. As Lodzinska has pointed out, introduction of the ions $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, and $Ba^{2+}$ has no effect on decomposition pH of the salt[25]: in the presence of these cations, potassium selenocyanate begins to decompose, when hydrochloric acid is added, at pH 5.5–4.9. In the presence of the cations $Cd^{2+}$, $Hg^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Fe^{3+}$, and $Cr^{3+}$, however, decomposition begins somewhat earlier, at pH > 6. The cations $Ni^+$, $Co^{2+}$, and $Cu^{2+}$ decompose the selenocyanate ion still earlier, at pH > 7. According to Lodzinska, even at concentrations of cobalt, nickel, or copper cations of $10^{-4}$ g-ion litre$^{-1}$ decomposition of $SeCN^-$ begins at a hydrogen-ion concentration of $10^{-8}$ g-ion litre$^{-1}$.

The electrical conductivity of aqueous solutions of potassium selenocyanate has also been studied; according to Birckenbach, the equivalent conductivity at infinite dilution is 119.5 at 18° and 138.2 at 25°.[26] The decomposition voltage of KNCSe was found to be 1.10 V.[6,27].

From a study of decomposition voltages and also calculation of the electron affinity of atoms and groups of atoms, Birckenbach concluded that the selenocyanate ion has properties closely similar to those of the halide ions. According to this worker, the selenocyanate ion should be placed before the iodide ion in the sequence of halide and pseudohalide ions:

$SeCN^-$, $I^-$, $SCN^-$, $CN^-$, $Br^-$, $N_3^-$, $Cl^-$, $OCN^-$, $CNO^-$, $F^-$.

## V. SELENOCYANATES OF HEAVY METALS†

Selenocyanates of heavy metals that were sparingly soluble in water were obtained before other selenocyanates. They were prepared by the action of a solution of potassium selenocyanate on the corresponding salt of the metal. Thus, Crookes obtained silver selenocyanate as a slightly soluble white compound[7]. Later silver selenocyanate was isolated by other workers[4,20], who found its density to be 4.602[20] and its solubility product to be $4.0 \times 10^{-16}$ at 18–20°.[27] Crookes noted that when potassium selenocyanate was added to salts of bivalent copper a brown precipitate was formed. He assumed that this was copper selenocyanate. However, the compound was not obtained in the pure state. Attempts to obtain the selenocyanate of univalent copper was also unsuccessful for a long time[28].

We have prepared the salt CuSeCN from acetone solution[29]: a solution of KNCSe is saturated with copper(I) chloride, and CuSeCN is precipitated by the introduction of a small quantity of water. The salt obtained in this way is a white powder, sparingly soluble in water, alcohol, and acetone. The solubility product of CuSeCN, measured potentiometrically at 20°, is $1.82 \times 10^{-10}$.

Crookes mentions the preparation of $Zn(SeCN)_2$ by dissolving zinc or its oxide in selenocyanic acid, but he gives no analytical results on the salt and says nothing about its properties[7].

Cadmium selenocyanate is obtained much more easily than the zinc salt from aqueous solution because of its lower solubility[30]. $Cd(SeCN)_2$ is obtained by mixing solutions of cadmium nitrate and potassium selenocyanate, rapidly filtering the solution, and drying the product[30]. This salt is also obtained from non-aqueous solutions. The solubility product of $Cd(SeCN)_2$ at 20° is $1.93 \times 10^{-5}$.[30] The salt is sparingly soluble not only in water but also in alcohol and acetone; it dissolves readily in the presence of an excess of selenocyanate or iodide ions.

Mercury selenocyanate, which was prepared by Cameron and Davy by the action of KNCSe on mercury(II) acetate solution, is very similar to the cadmium salt[23]. It was also obtained by Rosenheim and Pritze, using $HgCl_2$ and KNCSe as starting materials[31]. $Hg(SeCN)_2$ separates from water as a white mass; it is sparingly soluble in water, and readily soluble in the presence of selenocyanates, iodides, and cyanides of the alkali metals.

With its poor solubility in water, mercury(II) selenocyanate is very similar to the iodide and the thiocyanate. Cadmium selenocyanate, however, differs markedly from the iodide and the thiocyanate. Being sparingly soluble in water, in contrast to the latter, cadmium selenocyanate closely resembles the mercury salts. In solubility and thermal stability, $Hg(SeCN)_2$ is more reminiscent of the iodide than of the other halides. There is a still greater similarity in this respect between the salts of univalent mercury. Cameron and Davy also obtained mercury(I) selenocyanate by the action of potassium selenocyanate on mercury(I) nitrate[23]. The salt $Hg_2(SeCN)_2$, like $HgI_2$, has an olive green colour.

Of the elements of Group III of the Periodic System, only thallium selenocyanate is known; this was obtained by the action of potassium selenocyanate on an aqueous–alcoholic solution of thallium acetate[20], a yellow precipitate of TlSeCN, sparingly soluble in water, being formed. The specific gravity of TlSeCN is 5.462.[20]

Lead selenocyanate was obtained in the same way as the thallium salt[7,20,32]. Spacu prepared the salt Pb(OH)SeCN.[33] The compound $Pb(SeCN)_2$ is a finely crystalline pale yellow powder with a density of 4.694.[20,32] It turns red on exposure to sunlight. When heated, lead selenocyanate decomposes at a temperature somewhat above 100°, without reaching the melting point. At 20° a saturated aqueous solution of lead selenocyanate has a concentration of 0.00239 M.[32] It is practically insoluble in acetone and

† The term "heavy metal" is used by the Reviewers to include such transition metals as copper and zinc (Ed. of Translation).

alcohol. The solubility product of $Pb(SeCN)_2$ at 20° is $3.34 \times 10^{-7}$ (ionic strength of solution ~ 4.[32]

The problem of preparing selenocyanates of the transition metals — iron, cobalt, nickel, etc. — is considerably more complicated. Spacu showed that $Co(NCSe)_2$ exists in solution, but he dod not succeed in obtaining the compound in the solid state[34].

Crookes tried to prepare iron(II) selenocyanate by the action of HNCSe on FeO, but only free selenium was obtained[7]. Attempts to prepare iron selenocyanate by the action of aqueous solutions of potassium selenocyanate on an iron(II) salt solution were also unsuccessful.

## VI. COMPLEXES BASED ON METAL SELENOCYANATES

Because of the poor stability of the $SeCN^-$ ion, and because many cations become more stable when converted from hydrates to ammines, most work on the preparation of selenocyanato-complexes has been devoted to compounds containing ammonia or various organic amines in their structure.

Spacu and his coworkers studied compounds of this type. They succeeded in obtaining the following compounds with pyridine (Py)[34]: $MPy_4(NCSe)_2$ (with $Co^{2+}$, $Ni^{2+}$, $Mn^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Fe^{2+}$), $MPy_2(NCSe)_2$ (with $Cd^{2+}$ and $Zn^{2+}$), and $NiPy_6(NCSe)_2$. The salt $CoPy_4(NCSe)_2$ was converted into $CoPy_2(NCSe)_2$ when kept in a vacuum at 70°.

Besides pyridine, Spacu introduced hexamethylenetetramine (Hex) as a ligand and obtained the salt $MHex_2(H_2O)_4 \cdot (NCSe)_2$, where M = $Co^{2+}$, $Ni^{2+}$, $Mn^{2+}$, $Zn^{2+}$, or $Fe^{2+}$.[34] A large number of compounds were obtained with ethylenediamine[36-38]. The selenocyanates of nickel, cobalt, copper, cadmium, and manganese also form complexes with toluidine, benzidine, ammonia[33], and phenylhydrazine[39]. Quite recently the salt $Cu(NH_3)_4(NCSe)_2$ has been obtained from aqueous solution[40].

Other compounds containing amines are the complex salts $[(CH_3)_4N]_2[Co(NCSe)_4]$ and $[Et_4N]_2[Co(NCSe)_4]$, where $Et_4N$ is tetraethylammonium[41].

Spacu compared selenocyanates with the corresponding thiocyanates, and found little difference in their properties; salts containing amines with the SeCN group are somewhat less soluble than analogous salts with the SCN group.

Some molecular selenocyanates separate from liquid ammonia when selenium acts on metal cyanides[22]: magnesium, aluminium, and zinc selenocyanates have been obtained in this way. Zinc selenocyanate $Zn(SeCN)_2 \cdot 4NH_3$ melts with slight decomposition when heated in a vacuum to 100°. Magnesium selenocyanate $Mg(NCSe)_2 \cdot 4NH_3$ decomposes when heated to 135°. When heated in a vacuum to 70° $Al(NCSe)_3 \cdot 5NH_3$ loses 2–2.5 molecules of ammonia, but at 75° it decomposes completely.

By analogy with ammine complexes, it would appear that many selenocyanates, unobtainable under ordinary conditions, might be obtained from ketone and ether solutions. This applies in particular to salts of the transition elements. This hypothesis has been partially confirmed in the case of cobalt and nickel selenocyanates with dioxan, which will be discussed below.

## VII. COMPLEX FORMATION INVOLVING THE SELENOCYANATE ION AS LIGAND AND AS CENTRAL ION

Potentiometric study of the $Ag^+$–$SeCN^-$–$H_2O$ system has demonstrated the existence of $Ag(SeCN)_3^{2-}$ complexes with a dissociation constant of $1.3 \times 10^{-14}$.[28,42] With a higher concentration of KNCSe in aqueous solution, $Ag(SeCN)_4^{3-}$ is formed. Under conditions such that the solubility method in aqueous solution is applicable, it can be shown that AgSeCN is formed[42].

The salt $KAg_2(SeCN)_3$ has been obtained when aqueous solutions of potassium selenocyanate are saturated with silver selenocyanate[43]. This salt is stable in air and sparingly soluble in water. Colourless crystals of $KAg(SeCN)_2$ separate from aqueous solution as regular cubes, in addition to crystals of $K_3Ag(SeCN)_4$ and finely acicular colourless crystals of $K_2Ag(SeCN)_3$. The last salt is better prepared from alcoholic and acetone solutions[43]. It has also been shown by the solubility method in aqueous solution that the mixed complexes $Ag(SeCN)_2 \cdot SCN^{2-}$[44] and $AgI(SeCN)_2^{2-}$[45] are formed. The salts $K_2Ag(SeCN)(SCN)_2$, $KAg_2(SeCN)_2(SCN)$,[44] and $KAg_2(CNSe) \cdot I_2$[45] have been obtained crystalline; the complexes $AgI_3(SeCN)^{3-}$ and $Ag(SeCN)_3(SCN)^{3-}$ have been detected potentiometrically[45].

Both in the character of complex formation and in stability the selenocyanato-complexes are reminiscent of iodo- and thiocyanato-complexes[46,47]. They are, however, more stable than the thiocyanato-complexes. It is for this reason that silver forms comparatively readily mixed selenocyanatothiocyanato- and halogenoselenocyanato- - complexes[45].

It has also been found that selenocyanates, like halides and thiocyanates[48-51], form silver complexes of cationic type[52]. A study of the solubility of AgSeCN in aqueous solutions of $AgNO_3$ and $AgClO_4$ has shown that the complexes $Ag_2SeCN^+$, $Ag_3SeCN^{2+}$, and $Ag_4SeCN^{3+}$ are formed[52]. It is interesting to note that the solubility of AgSeCN at corresponding concentrations of $AgNO_3$ is very close to the solubility of silver iodide[51]. However, in contrast to the selenocyanate system, the iodide system has no complex with coordination number 4.[49-51]. Crystalline $[Ag_3SeCN] \cdot (NO_3)_2$ and $[Ag_2SeCN]ClO_4$ are obtained from aqueous solution. These salts are stable in air but are decomposed to AgSeCN by water[52].

It is also possible that some other metals form selenocyanato-complexes with a central anion. Thus, it may be assumed that similar complexes with mercury ($Hg_2SeCN^{3+}$) and even cadmium ($Cd_2SeCN^{3+}$) exist.

The formation of a cadmium complex $Cd(SeCN)_4^{2-}$ with a dissociation constant of $2.5 \times 10^{-4}$ has been demonstrated polarographically[28]. A potentiometric study of aqueous and aqueous–acetone solutions has revealed the existence not only of $Cd(SeCN)_4^{2-}$ but also of other complexes — $Cd(SeCN)_6^{4-}$, $Cd(SeCN)_5^{3-}$, $Cd(SeCN)_3^-$, $Cd(SeCN)_2$, and $Cd(SeCN)^+$ — the dissociation constants of which have been calculated[30].

As with the halides, mercury forms more stable selenocyanates than cadmium. Thus, the dissociation constant of $Hg(SeCN)_4^{2-}$ is $2.8 \times 10^{-30}$, and that of $Hg(SeCN)_3^-$ is $3.8 \times 10^{-27}$.[28]

The complexes $Hg(SeCN)Cl$, $Hg(SeCN)_2$, $Hg(SeCN)_3^-$, and $Hg(SeCN)_4^{2-}$ have been detected by the conductometric titration of an aqueous solution of $HgCl_2$ with KNCSe solution[53].

Some mercury selenocyanates have been obtained in the solid state[31]. The salt Hg(SeCN)Cl and also the salt $KHg(SeCN)_3$, which is sparingly soluble in cold water and alcohol, have been obtained from aqueous solution. The latter salt was previously obtained by Cameron and Davy[23]. Potassium tetrakisselenocyanatomercurate, readily soluble in water and alcohol, was obtained in the form of large amber-yellow plates. With the use of an aqueous solution of this salt the sparingly soluble compounds $MHg(SeCN)_4$, where M = Zn, Co, Pb, or Cu, have been isolated[31,53]. According to Swinarski and Lodzinska, the solubility of the $MHg(SeCN)_4$ salts in water, acetone, and aqueous alcohol decrease in the order Cd > Co > Zn.[54] The solubility product of $CuHg(SeCN)_4$ in aqueous solution is $1.59 \times \times 10^{-10}$.[55] The lattice parameters and the coefficient of thermal expansion of $CoHg(SeCN)_4$ crystals have been determined[56].

Formation of the sparingly soluble $M[Hg(SeCN)_3]_2$, where M = Zn, Pb, or Cu, has been demonstrated, and the double salt $4Co[Hg(SeCN)_3]_2.Co(CH_3COO)_2$ has also been prepared[53].

Complex mercury salts of mixed type $KHg(SeCN)(CN)_2$ and $KHg(SeCN)Hal_2$ were obtained by Cameron and Davy[23]; they were prepared by the action of mercury halides on an alcoholic solution of KNCSe.

The selenocyanate complexes of lead have been studied only recently. A potentiometric study of aqueous solutions has shown that $Pb(SeCN)_6^{4-}$ ($K_6 = 1.41 \times 10^{-4}$ at 20°) is formed[57]. This complex was also detected in a study of the heterogeneous $Pb(SeCN)_2$–KNCSe–$H_2O$ system by the solubility method[32]. The salt $K_4Pb(SeCN)_6$, which is sparingly soluble in water and acetone, was obtained from an aqueous–acetone (7 M with respect to acetone) solution of KNCSe by saturating it with lead selenocyanate[32].

The selenocyanates of the transition metals have been little studied. We have been able to demonstrate the existence of $CoNCSe^+$ and to calculate its dissociation constant ($K = 0.063$) by spectrophotometry[58]. The existence of the nickel complex $NiNCSe^+$ has been demonstrated in the same way[59,60].

Ablov and Samus' obtained dimethylglyoximatocobalt(III) complexes containing the selenocyanato-group[61]. Fine plates of the potassium salt and rhombic prisms of the ammonium salt $M[Co(DH)_2(NCSe)_2]$, where M = K or $NH_4$ [and DH = HON : C(CH$_3$).C(CH$_3$) : NO– (Ed. of Translation)], were obtained from an aqueous–alcoholic solution. A solution of the latter salt gives characteristic precipitates with $Cd^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Mg^{2+}$ cations. When hydrochloric acid is added to solutions of $K[Co(DH)_2(NCSe)_2]$, the acid $H[Co(DH)_2(NCSe)_2]$, which is sparingly soluble in water, is obtained; the action of alkali gives $[Co(DH)_2.(NCSe)H_2O].H_2O$.

When an alcoholic solution of potassium selenocyanate acts on $H_2PtCl_6$, a red-brown precipitate is formed, and when this is recrystallised from alcohol, it gives very fine hexahedral plates of $K_2Pt(SeCN)_6$[62,63]. If the preparation is carried out in aqueous solution, potassium hexakisselenocyanatoplatinae is obtained as a crystalline dihydrate[64]. Recrystallisation of this product from alcohol yields the anhydrous salt. Ammonium hexakisselenocyanatoplatinate $(NH_4)_2Pt(SeCN)_6$ is obtained as black rhombic crystals[65].

## VIII. SELENOCYANATO-COMPLEXES IN NON-AQUEOUS SOLUTIONS

As has been mentioned above, the selenocyanates are very sensitive to acids, and even to water. This appears to be due to the instability of the Se–C bond and also to the hydration of selenocyanate ions.

When it is considered that the introduction of non-aqueous solvents promotes a reduction in the hydration of ions[66], increased stability of the selenocyanates of many metals may be expected even in mixed solvents. The stability of the selenocyanate ion, and of complexes formed from it, is still more noticeably improved in solvents not capable of entering into solvolysis reactions with various salts. For this reason, even selenocyanates of the alkali metals are more stable in acetone and some other solvents than in water or alcohols. This is why the formation of copper(I) selenocyanato-complexes has been established in acetone by a study of the CuCl–KNCSe–$CH_3COCH_3$ system by the solubility method[29]. The salt KCu(SeCN)Cl is obtained as colourless crystals on crystallisation of the corresponding solution; it is decomposed by water and by alcohol with separation of CuSeCN[29]. Mixed selenocyanatothiocyanato-complexes of copper can also be shown to exist in acetone[44].

Copper(I) selenocyanate is very soluble in an acetone solution of KNCSe. It may be supposed that in this case, as with thiocyanates[67], the complex salts $K_2Cu(SeCN)_3$ and $K_3Cu(SeCN)_4$ are formed. However, the exact structure of the complexes formed on dissolution of CuSeCN has not been established, because the system undergoes rapid decomposition.

Reduction in the hydration of ions by the introduction of non-aqueous solvents, other conditions being similar, leads to the formation of higher complexes[66]. This is illustrated by silver selenocyanates. In aqueous solution the complex $Ag(SeCN)_3^{2-}$ is formed, but in a solution 7 M with respect to acetone, at the same concentrations of $NCSe^-$ ions, the complex $Ag(SeCN)_4^{3-}$ is formed[42]. A similar effect is observed in aqueous–methanolic and aqueous–dioxan solutions[68,69]. The complex $Ag(SeCN)_4^{3-}$ is mainly formed in high concentrations of methanol and in pure methanol[68].

From an alcoholic solution of potassium selenocyanate and gold(I) chloride, Clarke obtained fine, dark red crystals that rapidly decomposed[62]; he considered that these crystals corresponded to the salt $KAu(SeCN)_2$ (Au found 48.31%, compared with 43.94% calculated).

The interaction between potassium and cadmium selenocyanates in methanolic solution has been studied by electrical conductivity measurements, and the complex $Cd(SeCN)_3$ detected[30]. The salts $KCd(SeCN)_3.3CH_3COCH_3$, $K_2Cd(SeCN)_4.2CH_3COCH_3$, $K_2Cd(SeCN)_4$, $K_4Cd(SeCN)_6$, and also a number of cadmium halogenoselenocyanates have been obtained from acetone solution[70].

The dependence of the solubility of lead selenocyanate on the concentration of potassium selenocyanate in acetone solution has been studied, and formation of the complex $Pb(SeCN)_3^-$ demonstrated[32]. When the acetone solution is evaporated, the salt $KPb(SeCN)_3$ is obtained in fine silky yellowish green needles. The salt is readily soluble in acetone, but is decomposed by water[32].

We have studied the selenocyanato-complexes of cobalt and nickel in acetone and methanol solutions[58–60]. The formation of complexes from $MSeCN^+$ to $M(NCSe)_6^{4-}$, where

M = Co or Ni, has been demonstrated in these solutions by spectrophotometric and conductivity methods, and the dissociation constants of these complexes have been calculated.

The formation of nickel selenocyanato-complexes in dimethylformamide has also been studied. It has been shown that in this solvent complexes from $NiNCSe^+$ to $Ni(NCSe)_4^{2-}$ are formed. A comparison of the dissociation constants of nickel selenocyanates in different solvents shows that these complexes are most stable in acetone[71].

Complex selenocyanates of nickel and cobalt have been prepared from acetone solution[58-60]. Information on the composition, stability, and preparation of cobalt and nickel selenocyanates indicates that they are very similar to the thiocyanates[72,73].

Selenocyanates of manganese, cobalt, and nickel of composition $M(DMF)_4(NCSe)_2$ have been separated from dimethylformamide[40].

## IX. COMPLEX-FORMING CHARACTERISTICS OF THE $SeCN^-$ ION

The selenocyanate ion behaves as a pseudohalide ligand in complex-forming reactions. To determine the position occupied by this ion in the sequence of its analogues, we shall examine some selenocyanato-complexes and compare then with iodo-and thiocyanato-complexes.

From the dissociation constants of silver complexes of analogous composition with different ligands, it is easy to see that the selenocyanate ion is very close to the iodide ion in its complex-forming power[46,47]. The selenocyanato--complexes of silver are, however, more stable than the thiocyanato-complexes. In comparison with the latter, the selenocyanates separate more easily from solutions in equilibrium with a precipitate of the simple salt. Moreover, silver selenocyanates are easily formed as dinuclear complexes, which are reminiscent of iodo-complexes. Therefore, in their complexing power for silver ions selenocyanate and thiocyanate ions may be arranged in the series $I^- \geqslant NCSe^- > NCS^-$.

An analogous series is established on comparing the dissociation constants of thiocyanato-[74,75], iodo-[66,76], and selenocyanato-[36,57] complexes of lead, mercury, and cadmium.

It would seem that the above sequence of complex-forming power should be observed also in other cases. However, this is not so. Cobalt thiocyanates from $CoNCS^+$ to $Co(NCS)_4^{2-}$ are known in aqueous solution[77], but the selenocyanate ion forms only the simplest complex, and iodo-complexes of cobalt have not been detected in water at all. In this case, therefore, the sequence of complex--forming power $I^-$, $NCSe^-$, $NCS^-$ is in the reverse order. This applies to a still greater degree to nickel compounds[60,78].

Copper(II) thiocyanates have been described in the literature, but it appears that copper(II) selenocyanates are not formed[79,80].

## X. THE STRUCTURE OF SELENOCYANATES

The NCS group can be linked to metals through the nitrogen atom (isothiocyanate group), through the sulphur atom (thiocyanate group), and through the nitrogen and sulphur simultaneously (bridge thiocyanate group). It has been shown, for example, that in nickel and cobalt thiocyanato-complexes the ionic character of the M–NCS bond predominates, while in the thiocyanates of mercury, platinum, and silver the covalent character of the bond through sulphur predominates[81-83]. Since thiocyanates and selenocyanates are similar in properties, it is reasonable to suppose that the group NCSe can also form three types of bonds.

Two lines, at 2074 $cm^{-1}$ (2051) and 575 $cm^{-1}$, have been found in the Raman spectrum of aqueous solutions of KNCSe; these can be assigned to C–N and C–Se vibrations[84,85]. From this it was concluded that potassium selenocyanate had an ionic structure, and the structure $Se-C\equiv N$ was assigned to the $NCSe^-$ group. The same conclusion has been reached from study of the infrared spectra of KNCSe[41,86].

Examination of the infrared spectra of the compounds $CoA_2(NCSe)_2$ and $B_2Co(NCSe)_4$, where A is an amine and B is tetraalkylammonium or tetraarylarsonium, has shown that the selenocyanate group is attached to Co through N.[41,87,88].

Since $CoPy_2(NCS)_2$ and $CoPy_2(NCSe)_2$ have the same magnetic moment (5.1 $\beta$), an octahedral structure has been assigned to the latter compound. In solution in polar organic solvents, however, these compounds appear to have a tetrahedral configuration[35].

The compounds $CoHg(SeCN)_4$ and $CoHg(SCN)_4$ have been shown to be isomorphous[89]. Construction of Patterson projections confirmed the identity of the two structures. Therefore, in $CoHg(SeCN)_4$ the NCSe group forms a bridge between Hg and Co [as does the SCN bond in $CoHg(SCN)_4$[90]]; the selenocyanato-ligand is linked to mercury through the selenium, and to cobalt through the nitrogen[89]. The bidentate character of $NCSe^-$ in the $CoHg(SeCN)_4$ complex is obvious from infrared spectra[41,87]. The bridge structure also appears to occur in the silver selenocyanates[41]. In the $K_2Pt(SeCN)_6$ and $K_2Hg(SeCN)_4$ complexes the link between the selenocyanate group and the central atom is effected through the selenium[88].

A detailed study of the structure of the selenocyanates of the transition metals has begun in the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. Already results have been published of X-ray structure studies on the compounds $MA_4(NCSe)_2$ (where M = Co or Ni and A is dimethylformamide)[91]. These compounds are paramagnetic; the magnetic susceptibility of the cobalt salt is 3.22 $\beta$. X-Ray structure analysis has shown that in $MA_4(NCSe)_2$ the selenocyanate groups enter the inner sphere of the complex $[MA_4(NCSe)_2]$, which has an octahedral *trans*-configuration[91]. The NCSe group is linked to the central atom through the nitrogen, and the M–N=C angle is close to 180°.

A comparison of the stability of selenocyanato-complexes and their structure shows that those compounds in which the NCSe group is linked to the central atom through the selenium are more stable than the corresponding thiocyanates. Compounds in which the NCSe group is linked through the nitrogen, however, are less stable than the thiocyanates.

It will be seen from the above review of the literature that, right up to the 1950's, the number of metals that formed known coordination compounds with $NCSe^-$ ions was extremely small. Attempts to prepare selenocyanates of

a number of metals may have failed because aqueous solutions were used. Only selenocyanates of those metals that form stable complexes with $NCSe^-$ could be studied in water.

The range of existence of selenocyanato-complexes has been considerably extended by the use of non-aqueous solvents. With non-aqueous solutions it has become possible to study more fully both the compounds of the metals that form stable selenocyanates and the salts of such metals as cobalt, nickel, and copper, which do not form selenocyanato-complexes in water.

Comparison of results in the literature on selenocyanato-complexes shows that even metals with identical electron shells differ in their power of coordinating selenocyanate ligands. With the exception of the zinc subgroup, it is impossible in other groups of metals to trace a strict sequence in the stability of their complexes with their atomic number. Thus, in the copper subgroup, silver forms selenocyanato-complexes most easily. In Group III indium should form selenocyanato-complexes more readily than other metals in the tervalent state. Because of the high oxidation potential of $Tl^{3+}$, thallium, like lead, can form selenocyanates only in its lower valency state.

If the metals are compared according to Periods, the following points may be noted. In the Sixth Period the most stable selenocyanates in aqueous solution are formed by quadrivalent platinum and bivalent mercury, in the Fifth Period by silver and cadmium, and in the Fourth Period by cobalt. Therefore, as we go from the Sixth to the Fourth Period, the centre of complex formation is displaced to the left. From this it may be assumed that selenocyanates will be formed by iron, manganese, and other metals in this Period.

It is quite probable that in non-aqueous solvents selenocyanates not only of $Fe^{2+}$, $Fe^{3+}$, $Cr^{3+}$, $Mn^{2+}$, and $Zn^{2+}$, but even of gallium, tin, and other metals can be obtained.

Extension of the number of selenocyanates will permit this class of compounds to be characterised more fully and open the way to their practical use‡.


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‡ While this review was being prepared for the press, new papers appeared. The infrared spectra of *trans*-$[MA_4(NCSe)_2]$ (M = Ni, Co, Mn; A = dimethylformamide) and also of the compounds $Cu(NH_3)_4(SeCN)_2.H_2O$ and $KAg(SeCN)_2$ have been discussed[92]. The infrared spectra of some inorganic selenocyanates have been presented and reviewed[93]. A theoretical (semiempirical) analysis of the infrared spectra of selenocyanato-complexes has been made[94,95].

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# STUDY OF THE THERMAL STABILITY OF INORGANIC PEROXO-COMPOUNDS BY THE DIFFERENTIAL THERMAL ANALYSIS METHOD

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The inorganic peroxo-compounds are special higher forms of oxygen compounds of the elements and every year they acquire new fields of use. The diverse use of the different types of this broad class of compounds is determined not only by their oxygen content, which can be readily released in active form, but also by the singular nature of the bonding to oxygen in their molecules.

The presence of the peroxo-group, the so-called "oxygen bridge" was thought until recently to be sufficient for defining "inorganic peroxo-compounds". A detailed study of the structure and properties of a series of peroxo-compounds, made in the 'thirties of the present century, with the active participation of Soviet scientists, showed that this concept embraces at least nine groups of compounds, which are distinguished by the nature of the bond between the oxygen atoms in the bridge and by the nature of the bond between the oxygen bridge and the atoms of the element forming the peroxo-compounds. Some authors tend to include all the inorganic peroxo-compounds within the framework of complex compounds dividing them into three groups: polyoxides, peroxo-acids, and peroxohydrates. However, the group of polyoxides includes peroxo-compounds with a crystal lattice consisting of metal ions (predominantly of the Ia and IIa subgroups of the Periodic System) and the molecular anions $O_2^{2-}$, $O_2^-$, and $O_3^-$ respectively, which differ both in their structure and in the nature and length of the O–O bond. The bonds of the metal atoms with the oxygen bridge in these compounds are of the ionic type, whereas in other peroxo-compounds the peroxo-group as such or in the form $H_2O_2$ or $HO_2$ is joined to the atom of the element forming the peroxo-compound by a coordinate, not an ionic bond. It is therefore desirable to keep the division of inorganic peroxo-compounds into simple and complex.

The simple inorganic peroxo-compounds can be subdivided into four groups: (1) the hydrogen peroxides, which are characterised by the presence of the hydrogen peroxide ion HO [presumably $HO_2^-$ (Ed. of Translation)]; (2) the peroxides, characterised by the presence of the peroxide ion $O_2^{2-}$; (3) the superoxides, characterised by the presence of the superoxide ion $O_2^-$; (4) the ozonides, characterised by the presence of the ozonide ion $O_3^-$.

The complex peroxo-compounds can be subdivided into five groups: (1) peroxo-acids and their salts, in which the peroxo-group forms part of the complex anion, mono- and poly-nuclear representatives of this group being known; (2) peroxo-complexes which are neither peroxo-acids nor their derivatives, represented by compounds which include in the inner sphere a peroxo-group (peroxo-complexes), or hydrogen peroxide (perhydro-complexes [Russian nomenclature (Ed. of Translation)]), or the hydrogen peroxo-group (hydrogen peroxo-complexes); (3) peroxide hydrates — addition compounds of peroxides with water of crystallisation; (4) peroxohydrates — molecular compounds of

peroxides or salts analogous to crystal hydrates containing hydrogen peroxide of crystallisation; (5) hydrates of peroxohydrates — molecular compounds of peroxides or salts which contain both water of crystallisation and hydrogen peroxide of crystallisation.

Specific properties of compounds of each of the above groups have been described in a monograph[1] and an article[2].

A characteristic property of the peroxo-compounds, whether simple or complex, is the ability to lose oxygen in an active form during thermal decomposition or under the action of chemical agents.

To determine whether it is possible to use inorganic peroxo-compounds as sources of chemically bound oxygen it is necessary to have accurate information on their behaviour on heating.

Up to 1952, with the exception of Kapustinskii and Bayushkina's data[3] on the dissociation temperature of $BaO_2$, obtained by use of an apparatus which was a combination of a Kurnakov thermal analysis apparatus and a Beckmann manostat, and data on the thermal decomposition of several minerals under the action of sodium peroxide, obtained by differential thermal analysis[4], the literature does not contain objective information about the thermal stability of the inorganic peroxo-compounds based on the use of the last method. In the Peroxide Compounds Laboratory of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR since 1952 Makarov, Rode, Mironov, Vol'nov, Dobrynina, Grigor'eva, Firsova, and Chamova have widely used the method of differential recording of heating curves on a Kurnakov recording pyrometer for the thermal characterisation of representatives of the above-mentioned groups of peroxide compounds. It appeared that, depending on the type of peroxo-compound, the nature of the heating curves is different. In recent years the method of differential thermal analysis has been applied to peroxides by several foreign scientists: Margrave, Hoffman, Ghormley, Duval, etc.

It is necessary to note that unlike the manostat-pyrometric method used by Kapustinskii, which, as the author mentioned at the First Conference on Thermography[5] made possible the automation of the investigation of all three variables ($t$, $p$, and $c$), which determine the state of equilibrium of systems which dissociate with evolution of gas (liberation of oxygen, for peroxides), most of the heating curves for peroxo-compounds given in the present paper were recorded at a given external (atmospheric) pressure. Consequently, these curves reflect only the behaviour of the peroxo-compounds on heating under the real conditions of their use as sources of chemically bound oxygen and the value of the decomposition temperature thus obtained cannot be a basis for any rigorous thermodynamic calculations. Nevertheless, since these curves were obtained under comparable conditions, a comparison of them can throw light on the difference in structure of the individual groups of peroxo-compounds.

## STUDY OF THE THERMAL STABILITY OF THE PEROXIDES $M_2O_2$ AND $M^{II}O_2$†

Mironov[6] has widely used the thermographic method in investigating phase transformation diagrams of the $H_2O_2$–$H_2O$ system. Fig. 1 shows low-temperature heating curves

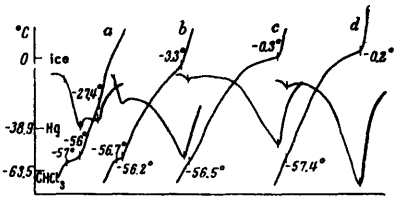



Fig. 1. Low-temperature heating curves of hydrogen peroxide solutions. $H_2O_2$, %: *a*) 77; *b*) 96.1; *c*) 99.3; *d*) 99.8.

for various compositions in this system, which can serve as a criterion of the purity of hydrogen peroxide. From the last curve of the diagram it is evident that thermography enables the presence of up to 0.2 wt.% water to be detected, which it is difficult to do by the usual chemical methods. Mironov[7] also took heating curves of the glassy substance which is formed when the dissociation products of water vapour in a glow discharge are frozen in a trap cooled with liquid air. The originality of the effects which appear on the curves and their difference from the effects obtained at low-temperature recording of solutions of hydrogen peroxide enabled the author to conclude that the glassy substance contained a compound of the type of higher peroxides of hydrogen. This conclusion was later also confirmed thermographically[8,9].

The heating curves for solutions of hydrogen peroxide of different concentrations in the region of positive temperatures [presumably above 0° (Ed. of Translation)] are characterised by the presence of an endothermic effect of boiling (at 151° for 100% $H_2O_2$) with a subsequent exothermic effect for the decomposition into water and oxygen, due to the liberation of heat (23.44 kcal mole$^{-1}$ for 100% $H_2O_2$).

Unlike the decomposition of hydrogen peroxide, the decomposition of alkali and alkaline earth metal peroxides into the oxide and hydrogen is accompanied by absorption of heat, as shown on the heating curves of lithium, sodium, calcium, and strontium peroxides[10–13]. It is not necessary to reproduce all these curves, since the effects characteristic for them also appear on the curves of the peroxide hydrates, which will be given below. It is also necessary to note that the effect at 510° on the heating curve of sodium peroxide[11] (Fig. 2), which was previously ascribed to fusion, really corresponds, according to new

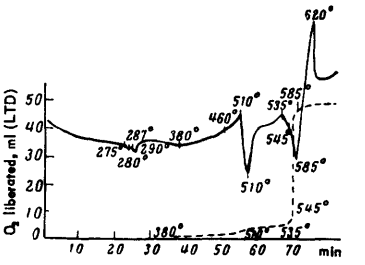



Fig. 2. Differential heating curve of sodium peroxide. Broken line: oxygen liberation curve.

† M denotes metal.

results[14], to the transformation of the hexagonal modification of $Na_2O_2$ (I) into another modification $Na_2O_2$ (II), the symmetry of which has not been determined. According to Tallman and Margrave[14], sodium peroxide melts above 596°.

## STUDY OF THE THERMAL STABILITY OF PEROXIDE HYDRATES, $M_2O_2.xH_2O$

There is considerable interest in the heating curves of the alkali and alkaline earth metal peroxide hydrates, which enable us to judge whether it is possible to obtain the peroxide in the anhydrous state. Fig. 3 shows the differential heating curves of lithium peroxide monohydrate[15] and sodium peroxide octahydrate[16,17]. On heating, lithium peroxide monohydrate loses water at 100–140° and forms the anhydrous peroxide. An endothermic effect, starting at 325°, corresponds to the decomposition of $Li_2O_2$ into $Li_2O$ and $\frac{1}{2}O_2$. On heating sodium peroxide octahydrate, it melts at 68°, dissolving in the water of crystallisation, and loses its active oxygen completely, being converted into sodium hydroxide dihydrate. An effect at 131° corresponds to the boiling off of the solution. Consequently, sodium peroxide cannot be obtained like lithium peroxide by dehydrating the hydrate formed in the oxide hydrate–hydrogen peroxide–water system.

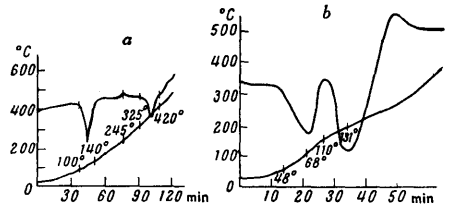



Fig. 3. Heating curves for:
*a*) lithium peroxide monohydrate $Li_2O_2.H_2O$; *b*) sodium peroxide octahydrate $Na_2O_2.8H_2O$.

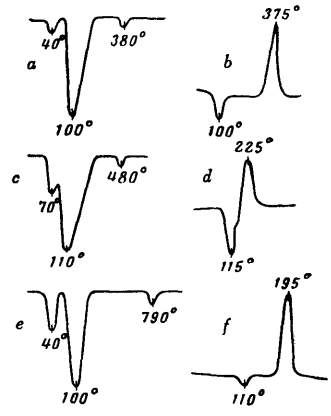



Fig. 4. Differential heating curves for peroxide hydrates of elements of Periodic Group II:
*a*) $CaO_2.8H_2O$; *b*) $MgO_2.xH_2O$; *c*) $SrO_2.8H_2O$; *d*) $ZnO_2.xH_2O$; *e*) $BaO_2.8H_2O$; *f*) $CdO_2.xH_2O$.

A marked difference is apparent on comparing the differential heating curves of calcium[12], strontium[18], and barium[19] peroxide octahydrates with those of the hydrated forms of magnesium[19], cadmium[19-21], and zinc[22] peroxides of gross composition $MO_2.xH_2O$ (Fig. 4). Those of the calcium, strontium, and barium peroxide octahydrates have three endothermic effects, corresponding respectively to incongruent melting, dehydration, and decomposition of the peroxide into the oxide and oxygen. With increase in the atomic weight of the element forming the peroxide, the stability of the latter increases: thermal decomposition starts at 380° for $CaO_2$, 480° for $SrO_2$, and 790° for $BaO_2$. On the heating curves of the hydrated forms of magnesium, zinc, and cadmium peroxides there is no fusion effect. The curves are characterised by the presence of a single endothermic effect within the limits 100–115°, corresponding to the removal of the mother-liquor, and a single exothermic effect, corresponding to decomposition to the oxide with liberation of oxygen and water. In this, with increase in the atomic weight of the element forming the peroxide the decomposition temperature decreases: $MgO_2$ 375°, $ZnO_2$ 225°‡, $CdO_2$ 195°. Owing to this difference and also because the oxides of these metals show less basic properties than calcium, strontium, and barium oxides, it can be suggested that the hydrated forms of magnesium, zinc, and cadmium peroxides are not hydrates of the true peroxides $MO_2$, but belong to a group intermediate between the peroxides of this composition and peroxo-acids. The probable structure of these compounds can be written (HO).M(OOH).$xH_2O$. The infrared spectra recently obtained[23] for these compounds also show the absence of water of crystallisation. If, for example, the magnesium peroxide hydrate had the actual formula $MgO_2.xH_2O$, its heating curve should show, after the removal of water, an endothermic effect for decomposition, as on the heating curve of, for example, $CaO_2.8H_2O$. The heats of the reactions $CaO_2 \rightarrow CaO + \frac{1}{2}O_2$ (-5.8 ± 0.5 kcal mole$^{-1}$) and $MgO_2 \rightarrow MgO + \frac{1}{2}O_2$ (-5.1 ± 1 kcal mole$^{-1}$) are very close.

## STUDY OF THE THERMAL STABILITY OF METAL PEROXIDE–HYDROGEN PEROXIDE ADDITION COMPOUNDS, $M_2O_2.xH_2O_2$, "PEROXOHYDRATES"

Differential heating curves of the alkali and alkaline earth metal peroxide–hydrogen peroxide addition compounds, that is, compounds in which hydrogen peroxide of crystallisation replaces water of crystallisation, are given in Fig. 5.[12,16,18,24-26] They show an exothermic effect of the decomposition of the crystallisation hydrogen peroxide in the range 45–65° with a subsequent endothermic effect of dehydration (with the sodium compound, fusion at 285°) at ~100° and the final endothermic effect of decomposition of the peroxide into the oxide and oxygen. On comparing the heating curves for the hydrated forms of magnesium, zinc, and cadmium peroxides (Fig. 4) with the heating curves of calcium, strontium, and barium peroxide–2-(hydrogen peroxide)s (Fig. 5), then the hypothesis that the first group of compounds contain hydrogen peroxide of crystallisation fails, since the exothermic effect corresponding to their decomposition does not precede the dehydration effect, as is characteristic for peroxide–(hydrogen peroxide) addition compounds.

‡ The report[21] that the decomposition of $ZnO_2$ at 200° is accompanied by an endothermic effect is evidently incorrect.

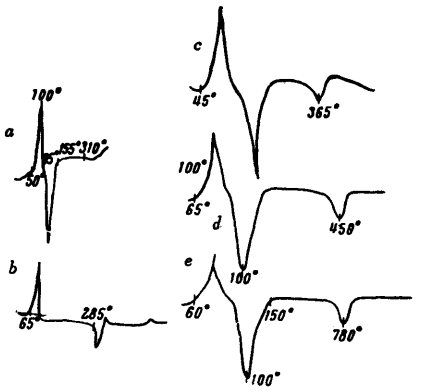



Fig. 5. Differential heating curves of the alkali and alkaline earth metal peroxide–(hydrogen peroxide) addition compounds:
*a*) $Li_2O_2.2H_2O_2$; *b*) $Na_2O_2.H_2O_2$; *c*) $CaO_2.2H_2O_2$; *d*) $SrO_2.2H_2O_2$; *e*) $BaO_2.2H_2O_2$.

## STUDY OF THE THERMAL STABILITY OF THE SUPEROXIDES $M^IO_2$

Only four representatives are known of this group of peroxide compounds: sodium, potassium, rubidium, and caesium superoxides. We have obtained the calcium, strontium, and barium superoxides[27] only admixed with peroxide and hydroxide of the metal. Rode[11,28] has made a detailed study of the behaviour of sodium superoxide on heating. It was found (Fig. 6) that in dry oxygen sodium superoxide starts to decompose at ~120°, in dry, $CO_2$-free air at 80–90°. In oxygen at 250° and in dry, $CO_2$-free air at ~215° it decomposes vigorously and endothermically with formation of sodium peroxide. Rode[29] also confirmed thermographically (Fig. 7) that sodium and potassium superoxides had two low-temperature polymorphic transformations, at -43° and -80° and at -75° and -120° respectively. As for the melting point of potassium superoxide, it must be pointed out that the values of 380°[30] and 440°[31] given in the literature were found over 30 years

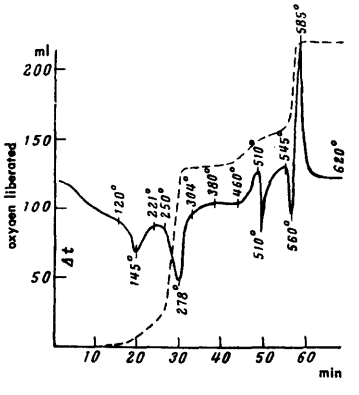



Fig. 6. Differential heating curve of sodium superoxide. Broken line: oxygen liberation curve.

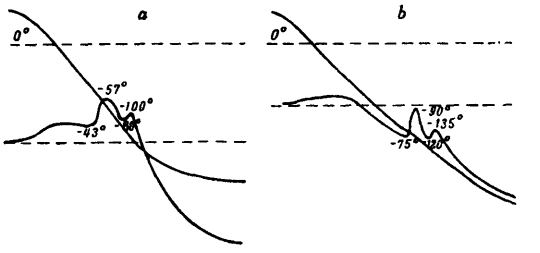



Fig. 7. Low-temperature heating curves for:
*a*) sodium superoxide $NaO_2$; *b*) potassium superoxide $KO_2$.

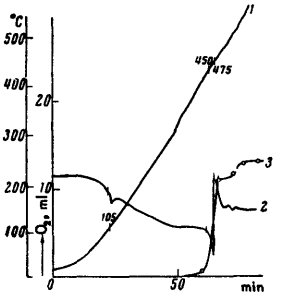



Fig. 8. Heating curves for caesium superoxides:
1) simple record; 2) differential record;
3) oxygen liberation curve.

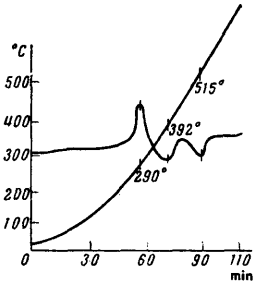



Fig. 9. Heating curve for a peroxide preparation containing calcium superoxide.

ago and were evidently obtained with insufficiently pure material. In the Peroxide Compounds Laboratory of the Institute of General and Inorganic Chemistry a heating curve has been recorded for caesium superoxide prepared in a pure form[45] (Fig. 8); it has an endothermic effect for fusion at 450°. The effect at 475° is due to the reaction of caesium oxide with the glass of the test-tube in which the recording was made. Fig. 9 shows the heating curve obtained by Vol'nov[27] for a preparation containing 16% calcium superoxide as well as calcium peroxide and hydroxide. The interpretation of this curve, together with chemical analysis and magnetic measurements, showed that the exothermic effect at 290° corresponds to the decomposition of

the superoxide and the endothermic effects at 392° and 516° correspond to the decomposition of calcium peroxide and hydroxide to the oxide.

## STUDY OF THE THERMAL STABILITY OF THE ALKALI METAL OZONIDES $M^{I}O_3$

Sokovnin and Matveev[32,33] recorded the heating curves of a new class of inorganic peroxo-compounds, discovered by Kazarnovskii, but obtained by their use of a new method: the reaction of the corresponding superoxides with $O_3$ in a pseudo-liquefied layer created by a current of ozonised oxygen, with subsequent extraction with liquid ammonia. Caesium ozonide with a purity of 92.5% was first obtained by this method[32]. The heating curve of potassium ozonide (Fig. 10), in agreement with the thermodynamic data which show that during the decomposition of the ozonide to the superoxide 5.5 kcal mole$^{-1}$ is released, is characterised by the presence of an exothermic effect for decomposition to $KO_2$ at 60° ± 2° and the endothermic effect of the decomposition of $KO_2$ to $K_2O_2$ at 390°. The oxygen liberation curve shows clearly how the process takes place in two stages[33]. The heating curve of caesium ozonide[32] (Fig. 11) is characterised by the analogous exothermic effect of the decomposition of $CsO_3$ to $CsO_2$ at 70–100°. The exothermic effect at 408° corresponds to the fusion and decomposition of the decomposition products of $CsO_3$. Both effects are confirmed by the nature of the oxygen liberation curve, shown by a broken line in the diagram. A comparison of the heating curves for $KO_3$ and $CsO_3$ shows that the limit of thermal stability rises with the atomic number of the elements.

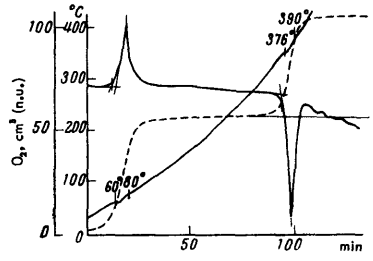



Fig. 10. Heating curve for potassium ozonide. Broken line: oxygen liberation curve.

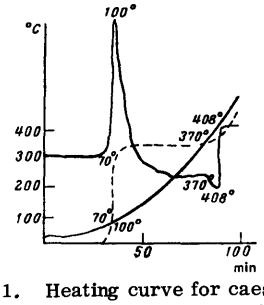



Fig. 11. Heating curve for caesium ozonide. Broken line: oxygen liberation curve.

## STUDY OF THE THERMAL STABILITY OF PEROXO--ACIDS AND THEIR SALTS

Peroxo-acids are quite unstable compounds which are difficult to isolate in the free state. Their salts have a greater thermal stability and can be used as initiators in some polymerisations. Grigor'eva and Selezneva[34] succeeded long ago in isolating crystalline hydrates of metaperoxo-acids of niobium and tantalum. The heating curves of these compounds are given in Fig. 12. The endothermic effects at 75–100° for $HNbO_4.H_2O$ and 100–145° for $HTaO_4.H_2O$ correspond to the decomposition of these compounds to the meta-acid with evolution of active oxygen and water[34]. The heating curves of the sodium salts of peroxoorthoniobic and peroxoorthotantalic acids $Na_3NbO_8$ and $Na_3TaO_8$ (Fig. 13) are characterised by the presence of an exothermic effect of the liberation of all four atoms of active oxygen at 130°.[34] The sodium salt of peroxoorthovanadic acid is decomposed in a similar manner, but at 115°.[35]

Fig. 14 shows the heating curves of several salts of dinuclear peroxo-acids: potassium peroxodicarbonate $K_2C_2O_6$,[36] potassium peroxodisulphate $K_2S_2O_8$,[37] and sodium peroxopyrotantalate $Na_4Ta_2O_{12}$.[35] The endothermic effect on the heating curve of the potassium peroxodicarbonate at

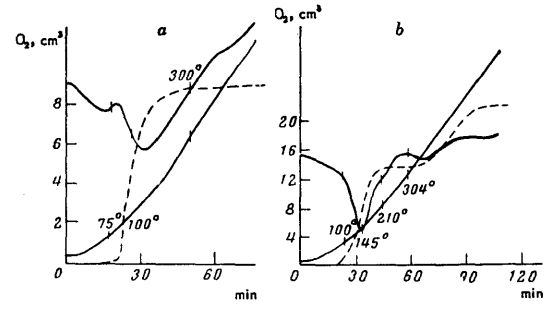



Fig. 12. Heating curve for hydrates of peroxoniobic and peroxotantalic acids:
*a*) $HNbO_4.H_2O$; *b*) $HTaO_4.H_2O$. Broken line: oxygen liberation curves.

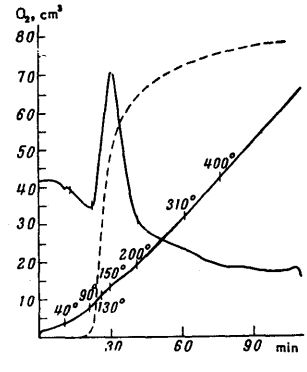



Fig. 13. Heating curves for sodium peroxoorthotellurate $Na_3TaO_8$. Broken line: oxygen liberation curve.

106° corresponds to its decomposition into carbonate with liberation of oxygen and carbon dioxide. The second effect at 198–200° corresponds to the decomposition of $KHCO_3$ impurity. On the heating curve of potassium peroxodisulphate the exothermic effect at 200° corresponds to the decomposition of this salt into pyrosulphate with liberation of oxygen. The endothermic effect at 350° corresponds to the fusion of pyrosulphate and the effect at 470° to the decomposition of the latter to sulphate with the liberation of sulphur trioxide. Sodium peroxopyrotantalate decomposes exothermically at 120° with liberation of all five atoms of active oxygen add the formation of $Na_4Ta_2O_7$. Potassium peroxopyrovanadate $K_4V_2O_{11}$ decomposes in a similar manner, but at 130–145°.[35]

Comparison of the heating curves shown in Fig. 14 suggests that when the decomposition of peroxo-salts is accompanied only by the liberation of active oxygen, this is shown by an exothermic effect (Figs. 14*b* and 14*c*). When the decomposition is more extensive, for example, by the reaction:

$$K_2C_2O_6 \rightarrow K_2CO_3 + CO_2 + {}^1/_2O_2$$

(Fig. 14*a*), the effect is endothermic.

Peroxide complexes which are not derivatives of peroxo--acids have been very little studied. Only one paper, devoted to the so-called uranium peroxide hydrates, has been published[38]. These compounds, which are peroxo--complexes and which contain a peroxo-group and water in the inner sphere, lose active oxygen stepwise on heating, with the formation of $U_3O_8$ finally at ~600°.

## STUDY OF THE THERMAL STABILITY OF SALTS WITH HYDROGEN PEROXIDE AND WATER OF CRYSTALLISATION

The heating curves of salts containing hydrogen peroxide of crystallisation have an exothermic effect for the decomposition of the peroxide into water and oxygen. In several alkali metal carbonate–hydrogen peroxide addition compounds (Fig. 15) this effect, which was studied by Chamova[39] and by Dobrynina[40], is preceded by the endothermic effect of the fusion of a salt in the crystallisation water. When the salt contains water of crystallisation in addition to hydrogen peroxide of crystallisation (the so-called hydrates of peroxyhydrates), the type of curves, as is evident from the example of $Na_2SiO_3.3H_2O_2.H_2O$,[41] is the same as for anhydrous hydrogen peroxide addition compounds (Fig. 16). But sometimes, as for example, on heating $Na_2CO_3.2H_2O_2.H_2O$ (Fig. 17), an endothermic effect, corresponding to the removal of water of crystallisation, precedes an exothermic effect of the decomposition of the

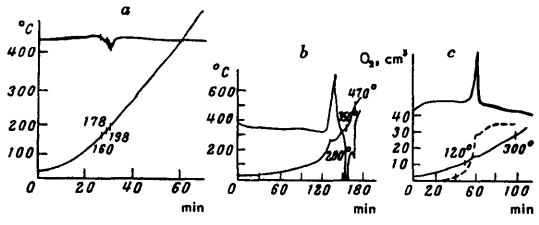



Fig. 14. Heating curves:
*a*) potassium peroxodicarbonate $K_2S_2O_6$; *b*) potassium peroxodisulphate $K_2S_2O_8$; *c*) sodium peroxopyrotantalate $Na_4Ta_2O_{12}$.

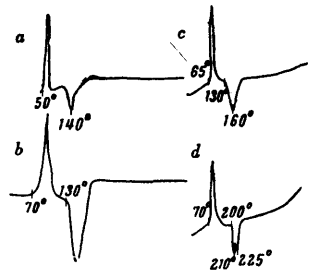



Fig. 15. Differential heating curves for hydrogen peroxide addition compounds of alkali metal carbonates:
*a*) $Na_2CO_3.2H_2O_2$; *b*) $K_2CO_3.3H_2O_2$;
*c*) $Rb_2CO_3.3H_2O_2$; *d*) $Cs_2CO_3.3H_2O_2$.

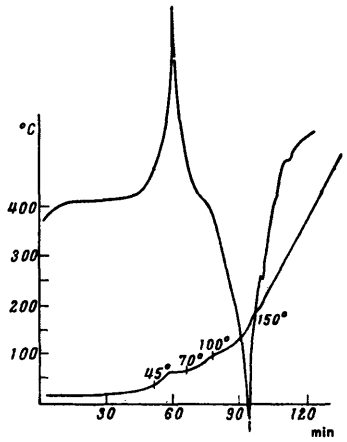



Fig. 16. Heating curve for sodium metasilicate–3-(hydrogen peroxide)–water, $Na_2SiO_3.3H_2O_2.H_2O$.

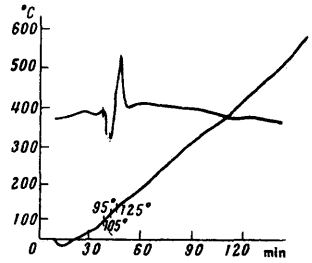



Fig. 17. Heating curve for sodium carbonate–2-(hydrogen peroxide)–water, $Na_2CO_3.2H_2O_2.H_2O$.

hydrogen peroxide of crystallisation. The curve permits the recommendation of temperature conditions for obtaining anhydrous sodium carbonate–hydrogen peroxide, which is widely used as a mild oxidant in the home and in the textile, food, and cosmetic industries. In some other salt–hydrogen peroxide addition compounds, for example, sodium sulphate–hydrogen peroxide[42], the endothermic

effect which corresponds to the incongruent melting of the compound precedes the exothermic effect of decomposition of hydrogen peroxide of crystallisation (Fig. 18).

Some bases – ammonia and urea – are also capable of forming molecular compounds with hydrogen peroxide. Their behaviuur on heating has been studied by Mironov[43], Lebedev[44], and Vol'nov[13]. Release of active oxygen in these compounds is shown on the heating curves by an exothermic effect at 40° and 80° respectively.

The example of several representatives of the groups of inorganic peroxo-compounds has shown that the use of differential thermal analysis in studying their thermal stability permits: (1) the rapid and objective determination of the nature and temperature limits of release of active oxygen: (b) the recommendation of a temperature regime for their production as hydrates, hydrogen peroxide addition compounds, or in the anhydrous state; (c) to recommend a temperature regime for their use in various oxidations; (d) to recommend temperature conditions for their safe storage; (e) to give a preliminary qualitative appraisal of the nature and strength of the bonding of the active oxygen in their molecules.

Depending on the group to which the peroxide compound belong, the heating curves are different:

1. The heating curves of the alkali and alkaline earth metal peroxides have an endothermic effect corresponding to the decomposition $M_2O_2 \rightarrow M_2O + \frac{1}{2}O_2$. With an increase in the atomic weight of the element forming the peroxide, the thermal stability increases. Barium peroxide is the most thermally stable compound of this group; it decomposes into oxide and oxygen at 790°.

2. The heating curves of alkali metal superoxides have successive endothermic effects for decomposition by the sequence $2MO_2 \rightarrow M_2O_2 + O_2 \rightarrow M_2O + \frac{1}{2}O_2$. The thermal stability of these compounds rises in the series Na–Cs.

3. The ozonides are the least stable of the simple (ionic) peroxides. Their heating curves have an exothermic effect for decomposition to superoxides by the reaction $MO_3 \rightarrow MO_2 + \frac{1}{2}O_2$ between 60° and 70°.




Fig. 18. Heating curve for sodium sulphate–3-(hydrogen peroxide), $Na_2SO_4.3H_2O_2$.

4. The heating curves of alkali and alkaline earth metal peroxide hydrates have an endothermic effect for decomposition by the reaction $M_2O_2 \rightarrow M_2O + \frac{1}{2}O_2$, which usually precedes the endothermic effects of incongruent melting and dehydration.

5. Unlike the alkaline earth metal peroxide hydrates, the hydrated forms of magnesium, zinc, and cadmium peroxides have heating curves with an endothermic effect corresponding to the loss of mother-liquor and the exothermic effect of decomposition. This can be explained by ascribing to these compounds the hydrogen peroxide form HO–M–OOH.

6. The heating curves of the salts of peroxo-acids have an exothermic effect at the thermal decomposition by the reaction $M_2E_2O_8 \rightarrow M_2E_2O_7 + \frac{1}{2}O_2$. When they undergo more extensive decomposition at the same time as they lose the active oxygen, there is an endothermic effect on their heating curves. The salts of the peroxo-acids exhibit considerable thermal stability and usually decompose above 130°. The peroxosulphates (~200°) are the most stable thermally.

7. The least stable of the peroxo-complexes are the molecular compounds with hydrogen peroxide – the "peroxohydrates" of peroxides and salts. Their heating curves have the exothermic effect of decomposition at 50–70°.


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# PHYSICOCHEMICAL INVESTIGATIONS AND METHODS OF PRODUCING COMPLEX FERTILISERS WITH THE USE OF UREA

G. L. Tudorovskaya and F. G. Margolis

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## I. INTRODUCTION

Urea is a highly concentrated fertiliser containing 46.6% nitrogen, free of inert materials, and is used either independently or in complex fertilisers which contain phosphorus and potassium as well as nitrogen. Furthermore, urea finds use as foodstuff for farm animals, is widely employed in plastics manufacture, in the pharmaceutical industry, and in medicine.

The increase in the demand by agriculture and industry for urea has brought about a considerable increase in the production in the USSR and abroad[1]. The greatest amount of urea is produced in Japan, where 85–90% of the total output is used as a fertiliser, compared with 60–65% in USA, and 20–40% in Europe.

In 1962 urea formed only 8% of the world production of nitrogenous fertilisers; in 1966 [1963 ?] this had grown to 17.5% calculated on nitrogen[2]. The production of urea for industrial purposes is also growing steadily.

In the USSR until recently the use of urea as a fertiliser was quite limited. In 1958 the total fraction of urea in the balance of nitrogenous fertilisers was 1% (calculated on

nitrogen). At the end of 1961 the level of production of the urea in the USSR had increased almost six times in comparison with 1958. In 1962 the USSR occupied third place in the world — after the USA and Japan — as regards output of urea.

According to the latest plan data in the USSR, owing to the improvement in the process the cost per unit of nitrogen in urea exceeds that in ammonium nitrate by 7–15%.[3] With the reduction in the cost of manufacture of urea and the increasing scale of production it is obviously finding wide application in agriculture as a component of fertilisers, both independent and complex.

To choose optimal conditions for carrying out the production of nitrogenous and complex fertilisers employing urea, several equilibrium systems have been studied. This work started in the USSR in the middle of the 'thirties; in recent years there have been further developments.

This article is a review of physicochemical investigations of systems which include urea and compounds containing nitrogen, phosphorus, potassium, and trace elements, and also the commercial methods of preparing fertilisers based on these systems.

## II. PHYSICOCHEMICAL INVESTIGATIONS

### 1. Solubility of Urea in Water and Ammonia

Various investigators have studied the urea–water binary system in detail[4–12]. A summary of the results obtained up to 1935 has been given in a monograph[11]. Soviet investigators subsequently studied the temperature region from complete solidification to 40°.[12–14].

Table 1 gives data on the solution compositions at the cryohydric points and the points of polymorphic transformations.

Various investigators have studied the solubility of urea in liquid ammonia[8,15]. The solubility of urea in liquid ammonia rises considerably with the temperature; starting from ~ 30° the solubility of urea in liquid ammonia exceeds its solubility in water. Urea and ammonia form the compound $CO(NH_2)_2 \cdot NH_3$; it can exist only in solutions containing an excess of ammonia, therefore the solubility curve for urea in liquid ammonia (Fig. 1) has a change in direction at the point $CO(NH_2)_2$ 77.9, $NH_3$ 22.1%, coinciding with the melting point of this compound, 46°.

Fig. 2 shows the $CO(NH_2)_2$–$NH_3$–$H_2O$ system; curves for the vapour pressure over saturated solutions are also given on this diagram.

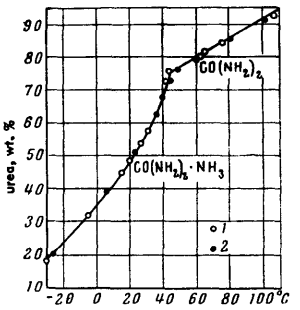



Fig. 1. Solubility curve for urea in liquid ammonia:
1) after Jänecke[8]; 2) after Scholl and Davis[15].

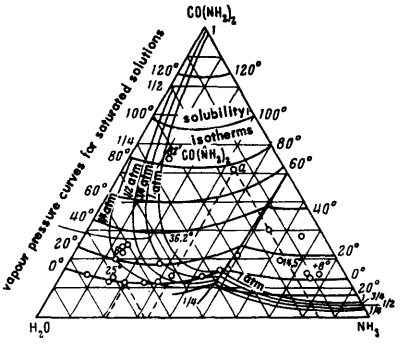



Fig. 2. Equilibrium diagram of the $CO(NH_2)_2$–$NH_3$–$H_2O$ system[8].

### 2. Systems Containing Urea and Nitrates

The $CO(NH_2)_2$–$NH_4NO_3$ anhydrous binary system has been studied by various authors[16,17]. Double compounds are not formed between the components; the eutectic point is at $NH_4NO_3$ 53.5%, 44.6°.[16] Soviet investigators have studied the viscosity and electrical conductivity of this system[18].

The $CO(NH_2)_2$–$NH_4NO_3$–$H_2O$ ternary system has been studied by the visual-polythermal method from 25° to complete solidification (-26.5°)[19] and by the isothermal method at 25°.[20] The polytherm (Fig. 3) is divided into seven crystallisation fields; in addition to the ice field there are three fields each for the polymorphic modifications of urea and ammonium nitrate. The existence of two series of solid solutions in the system has been suggested: urea in ammonium nitrate and ammonium nitrate in urea[19], but in the investigation of this system by the isothermal method solid solutions were not observed in the residues[20].

The electrical conductivity and viscosity of this system at 30° have also been studied[21]. The extrema on the curves in Figs. 4 and 5 are evidence of the formation of the complexes $NH_4NO_3 \cdot CO(NH_2)_2$ and $NH_4NO_3 \cdot 2CO(NH_2)_2$ in the solutions.

The common solubility in the $CO(NH_2)_2$–$NH_4NO_3$–$NH_3$–$H_2O$ system[22] was studied at 30° and 0° and various $NH_3$ : : ($NH_3$ + $H_2O$) ratios. The highest total solubility of the

TABLE 1.

| Solution composition at cryohydric point, wt. % | | t, °C | Solution composition at first inflection, wt. % | | t, °C | Solution composition at second inflection, wt. % | | t, °C | References |
|---|---|---|---|---|---|---|---|---|---|
| $CO(NH_2)_2$ | $H_2O$ | | $CO(NH_2)_2$ | $H_2O$ | | $CO(NH_2)_2$ | $H_2O$ | | |
| 33.0 | 67.0 | —10.8 | — | — | — | 53.3 | 46.7 | 22.5 | 12 |
| 32.9 | 67.1 | —10.9 | 40.7 | 59.3 | +1.1 | 57.2 | 43.8 | 29.2 | 13 |
| 32.9 | 67.1 | —11.0 | 40.7 | 59.3 | +1.1 | 54.5 | 45.5 | 24.4 | 14 |

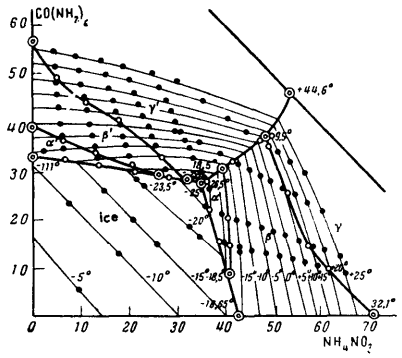



Fig. 3. Polythermal solubility diagram of the $CO(NH_2)_2$–$NH_4NO_3$–$H_2O$ system.

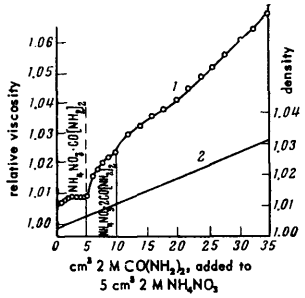



Fig. 4. Viscosity and density curves for the $CO(NH_2)_2$–$NH_4NO_3$–$H_2O$ system at 30°: 1) relative viscosity; 2) density.

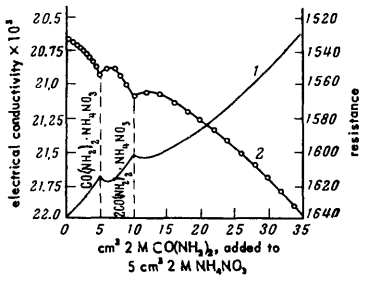



Fig. 5. Electrical conductivity curves for the $CO(NH_2)_2$–$NH_4NO_3$–$H_2O$ system at 30°: 1) electrical conductivity; 2) resistance.

salts at 30° — for 70% $NH_4OH$ and $NH_3$ : ($NH_3$ + $H_2O$) 0.7 — is 96.9%, of which 53.4% comes from the ammonium nitrate.

A complex of urea with ammonia starts to form at 0° and $NH_3$ : ($NH_3$ + $H_2O$) ratios of 0.4–0.5. At the ratio 0.4 the solid phase corresponds to the composition $NH_4NO_3$. $.CO(NH_2)_2$. $0.11NH_3$, at the ratio 0.5 to $NH_4NO_3.CO(NH_2)_2$. $.0.25NH_3$. It is suggested that as the $NH_3$ : ($NH_3$ + $H_2O$) ratio is increased the values of $n$ in the complex formed $CO(NH_2)_2.nNH_3$ will tend to unity.

The solubility of the salts at 30° increases with the $NH_3$ : ($NH_3$ + $H_2O$) ratio. At 0° such a relationship is not observed, owing to the formation of complexes.

On the basis of these results on the mutual solubility the authors [22] recommend for agricultural use a series of ammonia addition compounds, of composition given in Table 2.

Double compounds were not observed in a study of the $CO(NH_2)_2$–$NaNO_3$ anhydrous system [23]. The eutectic point is at $NaNO_3$ 29.5%, 83.9°.

The $CO(NH_2)_2$–$NH_4NO_3$–$NaNO_3$ ternary anhydrous system has been studied [23]. The ternary eutectic point is at $CO(NH_2)_2$ 45, $NH_4NO_3$ 47.5, $NaNO_3$ 7.59%, 37.1°.

The $NaNO_3$–$CO(NH_2)_2$–$H_2O$ three-component system was studied by the visual-polythermal method at temperatures from 40° to complete solidification (-19.55°). [24,25] The formation of an incongruently soluble compound $NaNO_3.CO(NH_2)_2.pH_2O$ was reported [25]. There are six crystallisation fields on the diagram (Fig. 6): ice, three fields of urea ($\alpha$, $\beta$, and $\gamma$ modifications), sodium nitrate, and the compound $NaNO_3.nCO(NH_2)_2.pH_2O$.

It was found that in the $CO(NH_2)_2$–$KNO_3$ binary system the eutectic point is at $CO(NH_2)_2$ 75.7, $KNO_3$ 24.3%, 110°. [26]

Fusion in the $CO(NH_2)_2$–$NH_4NO_3$–$KNO_3$ ternary system was also studied [26]. On the projection of crystallisation surface there is the field of the compound $2NH_4NO_3.KNO_3$, which melts incongruently at 170°. This field narrows to a transformation point at $CO(NH_2)_2$ 48, $NH_4NO_3$ 47, $KNO_3$ 5%, 66°. The ternary eutectic point is at $CO(NH_2)_2$ 44.3, $NH_4NO_3$ 49.9, $KNO_3$ 5.7%, 43° (Fig. 7).

TABLE 2.

| Chemical composition of ammines | | | | | | (NH₃ + H₂O) vapour pressure, mmHg, at | | | | Temperature of deposition of solid phase, °C |
|---|---|---|---|---|---|---|---|---|---|---|
| $NH_4NO_3$, % | $CO(NH_2)_2$, % | $NH_3$, % | $H_2O$, % | total N, % | organic N, % | 10° | 20° | 30° | 40° | |
| 45.1 | 15.2 | 20.1 | 19.6 | 39.41 | 7.09 | 550 | 708 | 917 | 1240 | —32.1 |
| 40.1 | 15.1 | 22.6 | 22.2 | 39.68 | 7.04 | 576 | 756 | 1034 | 1420 | —36.2 |
| 40.3 | 20.0 | 20.1 | 19.6 | 39.97 | 9.33 | 529 | 703 | 957 | 1310 | —29.6 |
| 50.0 | 10.0 | 20.1 | 19.6 | 38.71 | 4.66 | 453 | 616 | 108 | 1130 | —28.3 |

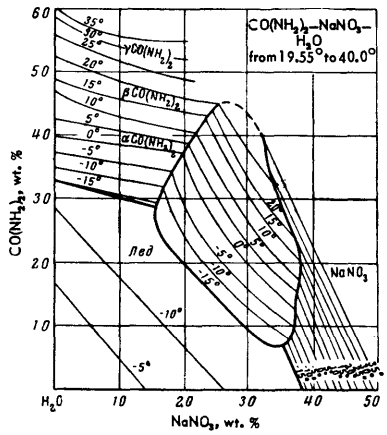



Fig. 6. Polythermal solubility diagram of the $CO(NH_2)_2$–$NaNO_3$–$H_2O$ system.

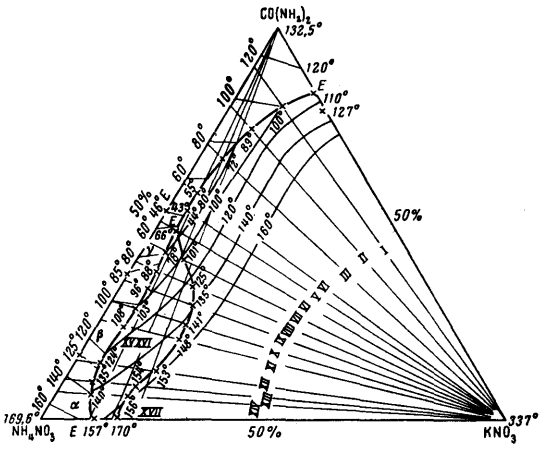



Fig. 7. Equilibrium diagram of the $CO(NH_2)_2$–$NH_4NO_3$–$KNO_3$ system.

Solubility in the $CO(NH_2)_2$–$KNO_3$–$H_2O$ system has been studied by several investigators [27,28]. Fig. 8 shows the diagram of the polytherms of this ternary system [27]; the investigation was by the visual-polythermal method, from 30° to complete solidification. Table 3 gives the compositions corresponding to the eutectic points according to the results of the different investigators.

Fig. 9 shows the 25° isotherm [29] of the $Ca(NO_3)_2$–$CO(NH_2)_2$–$H_2O$ system and the data for the system are also given in Table 4.

The compound $Ca(NO_3)_2.4CO(NH_2)_2$ was first isolated in 1918 by Bosch. A fertiliser of this composition is produced abroad; it has good physical properties, its hygroscopicity being less than that of calcium nitrate.

TABLE 3. Eutectic points in the $CO(NH_2)_2$–$KNO_3$–$H_2O$ system.

| Solution composition, wt. % | | | Temperature, °C | Reference |
|---|---|---|---|---|
| $CO(NH_2)_2$ | $KNO_3$ | $H_2O$ | | |
| 32.2 | 7.8 | 59.0 | —15 | 27 |
| 31.6 | 5.5 | 62.9 | —13.4 | 28 |

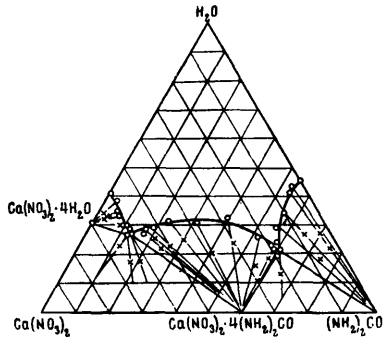



Fig. 9. Isothermal solubility diagram of the $Ca(NO_3)_2$–$CO(NH_2)_2$–$H_2O$ system at 25°.

TABLE 4. Invariant points in the $Ca(NO_3)_2$–$CO(NH_2)_2$–$H_2O$ system at 25°.

| Point No. | Liquid phase composition, wt. % | | | Solid phase |
|---|---|---|---|---|
| | $Ca(NO_3)_2$ | $CO(NH_2)_2$ | $H_2O$ | |
| 1 | 18.19 | 60.52 | 21.29 | $CO(NH_2)_2$—$Ca(NO_3)_2.4CO(NH_2)_2$ |
| 2 | 60.18 | 12.14 | 27.55 | $Ca(NO_3)_2.4H_2O$—$Ca(NO_3)_2.4CO(NH_2)_2$ |

## 3. Systems Containing Urea and Phosphates

Several papers describe the study of the common solubility of urea and various phosphates. The $CO(NH_2)_2$–$H_3PO_4$–$H_2O$ system was studied by the visual-polythermal and isothermal methods [11,30-32]. However, the information given by various authors on the presence of compounds in this system is contradictory. Matignon and Dodé [30] found the compound $CO(NH_2)_2.H_3PO_4$ and the compound $3CO(NH_2)_2.2H_3PO_4$ has been reported [11]. When solubility in this system was studied by the visual-polythermal method three crystallisation fields were observed: ice, urea, and solid solutions of the type $mCO(NH_2)_2.nH_3PO_4$. [31]

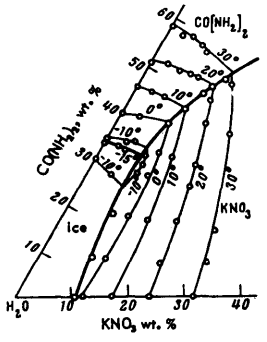



Fig. 8. Polythermal solubility diagram of the $CO(NH_2)_2$–$KNO_3$–$H_2O$ system.

According to recent information, in an isothermal study of solubility at 20° and 40° only urea, uronium phosphate, and their mixtures were observed in the solid phase [32]. Uronium phosphate dissolves congruently (Fig. 10).

The ammonium dihydrogen phosphate–urea–water system has been studied by the visual-polythermal method between -15.3° and 40° [33-35] and by the isothermal method at 25°. [20] It has one ternary point; chemical reaction between the components is not observed (Fig. 11). The cryohydric point is at $CO(NH_2)_2$ 28.8, $NH_4H_2PO_4$ 11.9, $H_2O$ 59.3%, -15.3°.

Solubility in the $(NH_4)_2HPO_4$–$CO(NH_2)_2$–$H_2O$ system was studied at temperatures from -16.6° to 30°. [14] The presence of the crystal hydrate of diammonium hydrogen phosphate $3(NH_4)_2HPO_4.2H_2O$ was confirmed (Fig. 12). Table 5 gives the invariant ternary points in this system.

The same work [14] gives the equilibrium diagram of the $CO(NH_2)_2$–$(NH_4)_2HPO_4$ system. The eutectic is at $CO(NH_2)_2$ 96.3, $(NH_4)_2HPO_4$ 3.7%, 126.7°.

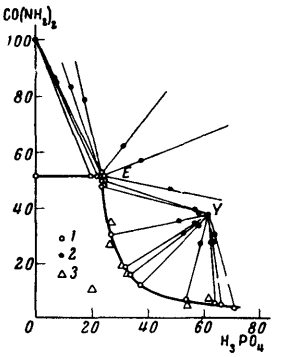



Fig. 10. Isothermal solubility diagram for the $CO(NH_2)_2$–$H_3PO_4$–$H_2O$ system at 20°. Phase compositions: 1) liquid; 2) solid; 3) liquid, calculated from the results of Blidin and coworkers[31]. *E* = uronium phosphate + urea. *Y* = uronium phosphate.

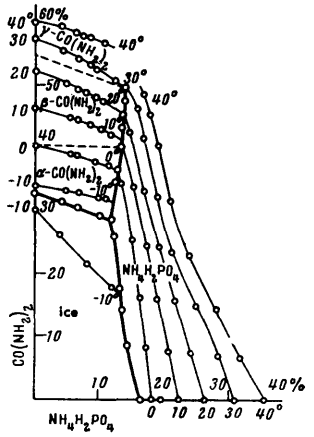



Fig. 11. Polythermal solubility diagram of the $CO(NH_2)_2$–$NH_4H_2PO_4$–$H_2O$ system.

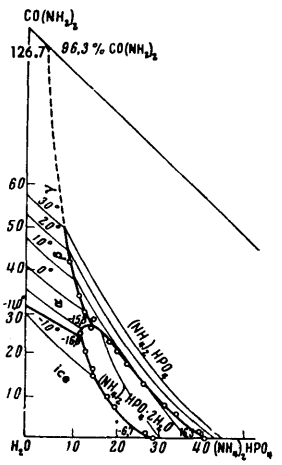



Fig. 12. Polythermal solubility diagram of the $(NH_4)_2HPO_4$–$CO(NH_2)_2$–$H_2O$ system.

TABLE 5. Invariant ternary points in the $(NH_4)_2HPO_4$–$CO(NH_2)_2$–$H_2O$ system.

| Point No. | Wt. % $CO(NH_2)_2$ | Wt. % $(NH_4)_2HPO_4$ | Wt. % $H_2O$ | per 100 moles dry salts: moles $CO(NH_2)_2$ | per 100 moles dry salts: moles $(NH_4)_2HPO_4$ | Crystallisation temperature, °C | Solid phase |
|---|---|---|---|---|---|---|---|
| 1 | 25.4 | 12.3 | 62.30 | 81.96 | 18.02 | —17.0 | ice + urea + $(NH_4)_2HPO_4.2H_2O$ |
| 2 | 26.7 | 15.90 | 57.4 | 79.87 | 20—13 | —16.2 | urea + $(NH_4)_2HPO_4$ + $(NH_4)_2HPO_4.2H_2O$ |

Solubility in the $KH_2PO_4$–$CO(NH_2)_2$–$H_2O$ system was studied by the visual-polythermal method from 35° to the temperature of complete solidification (-12.9°) [12] (Fig. 13). As the amount of potassium dihydrogen phosphate added is increased the temperature at the transformation point of one modification of urea into another falls from 22.5° to 1°. Evidently there is a region of restricted solid solutions of urea in $KH_2PO_4$ and the formation of compounds between the components is not observed.

## 4. Systems Containing Urea and Sulphates

Solubility in the $CO(NH_2)_2$–$(NH_4)_2SO_4$–$H_2O$ ternary system has been studied from -29° to 40°.[14] The polytherm diagram has six crystallisation fields: ice, solid solutions, the $\alpha$, $\beta$, and $\gamma$ modifications of urea, and the $(NH_4)_2SO_4$. There is one ternary point, at $CO(NH_2)_2$ 20, $(NH_4)_2SO_4$ 32, $H_2O$ 48%, -29°. Along its boundary with the urea field the solid solutions field stretches up to the eutectic of the $CO(NH_2)_2$–$H_2O$ binary system. As the temperature is raised the solid solutions field narrows and shifts to the urea side (Fig. 14).

The solubility of the $K_2SO_4$–$CO(NH_2)_2$–$H_2O$ system was studied by the visual-polythermal method from 25° to the temperature of complete solidification (-13°).[36] The presence of potassium sulphate in the solution has little effect

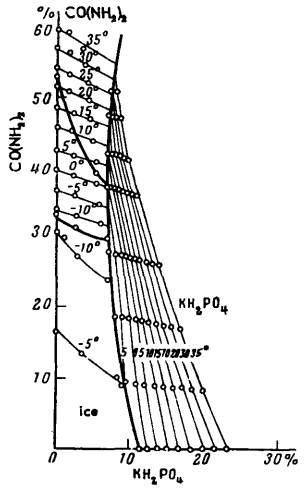



Fig. 13. Polythermal solubility diagram of the $KH_2PO_4$–$CO(NH_2)_2$–$H_2O$ system.

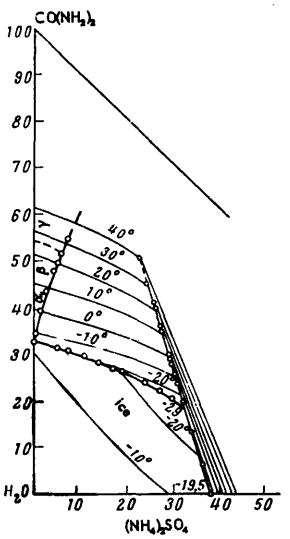



Fig. 14. Polythermal solubility diagram of the $CO(NH_2)_2$–$(NH_4)_2SO_4$–$H_2O$ system.

on the change in solubility of the urea. The ternary eutectic is at $CO(NH_2)_2$ 31.2, $K_2SO_4$ 4.9%, -13°.

The $CaSO_4$–$CO(NH_2)_2$–$H_2O$ ternary system was studied by the isothermal method[37–39] at 0°, 20°, 25°, 40°, and 70°. The compound $CaSO_4 \cdot 4CO(NH_2)_2$ is formed in the system (Fig. 15), and was first studied by Wittaker and coworkers[40].

Solubility in the $MgSO_4$–$CO(NH_2)_2$–$H_2O$ ternary system has been studied by the isothermal and visual-polythermal methods[41–45]. The complex $MgSO_4 \cdot 4CO(NH_2)_2 \cdot H_2O$ exists between 5° and 26° and decomposes at lower temperatures with liberation of urea, and at higher temperatures is converted into $MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$ (Fig. 16). The lower the temperature, the less the influence of urea on the solubility of magnesium sulphate.

5. Systems Containing Urea, Chlorides, and Other Compounds.

The KCl–$CO(NH_2)_2$–$H_2O$ system has been studied by several investigators[13,46,47] from -19.4° to 40°. There is no chemical interaction between the components of the

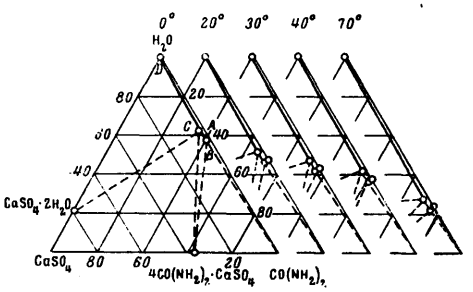



Fig. 15. Isothermal solubility diagrams of the $CaSO_4$–$CO(NH_2)_2$–$H_2O$ system (g per 100 g solution).

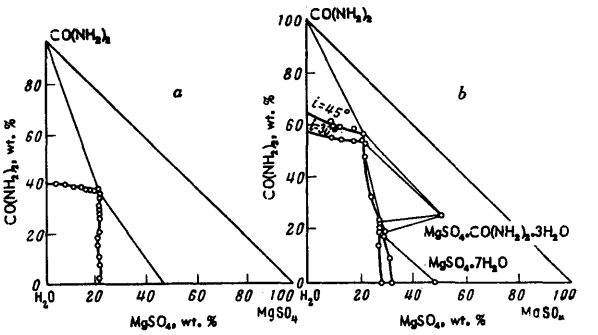



Fig. 16. Isothermal solubility diagrams of the $CO(NH_2)_2$–$MgSO_4$–$H_2O$ system: *a*) 0° isotherm; *b*) 30° and 45° isotherms.

system. The solubility of urea decreases in the presence of KCl. The ternary point of the system is at KCl 13.45, $CO(NH_2)_2$ 26.5%, -19.4°.

Solubility in the KOH–$CO(NH_2)_2$–$H_2O$ system has been studied[48]. Two solubility isotherms (0° and 30°) have been given. At 30° the isotherm has three parts, with the solid phases: $KOH \cdot H_2O$, $KOH \cdot 2H_2O$, and $CO(NH_2)_2$ (Fig. 17).

Several multicomponent systems have been studied to choose optimal conditions for the production of complex fertilisers. The $CO(NH_2)_2$–$NH_4NO_3$–$NH_4H_2PO_4$–$H_2O$ system was studied by the visual-polythermal method from -7° to 50° with $NH_4H_2PO_4$ : $NH_4NO_3$ weight ratios from 0.5 to 4 and total concentrations in the saturated solution of 30, 35, 37, and 40%,[49] and by the isothermal method at 25° and 50°.[20] The composition of the eutonic solution at 25° is: $CO(NH_2)_2$ 40.07, $NH_4NO_3$ 49.03, $NH_4H_2PO_4$ 0.78%.[20] The kinetics of the decomposition of urea in solutions in the presence of ammonium dihydrogen phosphate has been studied[20] at 50°. The 0° solubility isotherm in the $H_3PO_4$–$NH_3$–$CO(NH_2)_2$–KCl–$H_2O$ system has been studied[50]. In pursuing practical objectives, the authors studied restricted regions of this system in accordance with the agricultural requirements for the ratio $N : P_2O_5 : K_2O$ in liquid complex fertilisers. In addition, compositions of solutions for the molar ratios $NH_3 : H_3PO_4$ 1.7, 1.6, and 1.5. A linear relation was also found between the concentration of the total nutrients in solution and the temperature of crystallisation of the solid phase with which this solution is in equilibrium (Fig. 18).

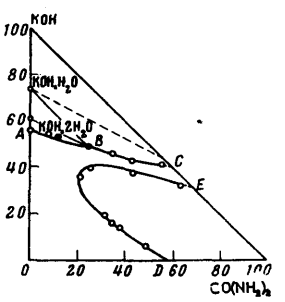



Fig. 17. Isothermal solubility diagram of the KOH–$CO(NH_2)_2$–$H_2O$ system at 30°.

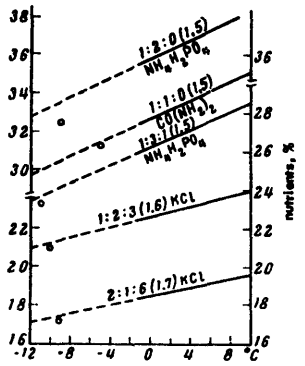



Fig. 18. Circles: measured values. Broken lines: extrapolated values. In parentheses: $NH_3:H_3PO_4$ molar values.

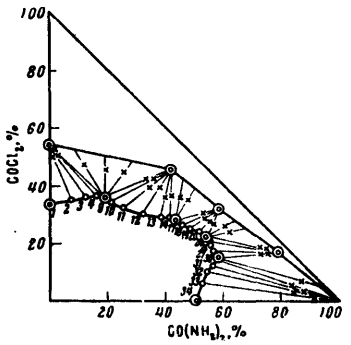



Fig. 20. Isothermal solubility diagram of the $CoCl_2-CO(NH_2)_2-H_2O$ system at 20°.

Solubility in the $CO(NH_2)_2-NH_4NO_3-NH_3-H_3PO_4-KCl-H_2O$ system at 0° was also studied only for selected ratios of the nutrients[50]. Fig. 19 gives a diagram of this system at 0°.

## 6. Systems Containing Urea and Trace Elements

In recent years several systems containing urea and compounds used as sources of trace elements (boron, manganese, copper, zinc, cobalt, etc.) have been investigated.

Mutual solubility in the $CoCl_2-CO(NH_2)_2-H_2O$ system at 20° has been studied[51] (Fig. 20, Table 6).

The 30° solubility isotherm of the $CoSO_4-CO(NH_2)_2-H_2O$ system[42,43] consists of four branches. Two complexes of cobalt and urea are formed in this system: $CoSO_4.2CO(NH_2)_2.4H_2O$ and $CoSO_4.6CO(NH_2)_2$ (Fig. 21).

In studying solubility in the $NiSO_4-CO(NH_2)_2-H_2O$ system[52] compounds analogous to those formed by urea with cobalt sulphate were found: $2CO(NH_2)_2.NiSO_4.4H_2O$ and $6CO(NH_2)_2.NiSO_4$. The system was studied at 25° and 40°.

TABLE 6. Invariant points of the $CoCl_2-CO(NH_2)_2-H_2O$ system.

| Composition of the solution, wt. % | | | Composition of the solid residues, wt. % | | Solid phase |
|---|---|---|---|---|---|
| $CoCl_2$ | $CO(NH_2)_2$ | $H_2O$ | $CoCl_2$ | $CO(NH_2)_2$ | |
| 33.79 | — | 66.21 | 50.64 | — | $CoCl_2-6H_2O$ |
| 36.01 | 19.87 | 44.62 | 47.72 | 11.67 | $CoCl_2.6H_2O+CoCl_2.2(NH_2)_2CO.2H_2O$ |
| 28.28 | 43.19 | 28.53 | 36.15 | 45.13 | $CoCl_2.2(NH_2)_2CO.2H_2O+CoCl_2.4(NH_2)_2CO.2H_2O$ |
| 23.03 | 54.62 | 22.35 | 25.70 | 60.64 | $CoCl_2.4(NH_2)_2CO.2H_2O+CoCl_2.10(NH_2)_2CO.2H_2O$ |
| — | 51.15 | 48.85 | — | 95.63 | $Co(NH_2)_2$ |

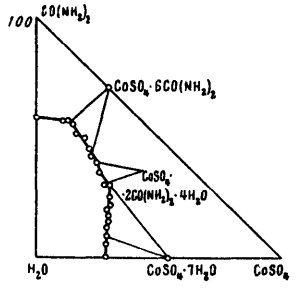



Fig. 21. Isothermal solubility diagram of the $CoSO_4-CO(NH_2)_2-H_2O$ system at 30°.

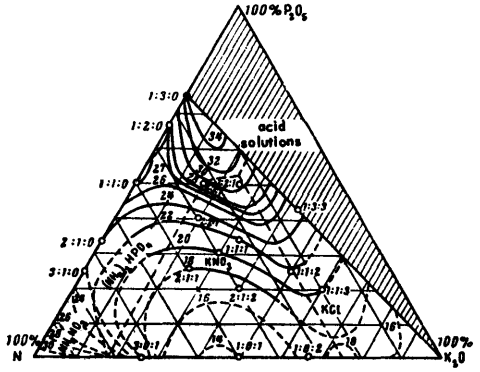



Fig. 19. Isothermal solubility diagram of the $CO(NH_2)_2-NH_4NO_3-H_3PO_4-NH_3-KCl-H_2O$ system at 0°.

The solubility of zinc sulphate in the presence of urea was studied by the visual-polythermal method at temperatures from -20.4° (the temperature of complete solidification) to 25°.[53] The ternary eutectic point is at $ZnSO_4$ 25.4, $CO(NH_2)_2$ 26.2, $H_2O$ 48.4%. Formation of complexes was not observed.

Solubility in the $CuSO_4-CO(NH_2)_2-H_2O$ system was also studied by the visual-polythermal method[42] from -18.4° to 30°. The solutions are viscous. The system tends to give supersaturated and supercooled solutions. The solubility of copper(II) sulphate rises from 12.5% at the eutectic point of the $CuSO_4-H_2O$ binary system to 23% at the ternary eutectic point, which suggests chemical reaction between the components. The concentrations of urea in solutions corresponding to the eutectic points of the binary and ternary systems are almost the same. The ternary eutectic

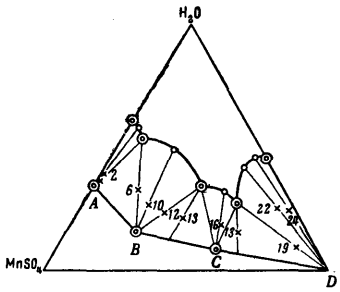



Fig.22. Isothermal solubility diagram of the $MnSO_4$–$CO(NH_2)_2$–$H_2O$ system at 20°: *A*) $MnSO_4.4H_2O$; *B*) $MnSO_4.CO(NH_2)_2.2H_2O$; *C*) $MnSO_4.4CO(NH_2)_2.2H_2O$; *D*) $CO(NH_2)_2$.

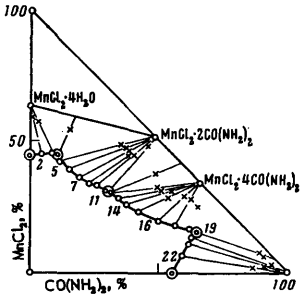



Fig.23. Isothermal solubility diagram of the $CO(NH_2)_2$–$MnCl_2$–$H_2O$ system at 30°.

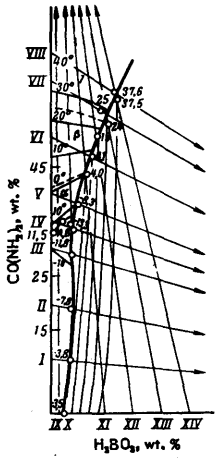



Fig.24. Polythermal solubility diagram of the $H_3BO_3$–$CO(NH_2)_2$–$H_2O$ system.

point is at $CO(NH_2)_2$ 32, $CuSO_4$ 23, $H_2O$ 45%, -18.4°. It has been suggested that two complexes of urea and copper(II) sulphate may be formed, by analogy with cobalt sulphate, in the liquid phase, but complexes have not been observed in the solid phase.

Solubility has been studied [54-56] in the $MnSO_4$–$CO(NH_2)_2$–$H_2O$ system at 10°, 20°, and 25° (Fig. 22).

The solubility in the $MnCl_2$–$CO(NH_2)_2$–$H_2O$ system was studied at 20° and 30° [57] and the specific gravity and viscosity of the equilibrium solutions were measured. Two compounds $MnCl_2.2CO(NH_2)_2.H_2O$ and $MnCl_2.4CO(NH_2)_2$ crystallise at 20° in addition to the two components, and the compounds $MnCl_2.2CO(NH_2)_2$ and $MnCl_2.4CO(NH_2)_2$ at 30° (Fig. 23).

Mutual solubility of the components in the $H_3BO_3$–$CO(NH_2)_2$–$H_2O$ system has been studied at temperatures from -14° (the temperature of complete solidification) to 50°. [58] Formation of compounds was not observed. The ternary eutectic point is at $H_3BO_3$ 3.7, $CO(NH_2)_2$ 36.5, $H_2O$ 59.8%, -14°. The polytherm of the ternary system is divided into three branches: ice, urea, and boric acid. The solubility of urea is almost unchanged in the presence of boric acid, but the solubility of boric acid rises slightly in the presence of urea (Fig. 24).

## III. TECHNOLOGY OF THE PRODUCTION OF COMPLEX FERTILISERS WITH USE OF UREA

The results of the physicochemical investigations were used to choose optimal conditions for various processes for the production of urea-containing fertilisers. Thus the production of the nitrogenous fertiliser, known on the world market under the trade name of "Calurea", is based on the production of a complex of urea and calcium nitrate. The ratio of the components in the compound corresponds to the formula $Ca(NO_3)_2.4CO(NH_2)_2$. This fertiliser displays better physicochemical properties than each of its constituents, that is, lower hygroscopicity and less deterioration on storage. When the calcium nitrate in this fertiliser is in excess then the mixture exhibits a greater hygroscopicity than calcium nitrate alone. The fertiliser is made by dissolving accurately measured quantities of urea in hot concentrated solutions of calcium nitrate (specific gravity 65° Bé) at 80–100°. The compound $Ca(NO_3)_2.4CO(NH_2)_2$ crystallises out on cooling [11]. Many patents have proposed different methods for obtaining fertilisers including $Ca(NO_3)_2.4CO(NH_2)_2$. [11,59-62] The mixtures can include salts of magnesium, calcium, and other metals. Fertilisers have also been patented in which urea is combined with calcium or magnesium basic nitrate, for example $Ca(OH)NO_3.2CO(NH_2)_2$. [63]

The existence of the compound $Ca(NO_3)_2.CO(NH_2)_2.3H_2O$ has been established. In comparison with "Calurea" it contains less urea and is readily granulated [64]. Urea is known to form solid solutions with some fertilising salts (for example, with ammonium sulphate, potassium phosphate, etc.) [12,14].

Several methods for preparing fertilisers containing urea and ammonium sulphate have been proposed [65,66]. Urea is dissolved in sulphuric acid at 80–1000° and the mixture neutralised with an excess of ammonia. Owing to the heat of reaction most of the water is vaporised. Then the mixture is dried and ground [65].

Mixed crystals of urea and $KNH_4HPO_4$ have been suggested for use as a fertiliser [67].

The widest use of urea is in the production of mixed fertilisers, which are composed of simple or double superphosphate, potassium salts, and other compounds. Urea is employed in these fertilisers predominantly as its ammines, often mixed with ammonium nitrate for the ammoniation of superphosphates [68-73].

Urea ammines cause hardly any corrosion of equipment made of ordinary steel.

Solutions obtained at one of the stages in the production of urea — at the exit of the synthesis column or after distillation — have also been suggested for use in the ammoniation of superphosphate. The fertiliser contains about 3.65% N, and 16.3% $P_2O_5$.[70]

Jensen has described[71] a process for the production of complex fertilisers containing urea. The experiments were made on a semi-plant apparatus using a TVA-type† ammoniator–granulator and a horizontal rotating drying drum. Urea ammines were used for the ammoniating solution and simple or double superphosphates and potassium chloride were employed. The author notes that no special difficulties were experienced in granulating complex fertilisers with $N:P_2O_5:K_2O$ ratios of 8:16:16, 10:10:10, or 5:20:20. The duration of the material in the granulator was 10 min, and the temperature of the product at entry 66–93°. It was in the drying drum for 15 min, and the temperature of the product on leaving was 66–121°. The hydrolysis of the urea was negligible.

Phillips[72] studied the conditions for granulating complex fertilisers containing simple or double superphosphate, potassium chloride, ammonium sulphate, etc. in an apparatus similar to that described. Ammoniating solutions of two compositions were used: ammines of ammonium nitrate and urea and ammonium nitrate ammine alone. It was noted that granulation proceeds best in working with solutions containing both ammonium nitrate and urea.

Jewell[74] studied, under laboratory conditions, the granulation of complex fertilisers with $N:P_2O_5:K_2O$ = = 10:10:18, obtained from superphosphate made from Moroccan phosphorite, ammonium nitrate or sulphate, urea, and potassium chloride. The amount of urea introduced into the fertiliser was varied from 2 to 15%. A mechanism has been suggested[74] for the hydrolysis of urea during the production and storage of complex fertilisers, depending on their acidity or alkalinity. The effect of moisture, acidity, and urea content on the stability of complex fertilisers has been determined.

The optimal conditions for obtaining and storing fertilisers so as to retain the stability of the product have been found, namely, entry temperature of product in drying $\geqslant$ 70°, reaching 90° during drying for $\geqslant$ 15 min. Temperature of storage of the fertiliser $\geqslant$ 35°, then the loss of nitrogen is negligible.

Several authors[11,73,75,76] note that to obtain fertilisers with good physicochemical properties, urea must be added in limited amounts. Several Japanese patents propose the manufacture of mixed fertilisers based on urea and superphosphate; the superphosphate should be neutralised without fail, for otherwise the urea reacts with the monocalcium phosphate to form uronium phosphate, dicalcium phosphate, and water[77] by the reaction:

$$Ca(H_2PO_4)_2\cdot H_2O+CO(NH_2)_2=H_3PO_4\cdot CO(NH_2)_2+CaHPO_4+H_2O.$$

Because of the presence of water the mixture becomes greasy, and unsuitable for spreading. Dolomite[78], ammonia[79,80], sodium hydrogen carbonate[81] are among the neutralising additions that have been suggested.

When neutralising additions are made, the monocalcium phosphate is partly or completely converted into dicalcium phosphate by the reaction:

$$CaH_2P_2O_8\cdot H_2O+CaCO_3+H_2O=2CaHPO_4\cdot 2H_2O+CO_2,$$

during which the hygroscopic moisture is converted into the water of crystallisation of the dicalcium phosphate. During the reaction of dicalcium phosphate dihydrate with urea, the latter accelerates the loss of the water of crystallisation[77]. Mixtures of dicalcium phosphate and urea exhibit approximately the same hygroscopicity as urea itself, with the exception of the instances when urea is present in small amounts.

Methods have been developed for making complex fertilisers with use of urea based on the products of the sulphuric acid[82–91] and nitric acid[92–102] treatment of phosphate raw materials. Thus, a Japanese patent proposes the addition of urea to a suspension of phosphogypsum in phosphoric acid, obtained by the decomposition of natural phosphate with sulphuric acid. The reaction is carried out at $\geqslant$ 80°. The suspension is then neutralised with ammonia and the product is dried at 70° to give a fertiliser with the composition (%): $CaSO_4.4CO(NH_2)_2$ 77.48, $NH_4H_2PO_4$ 20.86, $H_2O$ 1.9, $CaHPO_4.2H_2O$ traces, $P_2O_5$ 12.35, N 26.32. $N:P_2O_5$ 2.1:1.

Another Japanese patent[84] recommends the treatment of phosphorite with a mixture of sulphuric acid and urea followed by separation of the reaction products. The decomposition proceeds by the equation:

$$Ca_3(PO_4)_2+3H_2SO_4+12CO(NH_2)_2=2H_3PO_4+3[CaSO_4\cdot 4CO(NH_2)_2].$$

The reaction products contain calcium sulphate–4-urea in the precipitate and phosphoric acid and urea in the solution. Sodium alkylbenzenesulphonate is added to the reaction mixture to facilitate filtration. The yield of $H_3PO_4$ is 95%. Calcium sulphate is known to give a double compound with urea $CaSO_4.4CO(NH_2)_2$[40] which exhibits good physical properties. Apparently when urea is added to the product of the decomposition of phosphatic raw materials with sulphuric acid, which contain calcium sulphate, this double salt is formed. The Japanese investigators investigated the conditions for its production and determined its physicochemical constants and solubility in water[39,86–89].

Several patents recommend the use of phosphogypsum, which is a byproduct in the extraction method of making phosphoric acid, for mixing with urea.

Several articles and patents describe the production of urea-containing complex fertilisers based on the decomposition of phosphates with nitric acid. Japanese investigators published the first studies of the chemistry of the process[92,93]. Depending on the ratio between phosphorite, nitric acid, and urea, various reactions can take place, with the formation of calcium phosphates, uronium phosphate, and calcium nitrate–urea double compound.

An investigation of the hygroscopicity of the fertilisers produced showed that the best results are obtained when 1 mole $Ca_3(PO_4)_2$ takes not less than 4 moles conc. nitric acid (60%) and not less then 9 moles urea. The product contains $P_2O_{5\,tot}$ 9, $N_{tot}$ 24–25% (19–20% in the amide form).

Soviet investigators confirmed that the final products are double compounds: calcium nitrate–urea and uronium phosphate[94,95]. It was noted that uronium nitrate is

† TVA = Tennessee Valley Authority (Ed. of Translation).

formed as an intermediate. The following reactions take place:

(1) $Ca(NO_3)_2 \cdot 4H_2O + 2H_3PO_4 \cdot 5H_2O + 2CO(NH_2)_2 = 2CO(NH_2)_2 \cdot HNO_3 + Ca(H_2PO_4)_2 \cdot H_2O + aq$,

(2) $Ca(NO_3)_2 \cdot 4H_2O + 4CO(NH_2)_2 = Ca(NO_3)_2 - 4CO(NH_2)_2$,

(3) $2CO(NH_2)_2 \cdot HNO_3 + Ca(H_2PO_4)_2 \cdot H_2O + 4CO(NH_2)_2 = Ca(NO_3)_2 \cdot 4CO(NH_2)_2 + 2CO(NH_2)_2 \cdot H_3PO_4$.

Some authors propose to neutralise the nitric acid extract with CaO, $Ca(OH)_2$, $CaCO_3$, or ammonia before or after the introduction of urea [96-100]. Others add the urea without neutralisation [93,97,98].

It is recommended to add urea to the product of the decomposition of phosphatic raw materials with strong nitric acid (70%) — nitrosuperphosphate — which contains 6–8% free acid; this prevents the liberation of oxides of nitrogen from the product and facilitates the production of a fertiliser with good physicochemical properties [101,102].

Methods have also been proposed for the production of urea-containing complex fertilisers based on the treatment of phosphates with a mixture of sulphuric and nitric acids [97,103,104]. For example [104], a mixture of 100 g natural phosphate (31.1% $P_2O_5$), 68 g $K_2O$, and 50 g urea is treated with a mixture of 35 g $H_2SO_4$ (98%) and 17.23 g $HNO_3$ (50%). There is 16% excess of acid against the stoichiometric amount. The product is treated with 8 g $MgCO_3$. The fertiliser obtained contains: $P_2O_{5\,tot}$ 7.91, $P_2O_{5\,avail}$ 7.58, $P_2O_{5\,sol}$ 7.5, $N_{nitr}$ 5.43, $N_{urea}$ 5.06, $K_2O$ 8.52%.

A method for making complex fertilisers during urea synthesis has been proposed [105]. Phosphorus pentoxide is used to remove water from the sphere of reaction during the conversion of carbamate into urea and an excess of ammonia is introduced. The reactions are:

$$NH_4CO_2NH_2 = NH_2CONH_2 + H_2O;$$
$$3H_2O + P_2O_5 = H_3PO_4;$$
$$2NH_3 + H_3PO_4 = (NH_4)_2HPO_4;$$

and yield a mixture of urea and diammonium hydrogen phosphate. The introduction of phosphorus pentoxide lowers the temperature for the synthesis of urea, accelerates the process, and increases the yield of urea. It has been found that at 160° the conversion is 53% with respect to the $NH_3$, 48% with respect to the $CO_2$. The fertiliser contains N 31, $P_2O_5$ 33%.

A method for obtaining double concentrated fertilisers using urea and phosphorus pentoxide as raw materials has been patented in the USA. [106] In this method a solution of urea is mixed with $P_2O_5$, the mixture is cooled and ammonia is added, giving a melt containing urea and $NH_4H_2PO_4$; the slab is then granulated. The fertiliser contains N 24, $P_2O_5$ 31%.

A method has been proposed [107] for making highly concentrated fertilisers containing 60–81% nutrients by fusing urea with monocalcium phosphate and potassium metaphosphate. The melting point of the mixture is 122–129°. The fusion of urea, readily soluble $KH_2PO_4$, and $KPO_3$ (sparingly soluble in water) with the introduction into the melt of trace elements enables complex fertilisers to be produced with any combination of soluble and insoluble potassium phosphates and various ratios of nutrients. A disadvantage of the fusion process is the partial decomposition of the urea (2%). [107]

Shell Chemicals is commercially producing a fertiliser made by fusion sulphur with urea and granulating the product; it contains urea 40, sulphur 10%. [108]

In addition to the use of urea as a constituent of complex and complex mixed fertilisers, it (together with ammonia) is a principal source of nitrogen in the manufacture of liquid complex fertilisers. Unlike ammonium nitrate, urea weakly salts out ammonium phosphate, therefore liquid fertilisers based on it have a higher concentration of nutrients — 27%, instead of 15–17% for ammonium nitrate basis (liquid concentrated fertiliser does not crystallise at 0°).

Urea is known to form various polymeric compounds. The polymer with formaldehyde gives under certain conditions a fertiliser with a long-acting form of nitrogen. Such a fertiliser is especially effective on irrigated soils and under conditions of a moist climate. This increases the degree of utilisation of the nitrogen and decreases its loss.

The problems connected with the use of urea in liquid fertilisers and also the composition of the fertilisers which contain slow-acting forms of nitrogen will not be discussed in this article.

From this review it is evident that there have been many physicochemical investigations of systems which include urea and other fertilisers as components. Knowledge of the equilibrium systems allows optimal process conditions to be selected for obtaining urea-containing fertilisers of required composition, whether liquid or solid.


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# FLUORINATED STEROIDS

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When studying methods for introducing an oxygen substituent at position 11 of a steroid molecule, Fried and Sabo[1] in 1954 observed unexpectedly that 9α-fluoro-11β,17α,21-trihydroxypregn-4-ene-3,20-dione has a several times greater hormonal and anti-arthritic activity than has cortisol. This discovery formed the beginning of a new field of research — the synthesis of modified steroidal compounds — in steroid chemistry. The number of papers and patents which have appeared during the past decade on the chemistry and pharmacology of these compounds has already reached thousands. The introduction of additional alkyl groups, heteroatoms, and double bonds into a steroid molecule produces a considerable increase in the hormonal activity of natural steroids. Special interest attaches to fluorinated steroids among modified steroids, since the introduction of fluorine into a steroid molecule produces a great change in the physiological activity of the hormone.

## I. METHODS OF INTRODUCING FLUORINE INTO A STEROID MOLECULE

The synthesis of 9α-fluoro-11β,17α,21-trihydroxypregn-4-ene-3,20-dione was first accomplished by Fried and Sabo[1], who opened the 9β,11β-oxide by means of hydrogen fluoride. Since then the cleavage of oxides has become one of the main methods for introducing fluorine into many positions in the steroid molecule. However, the exceptionally high physiological activity of fluorinated steroids has led investigators to seek new methods for the synthesis of fluorinated steroids. Thus methods have been worked out for introducing fluorine on the basis of the reaction of steroid olefins with an *N*-halogeno-amide and hydrogen fluoride[2] and with lead tetrafluoride[3], the reaction of steroid ketones with sulphur tetrafluoride[4], and of hydroxy-compounds with silver fluoride or hydrogen fluoride and other reagents; perchloryl fluoride has been studied and used for the synthesis of fluorinated steroids[5].

The above methods enable compounds to be prepared having isolated fluorine atoms, as well as *gem*- and *vic*-difluoro-derivatives. By combining several methods it is possible to introduce successively into the steroid molecule two, three, and four fluorine atoms, which produces a marked increase in the physiological activity of the steroids (see Section II).

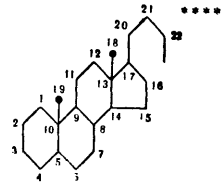
The scope of the various methods of synthesising fluorinated steroids is summarised in Table 1, from which it is seen that each method has its own specific field of application, seldom overlapping with those of other methods. Therefore the suitability of different processes for introducing fluorine at a given position in the steroid molecule can be compared only in a few cases. Thus the synthesis of 6-fluoro-steroids, for example, can be effected by three methods, based on the addition of fluorine-containing reagents to the 5–6 double bond. When the steroid contains one double bond, synthesis through the 5α,6α-oxides is mostly used. With polyunsaturated steroids the corresponding oxides are obtained unselectively and in very low yields, and it therefore becomes more convenient to apply the addition of mixed halogens. The addition of lead tetrafluoride has the advantage over both these methods that it enables fluoro-derivatives having the 6α configuration to be obtained directly.

### 1. Opening of Steroid Oxides by Fluorine-Containing Reagents

The introduction of a fluorine atom into a steroid molecule by opening an epoxide with hydrogen fluoride, which takes place by an $S_N2$ mechanism and leads to a *trans*-diaxial cleavage of the oxide ring, has become one of the principal methods for introducing a fluorine atom not only into position 9 but also into positions 2, 6, 12, 15, 17, and 20 in the steroid molecule, since the corresponding epoxides are quite accessible and the techniques are simple.

Fluorinating agents which have been used in these cases are, besides hydrogen fluoride, 48% hydrofluoric acid, potassium hydrogen fluoride, and the boron trifluoride–ether

TABLE 1. Preparative possibilities of various methods for the fluorination of steroids.



| Method | Fluorine introduced at position | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2α | 2β | 3α | 3β | 4 | 5α | 6α | 6β | 7α | 7β | 9α | 10β | 11α | 11β | 12α | 15α | 16α | 16β | 17α | 17β | 20α | 20β | 21 | 22 |
| Cleavage of oxides | | +*** | | | +*** | + | | + | | | + | + | | | + | + | | | + | | | + | | |
| Addition of mixed halogens to double bond | | | | | | | | + | | | | | | + | | | | + | | | | | | |
| Addition of $PbF_4$ to double bond | | | | | | +* | +* | | + | | | | | | | | | | | | | | | |
| Addition of $FClO_3$ to double bond | | | | | + | | | | | | | | | | | | | | | | | | | |
| Addition of HF to double bond | | | | | | + | | | | | + | | | | | | | | | | | | | + |
| Addition of $C_6H_5IF_2$ to double bond | | | | | | | | + | | + | | | | | | | | | | | | | | |
| Addition of $FClO_3$ to phenolic steroids | | | | | | | | | | | | + | | | | | | | | | | | | |
| Replacement of hydroxyls | | | + | + | | | + | | | | | | | + | | + | | | + | + | | | | |
| Replacement of toluene-p-sulphonate and methanesulphonate groups | | | + | + | | | | | | | | | | | | | + | + | + | | | | + | |
| Replacement of other halogens by fluorine | | | | + | | | + | | | | | | | | | | | + | | | | | + | |
| Replacement of hydrogen by fluorine ($FClO_3$) | + | | | | + | | + | + | | | | | | | | | + | + | | | | | + | |
| Replacement of >C=O by fluorine ($SF_4$) | | | +** | +** | | | | | | | | | +** | +** | | | | | +** | +** | +** | +** | | |

* Vicinal difluoride formed.

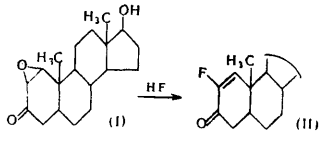
** Geminal difluoride formed.

*** Fluorine atom adjacent to double bond.

**** Here and subsequently the heavy black dots denote methyl groups.

complex. The effect of the solvent, the temperature, and the duration of the reaction, and also of neighbouring substituents, on the course of the reaction has been studied.

Relatively little work has been done on the action of fluorine-containing reagents on oxide groups in the A ring of a steroid molecule. Thus cleavage of the 1β,2β-oxide (I) with hydrogen fluoride is accompanied by dehydration and yields the 2-fluoride (II) containing a fluorine atom adjacent to a double bond[6]:

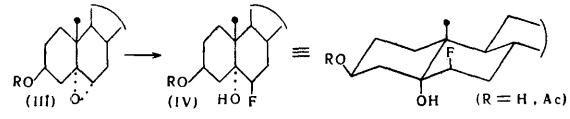


Fission of the 2α,3α-oxide under the same conditions gives the 2β-fluoro-3α-hydroxy-compound[7,8]. 4,5-Epoxides have been cleaved mainly with hydrochloric and hydrobromic acids, with the formation of 4-chloro- and 4-bromo-steroids[9,10].

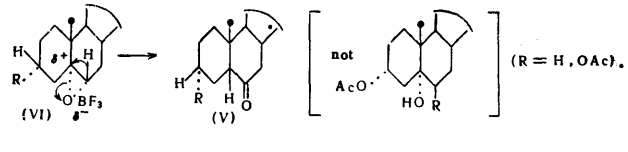
On the other hand, the cleavage of 5,6-epoxides has been subjected to quite detailed study on numerous examples and with various fluorinating reagents. The boron trifluoride–ether complex has been most widely used as such an agent, the reaction usually being conducted in benzene or in a mixture of benzene and ether at room temperature[11].

The opening of steroid 5α,6α-epoxides with the boron trifluoride–ether complex, first studied by Henbest and Wrigley[11,12], gives different products depending on the nature and the stereochemistry of the substituent attached to $C_{(3)}$. An epoxide which is unsubstituted at $C_{(3)}$ or else has a 3α-acetoxy-group (VI) gives as main product the corresponding $C_{(6)}$ ketone with rings A and B linked in the *cis*-configuration (V).

On the other hand, the 3β-hydroxy-epoxide — or its acetate (III) — undergoes cleavage by a quite different mechanism, the main product then being a fluorohydrin (IV).

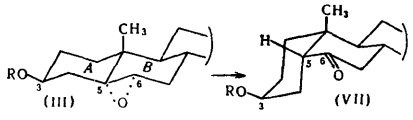


This course of the reaction was explained by considering the electronic and configurational factors. In unsubstituted epoxides (VI: R = H), boron trifluoride produces partial ionisation of the bond linking the epoxy-oxygen to the more alkylated $C_{(5)}$, promoting a simultaneous 1,2-hydride shift with the formation of a $C_{(6)}$ ketone (V).

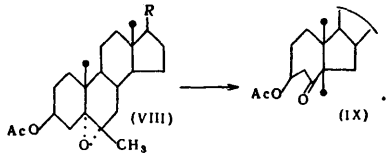


In the case of the 3β-alcohol (III) or its ester, however, two factors tend to prevent formation of the $C_{(6)}$ ketone. The first of these, the electronic factor, diminishes the partial ionisation of the bond linking the epoxy-oxygen to $C_{(5)}$ (this factor is necessary for formation of the $C_{(6)}$

ketone) owing to the increased inductive ($-I$) effect of the boron trifluoride–ether complex coordinated with the 3$\beta$--alcohol or ester. In this case the steric factor acts in the same direction, since formation of the $C_{(6)}$ ketone (VII) from (III) would have appreciably increased non-bonding 1,3-interactions in ring A, and the 3$\beta$-hydroxyl would have passed from the equatorial to the axial position.

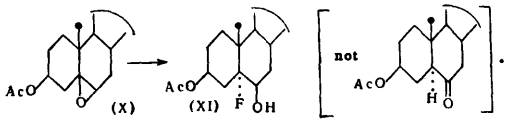


Thus in this case the second reaction, resulting in formation of the fluorohydrin (IV), should predominate. When position 6 is substituted (e.g. by a methyl group) the reaction of the 5$\alpha$,6$\alpha$-oxide (VIII) with boron trifluoride is anomalous, being accompanied by rearrangement to an *A*-homo--*B*-nor-compound (IX).[13]

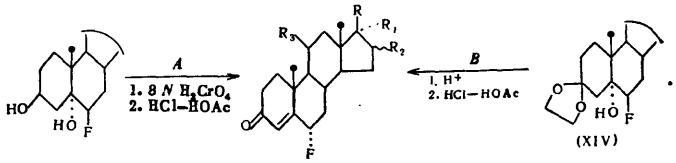


In the case of the 3$\alpha$-acetate of the 5$\alpha$,6$\alpha$-epoxide (VI: R = OAc), the above electronic and conformational factors act in opposite directions, but the predominance of the latter results in a very high yield of $C_{(6)}$ ketones (V).

5$\beta$,6$\beta$-Epoxides with no 3-substituent yield the $C_{(6)}$ ketone, whereas the 3$\beta$-acetoxy-compound (X) gives 5$\alpha$--fluoro-6$\beta$-hydroxy-derivatives (XI).



Bowers et al.[14], in an attempt to assess the role of electronic factors, studied the cleavage of 3-keto-5$\alpha$,6$\alpha$--epoxides with boron trifluoride. The above conformational factors, which play an important part in the fission of 3$\alpha$- and 3$\beta$-acetoxy-epoxides, are absent from this system, and therefore the composition of the reaction products is determined by competition between the increase in ionisation of the epoxy-oxygen under the influence of the boron trifluoride and its decrease due to the $-I$ effect of the keto-group. The latter obviously predominates, since treatment of 5$\alpha$,6$\alpha$-epoxypregnane-3,20-dione with the boron trifluoride–ether complex gives a 44% yield of the corresponding fluorohydrin.



Route *A*

(XIII)

(*a*) R = OH; $R_1 = R_2 = R_3 = H$
(*b*) R = $COCH_3$; $R_1 = R_2 = R_3 = H$
(*c*) R = $COCH_3$; $R_1$ = OAc; $R_2 = R_3 = H$
(*d*) R = $COCH_3$; $R_1$ = Br; $R_2 = R_3 = H$
(*e*) R = $COCH_2OH$; $R_1 = R_3$ = OH; $R_2$ = ...$CH_3$
(*f*) R = $COCH_3$; $R_1$ = OH; $R_2$ = Cl; $R_3 = H$
(*g*) R = OH; $R_1 = CH{=}CH_2$; $R_2 = R_3 = H$

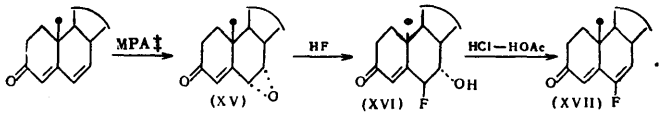
Route *B*

(*a*) R = OH; $R_1 = R_2 = R_3 = H$
(*b*) R = $COCH_3$; $R_1 = R_2 = R_3 = H$
(*c*) R = $COCH_2OH$; $R_1 = R_3$ = OH; $R_2$ = ...$CH_3$
(*d*) R = $COCH_2OH$; $R_1$ = OAc; $R_2 = R_3 = H$
(*e*) R = $COCH_2OH$; $R_1 = R_3 = R_2 = H$
(*f*) R = $COCH_2OH$; $R_1$ = OAc; $R_2$ = H; $R_3$ = =O

It was concluded from this that 3,3-ethylenedioxy--5$\alpha$,6$\alpha$-epoxides are suitable compounds for conversion into fluorohydrins, as was confirmed experimentally[14]. Thus the precursors of 6$\beta$-fluoro-5$\alpha$-hydroxy-compounds may be either 5$\alpha$,6$\alpha$-epoxy-3$\beta$-hydroxy-steroids and their acetates[11] or 5$\alpha$,6$\alpha$-epoxy-3,3-ethylenedioxy-steroids[14]. The last stage in the synthesis was the transition from 6$\beta$-fluoro-5$\alpha$-hydroxy-derivatives (XII) and (XIX) to the physiologically active 6$\alpha$-fluoro-4-en-3-ones (XIII), which was accomplished in two ways, *A* and *B*.[5-17] It was established that, when the 6$\beta$-fluoro-5$\alpha$-hydroxy-3-ones undergo isomerisation under the influence of hydrogen chloride in acetic acid, 6$\beta$-fluoro-analogues of 4-en-3-ones are formed, and these on further treatment are converted into 6$\alpha$-fluoro-4-en-3-ones. The scheme *A* has been used to synthesise the 6$\alpha$-fluoro-analogues of testosterone (XIII*a*), progesterone (XIII*b*),[15] 17$\alpha$-acetoxyprogesterone† (XIII*c*),[18] 17$\alpha$-bromoprogesterone (XIII*d*),[19,20] 16$\alpha$-methylcortisol (XIII*e*),[21,22] 16$\beta$-chloro-17$\alpha$-hydroxyprogesterone (XIII*f*),[23] 17$\alpha$-vinyltestosterone (XIII*g*),[24] and other derivatives[25-27]. Route *B* has provided syntheses of 6$\alpha$-fluoro-analogues of testosterone (XIII*a*), progesterone (XIII*b*), cortexone 17--acetate (XIII*h*), cortexone (XIII*i*), cortisone (XIII*j*),[14,17,28] and 16$\alpha$-methylcortisol (XIII*e*);[29] here, owing to the well--known instability of 17$\alpha$-hydroxy-20-ones to some types of Lewis acids, in the presence of which they undergo *D*-homo-rearrangement, the 17$\alpha$-hydroxy-group of the precursors was protected by acetylation ($R_1$ = OAc).

A modification of the above method is the synthesis of 6$\alpha$-fluorinated analogues of steroid hormones with the use of potassium hydrogen fluoride[30], hydrogen fluoride[31-39], or 48% hydrofluoric acid[40] to open the 5$\alpha$,6$\alpha$-oxides. In the last case 17$\alpha$-alkyl-6$\alpha$-fluorotestosterones[40], 6$\alpha$--fluorocortisone[41], 6$\alpha$-fluoro-16$\alpha$-methylcortisol[42], and other 6$\alpha$-fluorinated analogues[43-49] have been obtained.

6-Fluoro-steroids can also be prepared from 6,7-epoxides (XV) and hydrogen fluoride. Dehydration of the resulting 6$\beta$-fluoro-7$\alpha$-hydroxy-derivative (XVI) yields a steroid 6-fluoro-4,6-dien-3-one (XVII).[50-55]

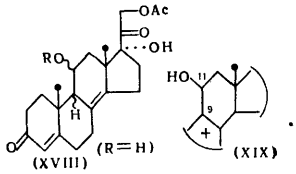


† The Russian text has been largely followed in the use of trivial names (Ed. of Translation).

‡ Monoperphthalic acid.

This procedure has been used to obtain 6-dehydro-6--fluoro-derivatives of 17α-ethynyltestosterone, progesterone, 17α-acetoxyprogesterone, cortexone, prednisone, etc.[50]

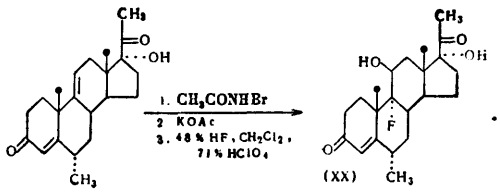
After Fried and Sabo's discovery of 9α-fluorocortisol[1,56], the cleavage of 9β,11β-epoxides of steroid hormones with hydrogen fluoride became the main method for introducing a fluorine atom into position 9 of a steroid molecule. Hirschmann et al.[57], and later Fried and Sabo[58], having carefully studied the reaction conditions, the kinetics, and the role of solvents, showed that, when the reaction is conducted in absolute chloroform, formation of 9α-fluoro--derivatives (obtained in 50% yield) is accompanied by that of a product (XVIII) containing no fluorine, the quantity of this compound depending on the reaction conditions. When the reaction is conducted in liquid hydrogen fluoride at -70°, (XVIII) becomes the main product.



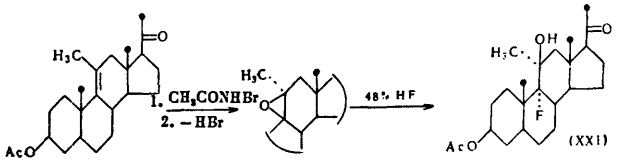

Formation of (XVIII) is probably due to inadequate concentration of the fluoride ion, resulting from the feeble dissociation of HF into $H^+$ and $F^-$ ions. Addition of a Lewis base (such as tetrahydrofuran) to the reaction medium raised the concentration of $F^-$ and diminished the quantity of (XVIII) with an increased yield of the fluorohydrin. Since, however, interaction of hydrogen fluoride with bases (in particular with tetrahydrofuran) lowers the acidity of the reaction medium, it is very important to select their optimum ratio. A kinetic study showed that, with a molar ratio of hydrogen fluoride to tetrahydrofuran of ~1.65 or above, the epoxide reacts at a sufficient rate at -30°. With a ratio of 1.94 the yield of the fluorohydrin reaches ~65%. The order in which the reagents are added is also important in this reaction: it is best to add a solution of the oxide in chloroform to a mixture of tetrahydrofuran and hydrogen fluoride cooled below -30°, which raises the yields to 75%. This reaction is kinetically of the first order with respect to the epoxide[57].

Fried and Sabo's method has been used to synthesise 9α-fluorinated derivatives of the pregnane[59-63] and androstane series[64-66]. Since 9α-fluorocortisol has found only limited application in medical practice owing to its broad spectrum of action[67], the same method has been used to prepare 9α-fluoro-analogues of corticosteroids containing also 2-alkyl,[68-72] 4-chloro,[73,74] 6-methyl,[75-79] 16-alkyl,[80-86] and 16-hydroxy-groups[75,76,87-94]. These substituents produce a considerable narrowing of the spectrum of biological action, at the same time intensifying the various types of activity (see Section II). For this purpose syntheses were made of compounds containing more than one fluorine atom, e.g. in the positions 6,9, 6,9,21, etc. A 9α-fluorine atom was introduced by Fried and Sabo's method into compounds already containing fluorine in position 6 or 21. In this way 6α,9α-difluoropregnanes[17,40,95-110] and 9α,21-difluoropregnanes[77,79,110,111] have been obtained.

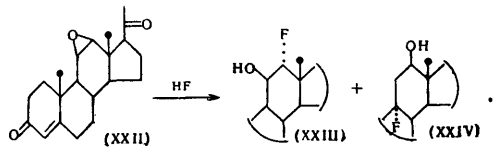
A somewhat modified method, involving the use of 48% hydrofluoric acid to cleave the 9β,11β-oxides, has been used to synthesise[112] 9α-fluoro-11β,17α-dihydroxy-6α--methylprogesterone (XX) and its 1-ene analogue:



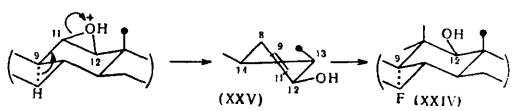

Introduction of a 9α-fluorine atom has been effected under the same conditions in the presence of an 11-methyl group[113,114]:




9α-Fluoro-analogues can be obtained also (together with 12-fluoro-derivatives) from 11β,12β-epoxides and hydrogen fluoride under the conditions employed by Fried and Sabo for the cleavage of 9β,11β-oxides. Thus in 1956 a paper appeared[115] on the synthesis of 12α-fluoro--11β-hydroxy- and -11-keto-progesterones. 11-Dehydroprogesterone gave with *N*-bromoacetamide a 45% yield of a bromohydrin, which formed in quantitative yield the 11β,12β-epoxide (XXII), from which the 11,12-fluorohydrin (XXIII) was obtained by the action of hydrogen fluoride in chloroform. In addition to a 70% yield of (XXIII), the hydrofluorination gives a 15% yield of the 9α-fluoro-12β-ol (XXIV). Application of the same reaction to an 11β,12β-epoxide in which ring A is saturated, and rings A and B are linked in the *cis* configuration, gives (XXIV) as the main product, whereas the 12α-fluoro-11β-hydroxy-derivative of type (XXIII) is formed only in small amounts[116]. This occurs also in the cleavage of 11β,12β-oxides of the spirostan series[117-119]:

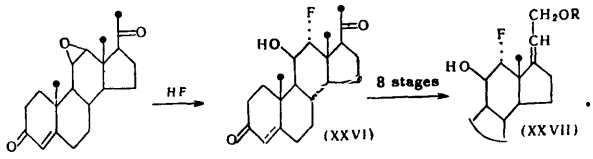



Formation of 9α-fluoro-12β-hydroxy-compounds of type (XXIV) from 11β,12β-oxides can be regarded as a simultaneous reaction involving the intermediate formation of the 9(11)-en-12β-ol (XXV) as an intermediate stage, followed by addition of HF to the resulting 9–11 double bond:

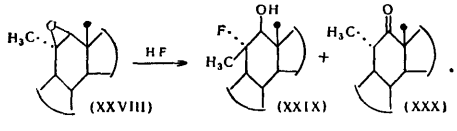



11β,12β-Epoxides have been used as starting materials for the synthesis of 12α-fluoro-analogues of androstane[120-123], progesterone[115,124,125], corticosterone[126-128], cortisone and prednisolone[129], 16α-hydroxyprednisolone[130],

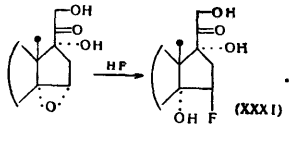
and other pregnanes[131-134]. For the synthesis of 12α--fluorocortisol, Fried et al.[135] tried to use 12α-fluoroprogesterone (XXVI) as intermediate, with subsequent introduction of the 17α- and 21-hydroxy-groups:



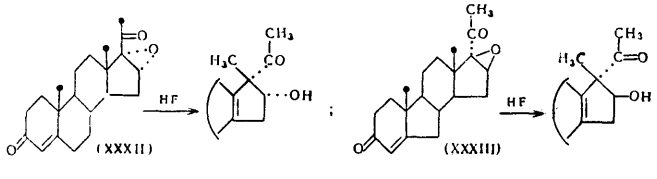

But it was found that, owing to steric and electronic factors, a 12α-fluorine atom prevents osmium tetroxide from approaching the 17–20 double bond, and the latter could not be oxidised in the compound (XXVII). This apparently explains the difficulty of cyclising the fluorohydrin (XXVI) to the oxide[135]. In order to avoid the effect of a 12α-fluoro--substituent, 11β,12β-epoxycortisone acetate was first synthesised, and smoothly converted in the usual way into the 12β-fluoro-analogue of cortisol. It is interesting that with 11α-methylated 11β,12β-epoxides (XXVIII) hydrogen fluoride reacts in two ways: under the influence of the electron-donor 11-methyl group, the oxide opens up with the formation of the 11α-fluoro-12β-hydroxy-11β-methyl derivative (XXIX), and this is accompanied by the acid--catalysed isomerisation of the epoxide to the 11α-methyl--12-one (XXX), the 12α-fluoro-derivative not being detected[136]:



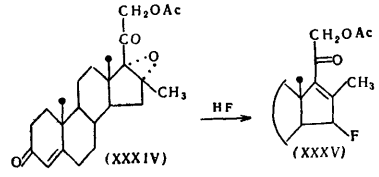

The 14α,15α-epoxide, in contrast to other steroid oxides, was extraordinarily stable towards such reagents as boiling acetic acid, trichloroacetic acid, etc.[137] Nevertheless, hydrogen fluoride[138,139] gives the normal *trans*-diaxial cleavage of the epoxide to form the corresponding 15β-fluoro-14α-hydroxy-derivative (XXXI):



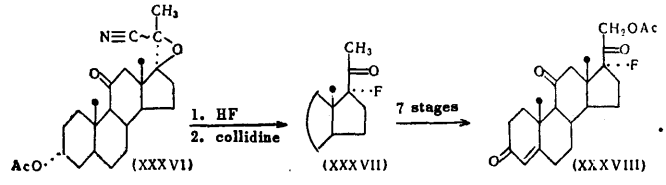

Attempts to cleave the 16α,17α-epoxide and obtain 16-fluoro-compounds, by using hydrogen fluoride under the conditions described for the cleavage of 5α,6α- and 9β,11β-oxides, were unsuccessful[140-144]. It was shown[145] that, when hydrogen fluoride acts on 16,17-epoxides, in particular 16α,17α- and 16β,17β-epoxyprogesterones (XXXII) and (XXXIII), the latter undergo the Wagner–Meerwein rearrangement, no fluorine-containing products being detected:



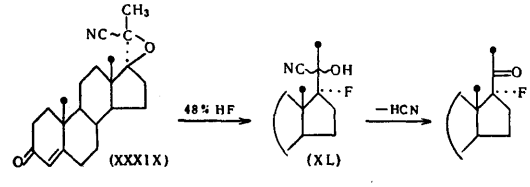

Fission of a 16α,17α-epoxide containing a 16β-methyl group (XXXIV) yielded the 15β-fluoro-16-methyl-16-ene (XXXV):[146]



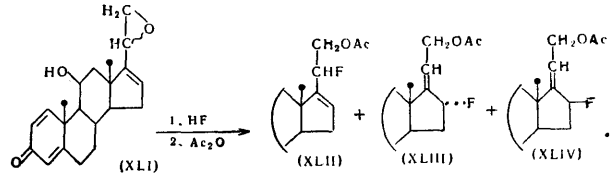

Attempts to introduce fluorine into position 17 by the cleavage of 16,17-epoxypregnanes with hydrogen fluoride were likewise unsuccessful. A similar reaction with 20ξ-cyano--17,20-epoxy-17α-pregnanes (XXXVI) was investigated for the introduction of fluorine at position 17.[147-149] In this case the 17,20-oxide ring is opened under the influence of hydrogen fluoride with the formation of a 17α-fluoro-20--hydroxy-derivative; subsequent elimination of hydrocyanic acid yields the 17α-fluoro-20-ketone (XXXVII). This route has been used for the synthesis of 11-dehydro--17α-fluorocorticosterone acetate (XXXVIII):[147]




It is interesting that in the case of progesterone derivatives the cyano-epoxide (XXXIX) does not react with anhydrous hydrogen fluoride, giving the fluorohydrin (XL) only with 48% hydrofluoric acid[148]:

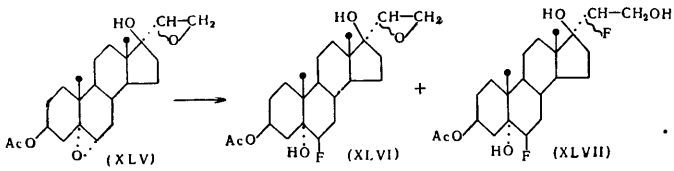



20ξ,21-Oxides have been least studied in relation to the action of fluorine-containing reagents. Until recently only the reaction of the 20ξ,21-epoxy-16-ene derivative (XLI) with hydrogen fluoride in the presence of acetic acid had been investigated[142,150]. The course of the reaction was ambiguous, the 16α (XLIII), 16β (XLIV), and 20ξ (XLII) fluorides being formed:




In the reaction of 5α,6α: 20ξ,21-dioxides, which are epimeric at $C_{(20)}$, with fluorine-containing reagents, it has been shown[24,151] that with one isomer (XLV) both oxide rings are cleaved with the formation of the 6β-fluoride (XLVI) and the 6β,20ξ-difluoride (XLVII). The entry of

fluorine at position 20 in the difluoride (XLVII) was established by nuclear magnetic resonance (with $^{19}F$).



(XLV) (XLVI) (XLVII)

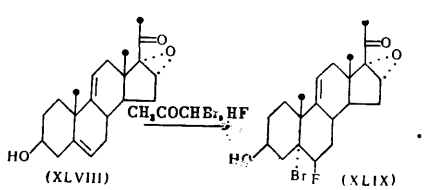
## 2. Preparation of Fluorinated Steroids From Olefinic Steroids

Direct addition of fluorine to carbon–carbon multiple bonds has not yet found application because of the extremely vigorous and uncontrollable reaction of fluorine both with C=C and with C–H bonds, even at low temperatures and with the halogen diluted with nitrogen.

Controlled addition of fluorine to olefins can be achieved only by replacing the gaseous halogen by various fluorine-containing reagents, among which have been used lead tetrafluoride, fluorine perchlorate, hydrogen fluoride, iodobenzene difluoride, trifluoroiodomethane, and difluorocarbene, as well as *N*-halogeno-amides together with hydrogen fluoride.

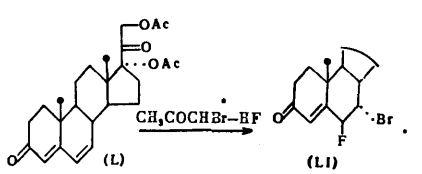
Addition of mixed halides. Fluorine can be introduced into a steroid molecule together with another halogen by the reaction of steroid olefins with *N*-halogeno-amides and hydrogen fluoride.

The halogeno-amides usually employed are *N*-bromo- and *N*-chloro-acetamide and *N*-chloro- and *N*-iodo-succinimide. The reaction is conducted at -80° in the presence of a proton-acceptor, must often pyridine or tetrahydrofuran, to increase the degree of ionisation of the hydrogen fluoride, which is present in large excess. This method of preparation enables fluorine to be introduced into positions 6, 11, and 16 of the steroid molecule, and is preferable to the cleavage of oxides, especially with polyunsaturated steroids, since the oxides of such compounds are obtained in very low yields. The present method is highly selective: in the case of 16$\alpha$,17$\alpha$-epoxy-3$\beta$-hydroxy-pregna-5,9(11)-dien-20-one (XLVIII), for example, reaction occurs primarily at the 5–6 double bond[152] with formation of the 5$\alpha$-bromo-6$\beta$-fluoro-derivatives (XLIX):



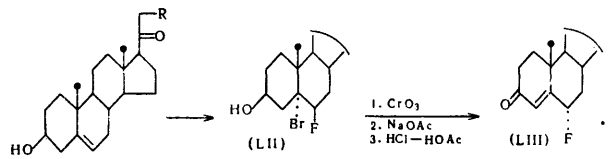
(XLVIII) (XLIX)

In the case of the 4,6-diene (L), however, the 7$\alpha$-bromo-6$\beta$-fluoro-derivative (LI) is formed[152,153]:



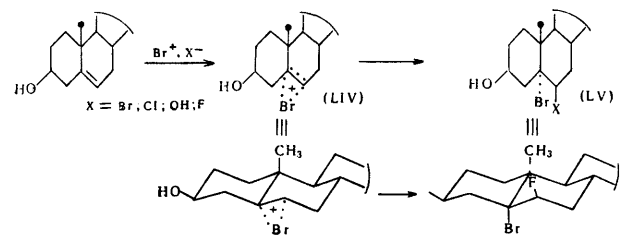
(L) (LI)

When the steroid molecule contains both 4–5 and 9–11 double bonds, the same pair of reagents add on at the latter bond[152,153]. This method of fluorination provides one of the best approaches to the biologically important 6$\alpha$-fluorinated steroid hormones[152,154–156]. Conversion of 6$\beta$-fluorinated (LII) to 6$\alpha$-fluorinated (LIII) compounds is accomplished by successive oxidation of the 3-hydroxy-group, dehydrohalogenation, and isomerisation in acetic acid:



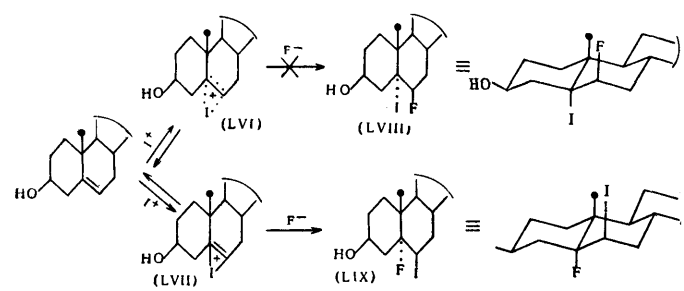
(LII) (LIII)

The halogenation of steroids with mixed halides, which is conducted in a polar medium, takes place by a mechanism of ionic addition. In the first stage an intermediate $\alpha$-bromonium cation (LIV) is formed. Approach of the bromine ion from the $\alpha$ region of the molecule is controlled by stereochemical factors[157]. Then the cation (LIV), on nucleophilic attack by the fluoride ion, forms the *trans*-diaxial cleavage product (LV).[158,159] Thus *trans*-diaxial addition of two halogens occurs in each case:



(LIV) (LV)

Reaction of steroids with *N*-iodosuccinimide and hydrogen fluoride shows an anomalous order of addition of the halogens, with the formation of a 5$\alpha$-fluoro-6$\beta$-iodo-derivative (LIX)[157] instead of the 6$\beta$-fluoro-5$\alpha$-iodo-compound (LVIII). This course of the reaction is explained by the existence of two possibilities — formation of an $\alpha$- or a $\beta$-iodonium cation (LVI) or (LVII) — in the first stage of the reaction:

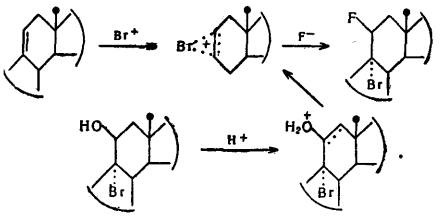


(LVI) (LVIII) (LVII) (LIX)

Two products (LVIII) and (LIX) can be formed on further attack by the fluoride anion. If formation of an iodonium ion is regarded as a reversible process, in which an equilibrium is present between the olefin and the two possible ions (LVI) and (LVII), the former (LVI) is kinetically preferred, as indicated above for the bromonium ion, in view of the preferred approach to the 5–6 double bond from the $\alpha$-region

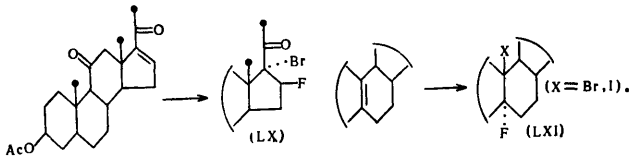
of the molecule. However, reaction of (LVI) with the fluoride anion yields the thermodynamically less stable (LVIII) of the two possible products (LVIII) and (LIX). From an examination of the non-bonding interaction of the iodine atom in these products, and also in view of the greater stability of secondary compared with tertiary iodides, it follows that (LIX) is more stable than (LVIII). Thus reaction involving the kinetically less preferred ion (LVII), but resulting in the thermodynamically more stable final product (LIX), is the dominant mode of addition of $I^+F^-$.

A particularly detailed study has been made of the addition of mixed halogens to the 9–11 double bond, which enables 9α-bromo(chloro, iodo)-11β-fluoro-derivatives to be obtained[153,160–167]. It was found that these products can be prepared from 9α-bromo-11-hydroxy-compounds by reaction with hydrogen fluoride in pyridine[160]. In both cases the reaction involves the 9,11-bromonium ion as intermediate stage, which is converted into the final product on nucleophilic attack by the fluoride ion:

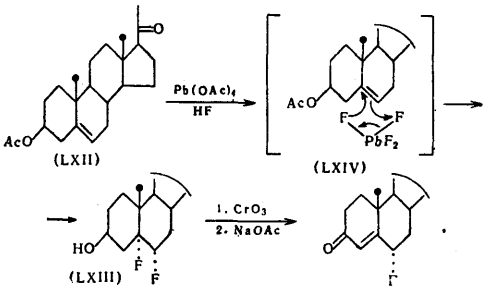


It is interesting that 9α,11β-difluoro-derivatives could not be obtained from 9α-fluoro-11β-hydroxy-steroids. It is probable that fluorine is too electronegative to form an onium ion[153,160].

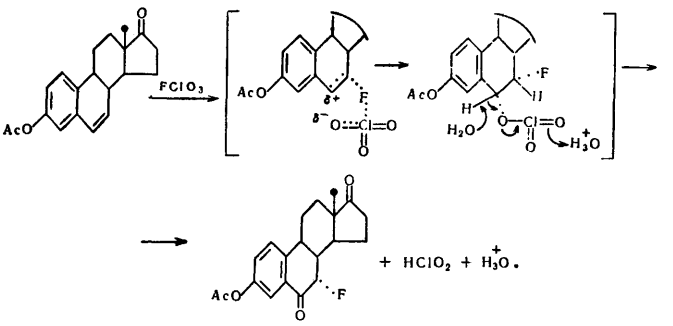
Addition of BrF to the 16–17 double bond enables 17α--bromo-16β-fluoro-derivatives (LX) to be obtained[152,153], while reaction of hydrogen fluoride and *N*-bromoacetamide or *N*-iodosuccinimide with 5–10 olefinic steroids yields 10β-bromo(or iodo)-5α-fluoro-derivatives of the type (LXI).[168]



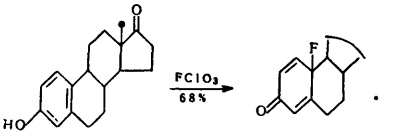
Addition of lead tetrafluoride to double bonds. Only one example of this reaction — with acetoxypregnenone (LXII) — is known at the present time. Lead tetrafluoride attacks this steroid at the instant of formation from lead tetraacetate and anhydrous hydrogen fluoride, the reaction being conducted in dichloromethane at -75°. The reaction product — the vicinal 5α,6α-difluoride (LXIII) — is formed in 27% yield based on the acetate (LXII) introduced into the reaction. The *cis*-addition of fluorine can be explained by the occurrence of reaction via a cyclic transition state (LXIV), in an analogous manner to the *cis* hydroxylation of steroids by osmium tetroxide. Oxidation of the 3β-hydroxyl with chromic acid and elimination of the 5α-fluorine by means of sodium acetate yield 6α-fluoroprogesterone; thus this reaction can serve also for the synthesis of 6α-fluorinated steroids[2,3,169]:



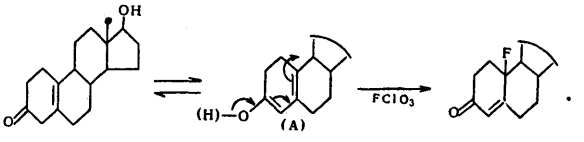
Addition of $FClO_3$. The action of perchloryl fluoride on steroids containing a double bond conjugated with an aromatic ring involves oxofluorination of the double bond, a reaction in which an oxo-group and a 7α--fluorine atom are simultaneously introduced into the steroid molecule. The suggested reaction mechanism is illustrated by the scheme[170]:



Reaction of steroids containing an aromatic ring A with perchloryl fluoride yields 10β-fluoro-19-norsteroids[171–174], the reaction being conducted in dimethylformamide at room temperature.

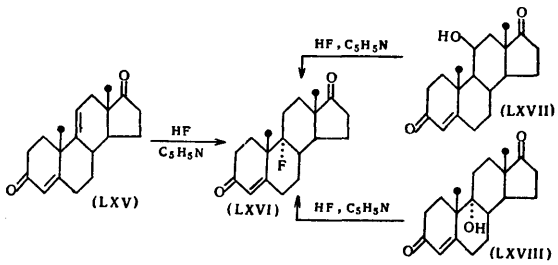


Compounds of the same type are formed from 3-oxo--5(10)-ene steroids[173], the enol (A) or the corresponding enolate ion probably being formed as an intermediate stage:

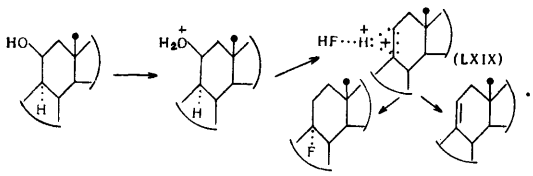


Addition of hydrogen fluoride (HF). The reaction of solutions of anhydrous hydrogen fluoride in pyridine with unsaturated steroids or the corresponding

hydroxy-compounds involves addition of HF to the double bond. An example of this reaction is provided by formation of the 9α-fluoroandrostenedione (LXVI) from the compound containing a 9–11 double bond (LXV), the 9α-hydroxy--derivative (LXVIII), and the 11β-hydroxy-derivative (LXVII). The 9α-configuration assumed for the fluorine atom is based on nuclear magnetic resonance spectra[175].

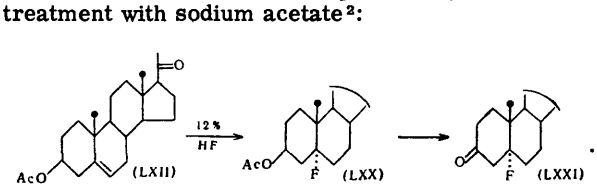



This reaction permits a 9α-fluorine atom to be introduced into derivatives of androstane and pregnane[176–179] without the simultaneous introduction of a hydroxy-group, as occurs in the cleavage of α-oxides. The most reasonable hypothesis is that hydrogen fluoride adds on, in accordance with the Markovnikov rule, to a double bond which is already present or is formed in the reaction. Actually, however, the matter is more complicated. Thus the yield of the 9α-fluoride (LXVI) is far higher from the 11β-ol (LXVII) than from the 9,11-dehydro-derivative (LXV); furthermore, paper chromatography of the reaction products shows that the fluoride (LXVI) is formed more rapidly from the 11β-ol (LXVII) than from the olefin (LXV). This suggests that 9α-fluoro-steroids may be formed directly from 11β-hydroxy-compounds. A probable mechanism of such a change involves protonation of the 11β-hydroxyl followed by elimination of the elements of water with formation of a solvated cation (LXIX), which can then be converted both into 9α-fluoro- and into 9,11-dehydro-compounds[175]:



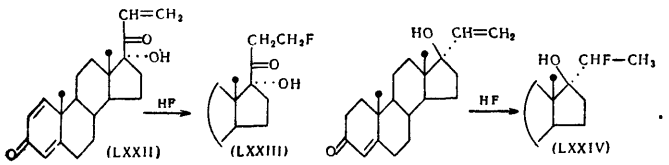

It is quite possible that the formation of 9α-fluoro-12β--hydroxy-steroids by the opening of 11β,12β-epoxides with hydrogen fluoride also occurs according to this scheme, and not by addition of hydrogen fluoride to an intermediate 9(11)-en-12β-ol, as has been assumed previously[117].

Addition of hydrogen fluoride to a 5–6 double bond is accomplished by a somewhat different method. Acetoxy-pregnenone (LXII) reacts with hydrogen fluoride only in the presence of a proton-acceptor (tetrahydrofuran), forming a 5α-fluoro-derivative (LXX); hydrolysis and oxidation of the latter under mild conditions give 5α-fluoropregnane-3,20-dione (LXXI), which splits off hydrogen fluoride on treatment with sodium acetate[2]:

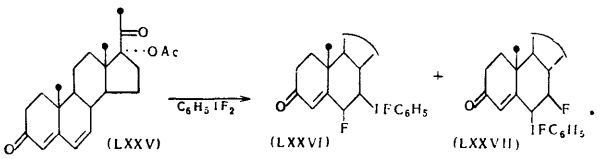



With the non-acetylated hydroxypregnenone under the same conditions, the action of hydrogen fluoride results in replacement of the 3β-hydroxy-group by the fluorine atom instead of addition to the 5–6 double bond.

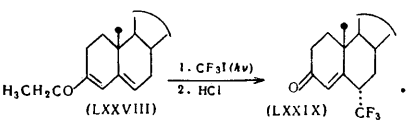
An example is also known of the addition of hydrogen fluoride to the 21–22 double bond§ in the compound (LXXII) with formation of the 22-fluoro-derivative (LXXIII),[180] and also to the 20–21 double bond of 17α-vinyltestoesterone to form the 20-fluoro-compound (LXXIV).[181] In these cases the reaction is also conducted in tetrahydrofuran with antimony trifluoride as catalyst.




Addition of iodobenzene difluoride $C_6H_5IF_2$. This reagent is formed *in situ* in chloroform solution from iodobenzene, hydrogen fluoride, and potassium hydrogen fluoride. Its reaction with the 4,6-diene (LXXV) gives a mixture of the compounds (LXXVI) and (LXXVII), containing fluorine in positions 6β and 7β, the adduced structures being assigned to them on the basis of nuclear magnetic resonance spectra[182].



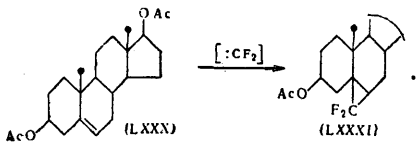

Addition of trifluoroiodomethane. Under the influence of ultraviolet radiation this reagent adds on to the 5–6 double bond of 3-enolic ethers of steroid 4-en--3-ones of the androstane and pregnane series (LXXVIII). Subsequent hydrolysis of the reaction products with hydrochloric acid yields 6α-trifluoromethylated steroids (LXXIX):[183–185]



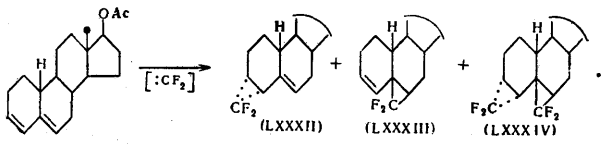

Addition of difluorocarbene. A peculiar method of introducing fluorine into unsaturated steroids is their reaction with difluorocarbene $CF_2$, which is formed when sodium chlorodifluoroacetate $CF_2ClCOONa$ is heated in high-boiling organic solvents[186]. Thus addition of difluorocarbene to the 5–6 bond of (LXXX) yields the 5β,6β--difluoromethano-derivative (LXXXI). The β configuration was assigned to the cyclopropane ring in (LXXXI) on the basis of steric hindrance to approach of the reagent from the α region, and is supported by the infrared and nuclear magnetic resonance spectra. It is interesting

§ Numbering as in formula in Table 1.

that the more bulky dichlorocarbene does not in general react with the 5–6 double bond in 10β-methylated steroids.



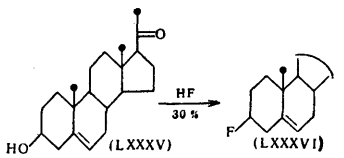

Addition of difluorocarbene to a 2–3 double bond gives two products, in which the three-membered ring has the 2α,3α and 2β,3β configuration respectively. Reaction with 3,5-dienes is more complicated, a mixture of the three products (LXXXII)–(LXXXIV) being formed.



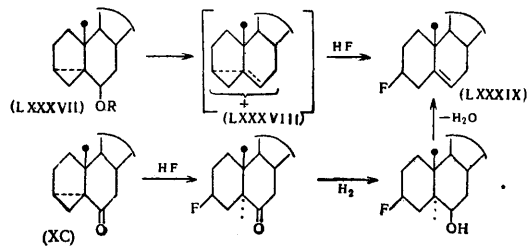

3. Replacement of Other Groups and Other Halogen Atoms by Fluorine

The last group of methods for synthesising fluorinated steroids comprises reactions in which other groups and also other halogens are replaced by fluorine. These include primarily the hydroxy-group and its toluene-*p*-sulphonyl or methanesulphonyl derivatives, which are replaced by fluorine on reaction with hydrofluoric acid or its salts. The substitution of fluorine for other halogens — bromine, chlorine, iodine — occurs in a similar manner. The present Section includes the reactions of perchloryl fluoride with compounds containing active hydrogen, and reactions of sulphur tetrafluoride with steroid ketones.

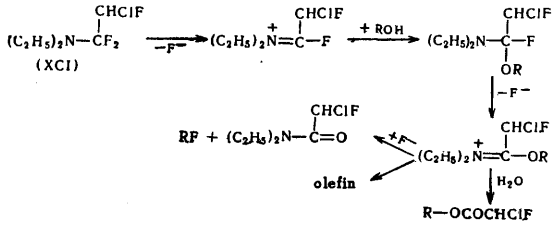
Replacement of hydroxyls by fluorine. This replacement occurs when certain steroid alcohols are treated with anhydrous hydrogen fluoride in tetrahydrofuran medium. Thus the hydroxypregnenone (LXXXV)[2] and its 16-dehydro-derivative[186–188] form 3β-fluoro-compounds (LXXXVI). The hydroxyl of 2-hydroxymethylated steroids is exchanged for fluorine under the same conditions[189].



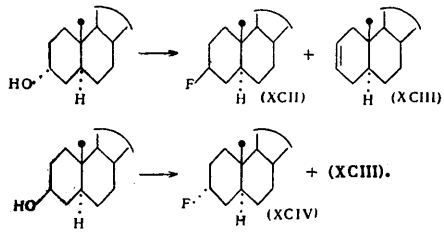

Analogous products are formed when 3,5-cyclosteroids of the androstane and pregnane series of the type (LXXXVII), where R = H or $CH_3$, react with hydrogen fluoride in benzene[190–192]. Reaction occurs via the homoallylic cation (LXXXVIII) and gives a 40–50% yield of the 3β-fluorinated derivatives (LXXXIX). Cleavage of the 3,5-ring occurs also when the 6-ketone (XC) is treated under the same conditions[190].




Replacement of hydroxyl by fluorine can be accomplished also by the action of *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine (XCI), which is formed when chlorotrifluoroethylene is passed through cooled diethylamine[193]. Products in which the hydroxyl has been split off and in which it has been esterified to form a chlorofluoroacetate are formed as side-products of this reaction and therefore the yields of the desired products do not usually exceed 20–50%. The reaction occurs according to the scheme[194,195] (in which R represents the residue of a steroid alcohol)



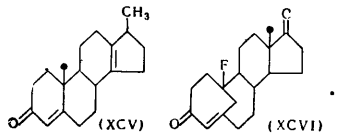

3α-Hydroxy-5α-androstan-17-one on treatment with the reagent (XCI) gives the 3β-fluoro-derivative (XCII), whereas its 3β-epimer yields the 3α-fluoro-derivative (XCIV), the reaction thus involving complete inversion of the configuration. In both cases the olefin — 5α-androst-2-en-17-one (XCIII) — is formed as a byproduct[194].




11α-Hydroxyprogesterone under these conditions forms a mixture of the 9α- and 11β-fluoro-derivatives, together with a small amount of the 9–11-olefinic derivative. The latter is the main product when the reagent (XCI) acts on 11β-hydroxyprogesterone[194]. Complete inversion of the configuration occurs when this reagent is used to substitute fluorine for a hydroxyl in the positions 6β,[194] 15β,[194,196,197] 17α,[198] and 17β.[194,195,198] Substitution of fluorine for hydroxy-groups in 2-, 16β-, and 19-hydroxymethylated steroids has also been reported[194,198–200].

The reactions of steroids with the reagent (XCI) can be complicated by various rearrangements. For example, testosterone yields, besides the normal reaction product, the Wagner–Meerwein rearrangement product (XCV), and

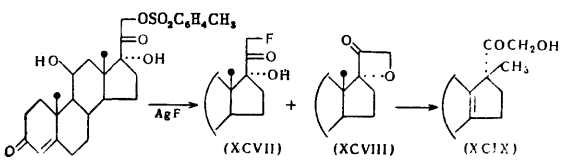
19-hydroxyandrostenediol gives the compound (XCVI), containing the bicyclo[4,4,1]undecane system[198].



(XCV) (XCVI)

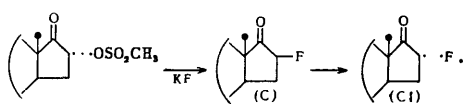
Replacement of toluene-*p*-sulphonate and methanesulphonate groups by fluorine. Since the direct replacement of hydroxyls by fluorine by the action of hydrofluoric acid may result in various rearrangements, and cannot be applied to polyols, methods have been worked out for accomplishing this substitution under milder conditions. One such method consists in converting the hydroxy-group into a toluene-*p*-sulphonate or a methanesulphonate, reaction of which with salts of hydrochloric acid enables the corresponding fluoro-derivatives to be obtained. The use of toluene-*p*-sulphonates is preferable, since they are formed more readily and give higher yields of the fluoro-derivatives (up to 75–90%)[201,202]. The reaction is conducted with potassium fluoride or silver fluoride in diethylene glycol, dimethylformamide, dimethyl sulphoxide, or acetonitrile[203–213].

The main field of application of this reaction comprises the conversion of 21-hydroxy-steroids into the corresponding 21-fluoro-compounds (XCVII). As a result of the considerable basic strength of the fluoride ion, the oxide (XCVIII) is often formed as a byproduct, and under the influence of acids rearranges to the compound (XCIX)[207,214,215].



(XCVII) (XCVIII) (XCIX)

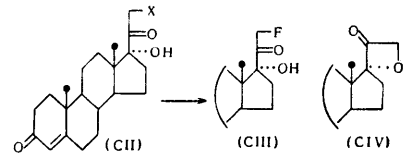
The action of potassium fluoride on methanesulphonates of 16$\alpha$-hydroxy-17-keto-steroids gives 16$\beta$-fluoro-compounds (C), which in the course of the reaction rearrange to the 16$\alpha$-fluoro-derivatives (CI).[216,217]



(C) (CI)

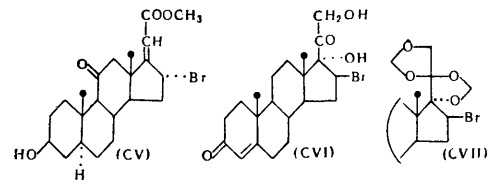
This reaction is employed also to substitute fluorine for hydroxy-groups in 6$\alpha$- and 16$\alpha$-hydroxymethyl-steroids[218–221]. Tetrabutylammonium fluoride $(C_4H_9)_4NF$ in acetone solution can be used instead of salts of hydrofluoric acid as source of fluoride ions in this reaction; under these conditions, structural rearrangements accompanying nucleophilic substitutions are diminished. The reaction involves a complete inversion of configuration: 3$\beta$-toluene-*p*-sulphonates give 3$\alpha$-fluoro-derivatives, whereas their 3$\alpha$-epimers yield the 3$\beta$-fluoro-compounds; testosterone toluene-*p*-sulphonate forms the 17$\alpha$-fluoro-derivative[222].

Replacement of other halogens by fluorine. This reaction is analogous to the replacement of alkane- and arene-sulphonates by fluorine. It occurs when potassium and silver fluorides act on halogenated steroids dissolved in acetonitrile or various alcohols. Ease of replacement by fluorine diminishes in the sequence iodine > bromine > chlorine. Thus when X = I, the main product of the action of salts of hydrofluoric acid on the compound (CII) is the fluoro-derivative (CIII) slightly contaminated with the 17,21-oxide (CIV); but when X = Cl, this oxide becomes the main product of the reaction[223,224]



(CII) (CIII) (CIV)

Interest attaches to the replacement of halogens in position 16 by fluorine. Whereas 16$\alpha$-iodooestrone[225] and the 16$\alpha$-bromo-steroid (CV)[226] form 16$\beta$-fluoro-derivatives, the reaction thus entailing an inversion of configuration, with 16$\beta$-bromocortexone (CVI) or its bismethylenedioxy-derivative (CVII) the configuration is preserved during the reaction, and 16$\beta$-fluoro-derivatives are produced[227–230]. The reasons for this difference in the stereochemical course of the reaction have not yet been elucidated.

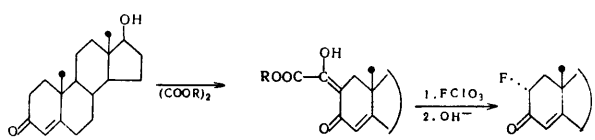


(CV) (CVI) (CVII)

Replacement of halogens by fluorine has been used also to prepare 3$\beta$-fluorinated[231], 6$\alpha$-fluorinated[232], 6$\alpha$-fluoromethylated[233], and 16$\beta$-fluoromethylated[234] steroids. Being one of the principal methods for introducing fluorine into position 21 (because of activation of the 21-halogen by the adjacent $C_{(20)}$ carbonyl group[235–245]), this route serves also for the preparation of polyfluorinated steroids[246–250].

Replacement of hydrogen by fluorine. In contrast to bromination or chlorination, the direct fluorination of steroid ketones in the $\alpha$-position is impossible. Indirect routes are therefore necessary for this purpose, by the action of fluorine-containing reagents, e.g. perchloryl fluoride $FClO_3$, on those derivatives of keto-steroids in which the activity of the $\alpha$-hydrogen has been substantially increased.

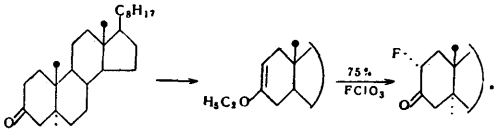
The first scheme for introducing fluorine into keto-steroids comprises three stages — preparation of an alkoxalyl or hydroxymethylene derivative of the steroid, followed by treatment with sodium ethoxide and perchloryl fluoride, and finally alkaline hydrolysis of the product to remove the alkoxalyl group — an example being the synthesis of 2$\alpha$-fluorotestosterone[251]:



A fluorine atom can be introduced into steroids by this method not only at the 2$\alpha$ position[5,170,251–262] but also at

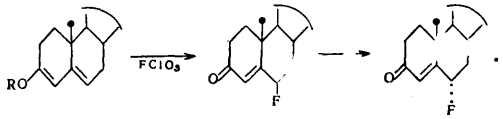
the 16$\alpha$, 16$\beta$,[263-268] and 21 [251,256,268] positions. In the two latter cases not only monofluoro-derivatives (16$\alpha$ or 21) can be obtained but also difluoro-compounds[270-272].

In the second scheme for the fluorination of keto--steroids, solutions of derivatives of the enolic form of these steroids in organic solvents are treated with perchloryl fluoride. Thus 2$\alpha$-fluorocholestan-3-one is formed from cholestanone via 3-ethoxycholest-2-ene:[269]

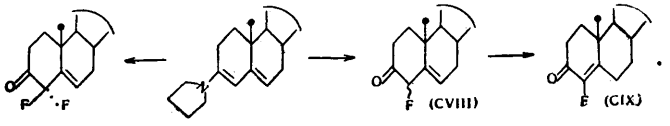


Enamines of 3-keto-5$\alpha$-steroids[273] react similarly, as also acetates of the enolic form of 17-keto-steroids[274]. In the latter case the yield of 16$\alpha$-fluoro-17-keto-steroids can be considerably increased by replacing the acetates by the acetamide derivatives of the enolic form[274-277].

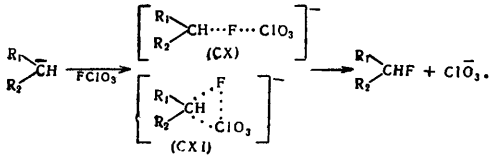
The reactions of perchloryl fluoride with derivatives of the steroid 4-en-3-ones are rather more complicated, the composition of the reaction products depending on the conditions and the type of enolic derivatives. Thus acetates[48,277] and ethyl ethers[269,278-280] of the enolic form of these steroid derivatives yield 6$\beta$-fluoro-compounds, which can be isomerised under the reaction conditions to the 6$\alpha$-fluoro-derivatives:



In contrast to this, the fluorination of pyrrolidine enamines of steroid 4-en-3-ones yields 4-fluorinated products. When the reaction is conducted in methanol[281-285], 4$\xi$--fluoro-5-ene derivatives (CVIII) are obtained, which in the presence of acids isomerise to 4-fluoro-4-enes (CIX); when the reaction was conducted in ether[284,286], only 4,4--difluoro-5-ene derivatives were isolated.



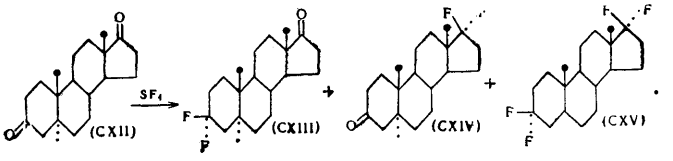

Since perchloryl fluoride has no dipole moment[287], it is difficult to predict *a priori* the type of ionisation and the mechanism of fluorination with this compound. It is possible that perchloryl fluoride will dissociate in different ways depending on the conditions[288,289]. It is assumed in most cases that the fluorine is electrophilic in character in this reaction, i.e. that fluorination consists in attack by an $F^+$ ion on a carbanion or a carbon atom of a double bond having a greater electron density. This view is supported by the formation of axial $\alpha$-halogeno--ketones both on fluorination with perchloryl fluoride and in the reaction of ketones with $Br^+$.[48,172,269] It is probable that in this case fluorination is a single-stage process, involving transition states of the type (CX) or (CXI):[290,291]




Conversion of carbonyl group into a *gem*--difluoro-derivative. Treatment of steroid aldehydes or ketones with sulphur tetrafluoride ($SF_4$) enables two fluorine atoms to be introduced simultaneously into the steroid molecule. This reaction is conducted at room temperature with hydrogen fluoride, boron trifluoride, or other fluorides ($AsF_3$, $TiF_4$, $PF_5$), as catalyst[292]. Although hydrogen fluoride is a less active catalyst than boron trifluoride its use is to be preferred, since fewer byproducts of the reaction are then formed[293]. Hydrogen fluoride can be generated directly during the reaction by adding to the mixture a quantity of ethanol, which forms hydrogen fluoride on reaction with sulphur tetrafluoride[4].

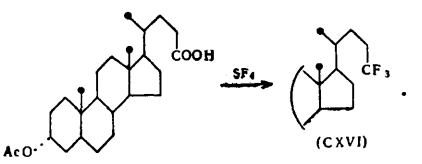
Comparatively mild reaction conditions ensure that esters, acetals, and bismethylenedioxy-derivatives shall be stable, and permit considerable expansion of the field of application of the reaction among such multifunctional compounds as steroids. Reaction with sulphur tetrafluoride has been used to introduce two fluorine atoms into positions 3, 11, 17, and 20 of the steroid molecule[4,293-297], and also to obtain 2- and 6-difluoromethylated steroids from the corresponding hydroxymethylene derivatives[293,298-300].

Compounds containing more than one carbonyl group in the molecule can react either at one or at all the reaction centres. Thus 5$\alpha$-androstane-3,17-dione (CXII) forms a mixture of di- and tetra-fluorinated derivatives (CXIII)--(CXV), with fluorination at $C_{(3)}$ predominating in the ratio 3:1.[4]




The reactivity of carbonyl groups in different positions in the steroid molecule towards sulphur tetrafluoride was found to decrease in the sequence 3-one $\simeq$ 6-formyl > 17--one > 20-one > conjugated 3-one > 11-one.[293]

Steroid acids on reaction with sulphur tetrafluoride form trifluoromethylated derivatives. Thus acetoxy--lithocholic acid yields the 24-trifluoro-derivative (CXVI):[293]

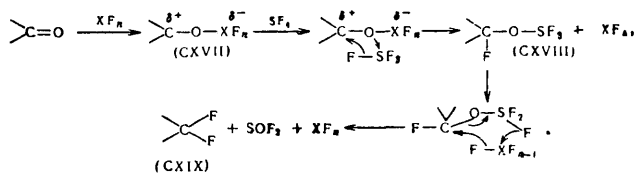



The reaction probably involves the intermediate formation of the acid fluoride, the hydrogen fluoride which is thus

evolved catalysing the further changes, so that in this case separate addition of a catalyst is not necessary[293]:

$$R{-}CO_2H + SF_4 \rightarrow R{-}COF + HF + SOF_2,$$
$$R{-}COF + SF_4 \rightarrow R{-}CF_3 + SOF_2.$$

Several schemes have been suggested for the mechanism of the reaction of ketones with sulphur tetrafluoride, the most probable of them being[293,294]



According to this scheme, the ability of $XF_n$ to catalyse the reaction is associated with its ability to polarise the carbonyl group as a Lewis acid. The first stage in the reaction consists in formation of the complex (CXVII) between the carbonyl group and the catalyst. Attack by a sulphur tetrafluoride molecule on this complex yields the adduct (CXVIII), cleavage of which by means of the catalyst forms the difluoride (CXIX).

## II. PHYSIOLOGICAL ACTIVITY OF FLUORINATED STEROIDS

The introduction of fluorine atoms into steroid compounds results in fundamental and varied changes in their physiological activity. The changes of greatest interest and practical importance are found in the corticosteroid series. The introduction of fluorine affects primarily the hormonal activity of these compounds — their control of the metabolism of carbohydrates (glucocorticoid activity) and salts (mineralcorticoid activity). The discovery of the anti-arthritic, antiallergic, and anti-inflammatory properties of modified corticosteroids extended the therapeutic effects of these compounds beyond the range of natural hormonal activity, and enabled their clinical application to be greatly expanded. At the present time fluorinated steroids are employed for the treatment of various types of arthritis, Addison's disease, dermatoses, etc. Since fairly detailed reviews are available in this field[67,301,302], only a brief account with the most recent results need be given here.

Introduction of fluorine at the 2$\alpha$ position in ring A of a steroid molecule lowers all forms of hormonal activity[253]; nevertheless, anti-tumour activity has been observed in 2$\alpha$-fluorotestosterone[254]. The only compound containing a 3$\beta$-fluorine atom which has been studied is 17$\alpha$-acetoxy-3$\beta$-fluoropregn-5-en-20-one, and this on oral application has three times the gestagenic activity of 17$\alpha$-acetoxyprogesterone[192]. Replacement of the 4-hydrogen atom by fluorine lowers the androgenic, gestagenic, and corticoid activities[284,303].

Compounds containing a 6$\alpha$-fluorine atom have, in comparison with the corresponding unsubstituted compounds, far greater glucocorticoid, anti-inflammatory, and thymolytic activities and at the same time diminished mineralcorticoid activity[17,28,40,304]. Increased anti-arthritic activity in 6$\alpha$-fluorocorticoid steroids has also been reported, although the increase is not quite so large as with the 9$\alpha$-fluoro-analogues[305]. The gestagenic and anabolic activities of the 6$\alpha$-fluoro-derivatives of progesterone and testosterone are also considerably enhanced[18,40,306]. On the other hand, the 6$\beta$-fluoro-epimers have a lower gestagenic activity than the unsubstituted compounds[306]. 6$\alpha$-Fluoromethylated steroids, like the 6$\beta$-fluoro-compounds, possess increased glucocorticoid and diminished mineralcorticoid activities[218].

The therapeutic effects produced by the introduction of a 9$\alpha$-fluorine atom have been studied the most widely. It has been reported that the glucocorticoid activities of the 9$\alpha$-fluoro-analogues of cortisol and corticosterone exceed those of the unsubstituted compounds by factors of 8 and 3.5 respectively[80,115]. The mineralcorticoid, thymolytic, anti-inflammatory, and anti-arthritic activities are correspondingly increased too[76,80,304,305,307-309]. 9$\alpha$-Fluoroprogesterone has a greater gestagenic activity than has unsubstituted progesterone[63,175]; nevertheless, the 9$\alpha$-fluoro-11$\beta$-hydroxy-analogue has a lower progestative activity than the unsubstituted compound[310-312]. Analogous effects are found in the androstane series. The introduction of 9$\alpha$-fluorine into testosterone propionate increases the androgenic and anabolic activities of the steroid roughly fivefold[175], whereas 9$\alpha$-fluoroandrostan-11$\beta$-ols have an appreciably diminished androgenic activity[66]. Enhanced aldosterone-blocking activity is also noted when 9$\alpha$-fluorine is introduced into 17-spirolactones of the androstane series[313]. 9$\alpha$-Fluoro-11$\beta$,17$\alpha$-dihydroxy-6$\alpha$-methylpregna-1,4-diene-3,20-dione is an effective anti-tumour agent, arresting the growth of mouse adenocarcinoma and rat fibroadenoma[314].

An 11$\beta$-fluorine atom is introduced only together with another halogen — bromine, chlorine, or iodine — in the 9$\alpha$ position. In comparison with the corresponding unsubstituted compounds, such dihalogenated derivatives of progesterone have lower gestagenic activity[160,162], those of testosterone lower anabolic and androgenic activities[166], and those of cortexolone lower glucocorticoid activity[315].

12$\alpha$-Fluorinated analogues of corticosterone and 11$\beta$-hydroxyprogesterone have enhanced glucocorticoid activity, which is approximately equivalent to that of the corresponding 9$\alpha$-fluoro-derivatives[311,312]. Nevertheless, 12$\alpha$-fluorocortisone possesses neither glucocorticoid nor mineralcorticoid activity[135]. There are also data indicating enhanced gestagenic and anti-oestrogenic activity in 12$\alpha$-fluoro-11$\beta$-hydroxyprogesterone compared with progesterone itself[311,312].

Introduction of a fluorine atom into the 16$\alpha$ position increases the glucocorticoid and anti-inflammatory activity and sharply diminishes the mineralcorticoid activity[142,150]. Analogous effects are produced by introducing a 16$\alpha$-fluoromethyl group into a steroid[219]. Yet 16$\beta$-fluorinated steroids have diminished glucocorticoid and anti-inflammatory activity in comparison with the unsubsituted compounds[142,316]. The 17$\alpha$-fluoro-analogue of progesterone is a rather less active gestagen than is progesterone[148].

Compounds containing a fluorine atom in position 21 have glucocorticoid and mineralcorticoid activity intermediate between those of the relatively inactive 21-deoxy-compounds and the highly active 21-hydroxy-analogues[214,301]. 21-Fluoroprogesterone is a more active gestagen than is progesterone by a factor of 2–4.[223,224]

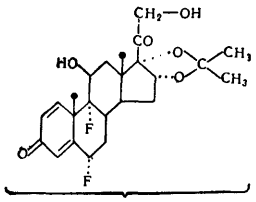
Data on the effect of fluorine atoms on the main forms of physiological activity of steroids are summarised in Table 2.

TABLE 2. Physiological activity of fluorinated steroids (+ = enhancement of activity; - = diminution in activity).

| Position of F | Activity compared with unsubstituted compound | | | | Position of F | Activity compared with unsubstituted compound | | | |
|---|---|---|---|---|---|---|---|---|---|
| | gestagenic | glucocorticoid | mineralocorticoid | anti-inflammatory | | gestagenic | glucocorticoid | mineralocorticoid | anti-inflammatory |
| 2α | − | − | − | | 12α | + | + | − | |
| 3β | + | | | | 16α | | + | − | + |
| 4 | − | − | − | | 16β | | − | | |
| 6α | + | + | − | + | 17α | − | | | |
| 6β | − | | | | 21 | + | + | + | + |
| 9α | + | + | + | + | | | | | |

The clinical application of corticosteroids is impeded by the fact that many of them show mineralcorticoid activity, which on prolonged treatment produces oedema and a rise in blood pressure[317]. In order to obtain compounds suitable for practical application, therefore, it was necessary to suppress the mineralcorticoid activity, which in this case was a secondary effect. This was achieved by introducing appropriate substituents into the molecule, in particular fluorine atoms in positions 6α and 16α. The same effect can be obtained by introducing into the molecule a 1–2 ethylenic bond[60,62,305,312], methyl groups in positions 2α,[304,305,312] 6α,[301,304,305] and 16α and 16β,[80,83,96,304,305,318-320] or a 16α-hydroxy-group[87,301,305]. There occurs not only a sharp drop in mineralcorticoid activity but also a substantial increase in glucocorticoid and anti-inflammatory activity.

Results obtained for the modification of the cortisol molecule (Table 3) show that, when the molecule contains more than one modifying substituent, their effects on the activity are additive. This has enabled compounds to be prepared which have an extremely high level of physiological activity, exceeding that of natural corticosteroids several hundredfold. It must also be noted that 16α,17α-acetals of 16α-hydroxycorticosteroids, which are not included in Table 3, have 3–4 times the anti-inflammatory activity of the unsubstituted compounds[95,321,322].



Dexamethasone (9α-fluoro-11β,17α,21-trihydroxy-16α--methylpregna-1,4-diene-3,20-dione) and triamcinolone (16α,21-diacetoxy-9α-fluoro-11β,17α-dihydroxypregna-1,4--diene-3,20-dione) have been used in medical practice as antiarthritic and anti-inflammatory remedies[305]. Synalar (6α,9α-difluoro-11β,21-dihydroxy-16α,17α-isopropylidenedioxypregna-1,4-diene-3,20-dione) is used in the treatment of psoriasis and skin diseases[326].

The problem of the particular mechanism by which the introduction of fluorine affects physiological activity has not yet been solved. Fried[115,311] suggested that this effect was associated with the inductive (-*I*) effect of the fluorine atom on the neighbouring oxygen-containing group in position 11. This hypothesis was based on the parallelism observed between the effect of various 9α-substituents on the

TABLE 3. Physiological activity of analogues of cortisol.

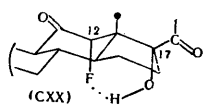
| Substituents in cortisol molecule | | | | Physiological activity | | | Refs. |
|---|---|---|---|---|---|---|---|
| 1–2 | 6α | 9α | 16α | glucocorticoid (cortisol = 1) | anti-inflammatory (cortisol = 1) | mineralocorticoid (cortexone = 1) | |
| | F | | | 10 | | | 17 |
| | | F | | 8 | 10 | 2.7 | 80, 301 |
| | F | F | | 50 | 100 | | 17,96 |
| Δ | F | | | 81 | 8 | | 17, 40, 305 |
| Δ | | F | | 43 | 20 | 4 | 62, 80 |
| Δ | | | F | 8 | 16 | | 142, 150 |
| | F | | $CH_3$ | 40 | 5 | | 96, 97 |
| | | F | $CH_3$ | 12 | 14 | | 80 |
| Δ | F | | $CH_3$ | 160 | 50 | | 97, 305 |
| Δ | | F | $CH_3$ | 17 | 40 | | 80, 326 |
| Δ | $CH_3$ | F | | 120 | 24 | 0.1 | 301 |
| Δ | $CH_3$ | | F | 25 | 20 | | 278 |
| Δ | | F | OH | 13 | 5 | | 87, 95 |
| Δ | F | F | | 427 | 200 | | 17, 40, 96 |
| Δ | F | | F | 116 | 100 | | 278 |
| Δ | | F | F | 60 | 75 | | 150, 301 |
| | F | F | $CH_3$ | | 50 | | 96 |
| | F | F | OH | | 15 | | 95 |
| Δ | F | F | $CH_3$ | 730 | 165 | | 96, 97,305 |
| Δ | $CH_3$ | F | F | 250 | 190 | | 278 |
| Δ | F | F | F | 425 | 480 | | 278 |

TABLE 4. Glucocorticoid activity of 9α-substituted cortisols and acid dissociation constants of the substituted acetic acids[312].

| Substituent | Glucocorticoid activity | Acid dissociation constant $10^5 K_a$ |
|---|---|---|
| Fluorine | 10.7 | 217.00 |
| Chlorine | 4.7 | 155.00 |
| Bromine | 0.3 | 138.00 |
| Iodine | 0.1 | 75.00 |
| Hydroxyl | 0.2 | 16.00 |
| Methoxyl | <0.2 | 33.00 |
| Hydrogen | 1.00 | 1.82 |

activity of a steroid hormone and their inductive effects assessed from the strengths of the corresponding substituted acetic acids (Table 4).

This hypothesis was regarded as supported also by the presence in 12α-fluoro-steroids (12α-fluorocorticosterone[115] and 12α-fluoro-11β-hydroxyprogesterone[311]) of enhanced glucocorticoid activity of the same order as in the 9α-fluoro-analogues, which are symmetrically substituted about $C_{(11)}$. The difficulty presented by the absence of glucocorticoid or mineralcorticoid activity in 12α-fluorocortisone[135] could be bypassed on the assumption that in this case such absence resulted from the formation of a hydrogen bond between the axial 12α-fluoro- and 17α--hydroxy-groups (CXX).



(CXX)

However, recently discovered facts have considerably diminished the value of this hypothesis. The acetate of 9α-fluorocortexone, *containing no oxygen in position 11*, shows twelve times the mineralcorticoid activity of cortexone acetate[177]. This indicates that the increase in hormonal activity accompanying introduction of 9α-fluorine is not due to an inductive effect on a neighbouring oxygen function. It is evidently more probable that modified hormones are less rapidly metabolised by the organism, and

thus remain for a longer period in an active state in the latter[323]. In particular, the presence of fluorine atoms may prevent one of the normal metabolic processes, hydroxylation. It is interesting in this connection that the most active fluorinated steroids have the fluorine atoms in the positions 6, 9, 16, and 21, i.e. in those positions in which enzymic hydroxylation of steroid hormones occurs in the animal organism[324].

The enhanced activity of fluorinated steroids has been explained also by a diminution in their bonding by blood plasma[325]. Real progress in explaining the phenomena observed in this field can be made only when a deeper understanding has been obtained of the molecular mechanism of the action of steroids, about which almost nothing is known at the present time[324].


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# THE PHOSPHORYLATION OF CELLULOSE

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## I. INTRODUCTION

Although a large number of monographs and reviews have been published on the chemical modification of cellulose, questions associated with the phosphorylation of this important polysaccharide are treated superficially and incidentally in them, or even omitted altogether, as has been done in the latest treatise on the chemistry of cellulose [1].

The task of the present paper is to fill the gap: it represents the first attempt to collect together all the information on methods of preparation as well as the properties and practical application of phosphorus-containing derivatives of cellulose. The paper summarises investigations on the phosphorylation of cellulose, made mainly during the past thirty years, recent progress being reported in the greatest detail. A special place is given to describing the achievements made in the practical application of phosphorus-containing cellulosic materials.

The large amount of experimental work on the preparation of phosphorus-containing cellulose derivatives can be divided into two groups, according as phosphorylation is effected with derivatives of acids containing quinquevalent or tervalent phosphorus. The first group is in turn divided into two subgroups, the first of which comprises

papers on procedures for the direct phosphorylation of the polysaccharide, i.e. the replacement of the hydrogen atoms of hydroxy-groups by phosphorus-containing acid radicals; the second subgroup contains other methods for the chemical bonding of phosphorus to the macromolecular chain (indirect phosphorylation). A large number of papers and especially patents are devoted to the problem of conferring particular properties on cellulosic materials by impregnating them with compositions which include phosphorus compounds. In the latter case the formation of chemical bonds between cellulose and the phosphorus component has not in general been established, and therefore this question is not discussed in the review†.

The large number of publications on the preparation of phosphorylated celluloses is due to the growing technical interest in them. An important application of these products is the production of non-flammable textiles. The introduction of phosphorus into cellulose confers on articles made from it the ability to withstand the action of a flame‡. Cloth made from phosphorus-containing cellulose and clothes manufactured from it can be employed in firefighting, in furnace work, in the army, etc. [2-16]. Phosphorus-containing celluloses are used in several cases in the production of shrink-resistant [17] and crease-resistant [18,19] fabrics, which are resistant to water [8,20,21] and possess antiseptic [20,22] and rotproof [21,23,24] properties.

Phosphorylated celluloses are novel, as yet little studied, but promising ion exchangers. Their desirable properties are their hydrophilic character, in some cases high selectivity of ion-exchange action, and characteristic physical properties. In contrast to most other known adsorbents, these substances may be in the form of powders, wadding, or sheets, and are therefore employed in different ways in the ion-exchange process. They are used not only in the form of columns but also in other ways: thus a very promising procedure at the present time is continuous ion exchange by means of an endless belt of phosphorylated cotton [25]. The use of phosphorylated celluloses has been recommended for the isolation of $Th^{4+}$, $Ti^{4+}$, $U^{4+}$, $Ce^{4+}$, $Fe^{2+}$, $ZrO^{2+}$, $UO^{2+}$, $Hf^{2+}$, $Cu^{2+}$, and other ions from synthetic and technical solutions [22,25-46].

In some cases these esters are employed in radiometric instruments for the control of waters containing small concentrations of radioactive elements [47]. References have also appeared to the use of cellulose phosphates for the purification and separation of proteins, vitamins, and other important natural products [48-55].

Phosphorylated celluloses are fairly efficient cation exchangers: the ion-exchange properties of these compounds and other ion exchangers of similar type are compared in the accompanying Table [37].

Ion-exchange processes have been studied mainly with cellulose specimens containing acid phosphate groups, which, as is well known [56-58], are not always the most suitable for bonding a particular ion. Phosphonates, phosphoramidates, and phosphonamidates of cellulose have not yet been assessed from this point of view, which reveals certain prospects for the preparation of novel polymeric complexing agents. The usefulness of such researches is supported by the appearance of papers on the application to ion exchange of celluloses which have been impregnated with certain phosphorus-containing extractants for metals [59-61].

TABLE.

| Ion exchanger | Exchange capacity, mg-equiv. $g^{-1}$ | pH at half capacity |
|---|---|---|
| Cellulose phosphate, 1st H atom | 1.3 | 1.5 |
| Cellulose phosphate, 2nd H atom | 2.6 | 7.5 |
| Sulphoethylated cellulose | 0.5 | 0.5 |
| Carboxymethylated cellulose | 0.3 | 3.7 |
| Diethylaminoethylated cellulose | 0.3 | 7.7 |

Phosphates and phosphonates of cellulose are of interest to several investigators concerned to establish a relationship between the physicochemical characteristics of substances and their structure [62,63].

## II. PHOSPHORYLATION OF CELLULOSE BY DERIVATIVES OF ACIDS OF QUINQUEVALENT PHOSPHORUS

### 1. Phosphorylation by Acid Chlorides

The most widely used method for preparing esters of phosphorus acids is the reaction of alcohols or their alkoxides with the corresponding acid chlorides [64,65]. Several variants of this process have been used for the phosphorylation of cellulose. Work was published in 1932 on the reaction of cellulose with phosphorus oxychloride in the presence of phosphoric acid with and without a solvent present, a highly degraded, water-soluble product being obtained [66]. A less degraded material is obtained by employing cellulose which has first been treated with alkali [26,49,67-70], a water-insoluble phosphate being formed when the reaction is conducted in absolute benzene [26].

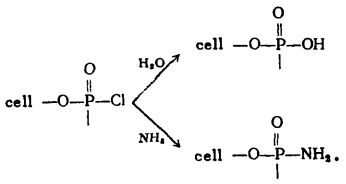
Much attention has been paid to the phosphorylation of cellulose with phosphorus oxychloride in the presence of ammonia [71] or pyridine [25,27,35,72,73], when a polysaccharide containing rather more than 9% of phosphorus could be obtained (the phosphorus content was somewhat higher when hydrocellulose was used [27]). Under the conditions of esterification, partial replacement of the hydroxy-groups of the polysaccharide by chlorine is observed [25]. Phosphorylation in the presence of pyridine is also accompanied by considerable degradation of the product. Thus the preparation of a cellulose phosphate containing 3.5% of phosphorus involved a loss of strength of 50%, and the loss increases with rise in the phosphorus content [27]. There are indications that, in the presence of pyridine, phosphorus oxychloride will phosphorylate derivatives of cellulose, e.g. ethyl- and hydroxyethyl-cellulose and cellulose acetate [27,73].

Treatment of cellulose with phosphorus oxychloride yields mainly phosphorochloridates, apparently consisting mainly of Cell–O–$POCl_2$ residues [27]. The lability of the chlorine atoms in these compounds corresponds to that in ordinary alkyl (or aryl) phosphorochloridates [64,65]. They are exchanged for hydroxyl on treatment with water, and

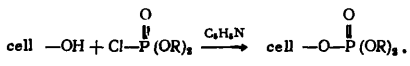
† Detailed accounts of the modification of the properties of cellulose by impregnation with phosphorus-containing compositions will be found in several monographs [2-4].

‡ Several theories have been put forward to explain from various points of view the non-combustibility of phosphorylated celluloses [2,4,5].

for an amino-group with ammonia, cellulose phosphates and phosphoramidates respectively being formed[70]:



Cellulose is phosphorylated also by alkyl (and aryl) phosphorochloridates in the presence of tertiary amines [10,74-79], when mixed phosphoric esters are formed, e.g.



Derivatives of cellulose undergo similar reactions[73,80].

References have recently appeared to the possibility of the phosphorylation of cellulose with phosphoramidochloridates[81] and with phosphonochloridates[76,77,81-83], the products containing fragments in which phosphorus–carbon and phosphorus–nitrogen bonds are present. Phosphoramidochloridates obviously phosphorylate cellulose partly also by a mechanism involving alcoholysis of phosphoramidates[81].

The interaction of cellulose with polyphosphonitrilic chlorides in the presence of pyridine has been described[19,84], but there is no rigorous evidence of the formation of macromolecular glycosylphosphonitriles.

## 2. Phosphorylation by Acids

At ordinary temperatures cellulose hardly reacts at all with phosphoric acid, but only swells and partly dissolves in it[85,86]. Nor are cellulose phosphates obtained on heating, owing to degradation of the polysaccharide[87,88]. Unsatisfactory results have been obtained also for phosphorylation with phosphoric acid in the presence of sulphuric acid[89] or of phosphorus pentoxide[90], only water-soluble oligomers being obtained in these cases. An only slightly degraded product containing a few per cent of phosphorus was obtained by Ermolenko and Kaputskii, who acylated cellulose with phosphoric acid (0–10°), the reaction being activated with oxides of nitrogen[91,92]. These workers consider that macroradicals are produced by the action of nitrogen dioxide on cellulose, and it is these which are responsible for phosphorylation.

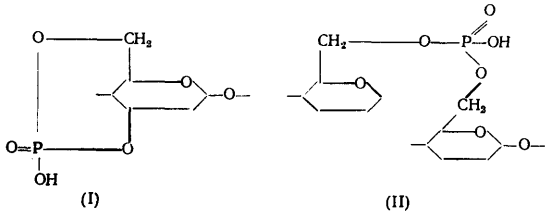
Considerably better results were obtained for the phosphorylation of cellulose with phosphoric acid in the presence of ammonia and other compounds containing nitrogen. The reaction is often conducted under relatively mild conditions, and in several cases it is possible to obtain cellulose phosphates with little degradation. The addition of nitrogenous bases is necessary to neutralise the phosphoric acid, and consequently to diminish its dehydrating effect. It is possible that urea increases the reactivity of cellulose, since the latter is known to be able to change its supermolecular structure under the influence of nitrogeneous bases[93].

The esterification of cellulose with phosphoric acid in the presence of urea was first accomplished towards the end of the 1930s[6,94]. A large (mainly patent) literature then appeared on new variants of the phosphorylation of cellulose with phosphoric acid in the presence of amines, urea, dicyanodiamide, melamine, guanidine, formamide, and other compounds containing nitrogen[6,8,16,18,20,31-34,37,39,95-120]. It has recently been proposed to conduct the process also in the presence of 2-alkoxyethanols and sulphonates[108]. The technique of this reaction is simple and convenient, and it has therefore been applied in industry. The phosphorylation of cellulose is usually accomplished by heating the reaction mixture at 130–200° for from 15 min to several hours. In order to obtain a more homogeneous product and increase the reactivity of the cellulose, it has been proposed to subject the initial compound to preliminary scouring, desizing, and mercerisation[6].

In spite of the extensive literature on this method of phosphorylation, the effectiveness of the reaction has been obscure until quite recently. Many authors do not indicate the phosphorus content of their products, and sometimes publish extremely contradictory results. Thus the synthesis of a cellulose phosphate containing 11–13% of phosphorus has been reported[33], whereas similar work[101,103] has given specimens containing only 4–6% of phosphorus. The most careful investigation[102] has shown that a phosphorus content of 9% can be obtained only by repeating the phosphorylation procedure three times.

The structure of the cellulose phosphates obtained has not yet been finally elucidated. Most authors suggest that phosphorylation involves mainly the primary hydroxyls of the glucose units[3,120], but this has not been proved. Some research workers[6,26,31,120] regard the products obtained as primary and secondary phosphoric esters, pointing out that monoalkyl phosphates are formed on heating to 150°, and dialkyl phosphates above 150°.

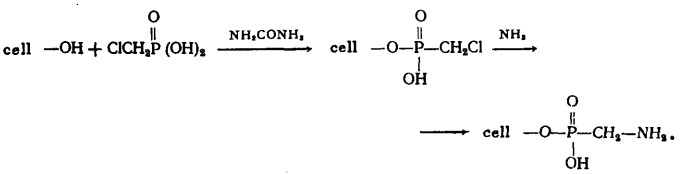
The secondary esters can be of two types — cyclic (I), in which the phosphorus atom is linked by the two bonds with only one glucose unit, and cross-linked (II).



(I) (II)

Several authors associate the formation of structures (I) or (II) with the appearance of definite properties in the resulting compounds, e.g. the cross-linking of the macromolecules through phosphorus with the acquirement of rotproof properties[98].

Alkyl phosphates[124,125] and *NNN'N'*-tetramethylphosphorodiamidic[81], chloromethylphosphonic, and hydroxymethylphosphonic[123] acids[42,43], besides phosphoric acid, can react with cellulose in the presence of nitrogen bases. Above 130° this reaction is accompanied by secondary ammonolysis of the chloromethylphosphonate, with formation of the cellulose aminomethylphosphonate[43]:



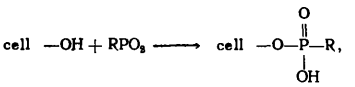
Phosphorylated celluloses obtained by the above method often possess poor mechanical properties, and are therefore unsatisfactory to the consumer. Recently, in order

to obtain less degraded products, phosphorylation has frequently been achieved with poly(vinyl phosphate)[28,30,40,103,124,125]. The loss in mechanical strength of the specimens thus obtained corresponds to the loss for cellulose phosphates containing one-third to one-quarter of the phosphorus content[103]. The mechanism of the reaction has not yet been elucidated; it is suggested that, depending on the conditions, either trans-esterification of poly(vinyl phosphate) by the cellulose or condensation with formation of a mixed phosphate of the two macromolecular compounds can occur[28].

Towards the end of the 1940s reports had appeared in the literature of the phosphorylation of cellulose with pentaerythritolphosphoric acids[126-133]. Reaction is usually complete at 130–180° in 15 min. The phosphorus content of the resulting phosphates does not exceed 3%. No comparison has yet been made of the characteristics of phosphorylated celluloses obtained in this way and by other methods. Nor are data available on the mechanism of this reaction.

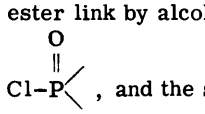
### 3. Phosphorylation by Other Reagents

Anhydrides of phosphoric acids are interesting phosphorylating agents for cellulose. The use of phosphorus pentoxide for this purpose has been patented[134,135]. Derivatives of meta-, pyro-, and poly-phosphoric acids have also found application[104,108,109,114,118,119,136]. It has recently been proposed to obtain acid phosphonates of cellulose by phosphorylating the latter with phosphonic anhydrides[137]:

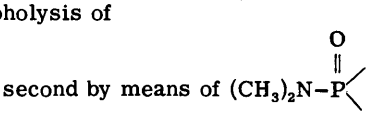


where R = $CH_3$, $C_2H_5$.

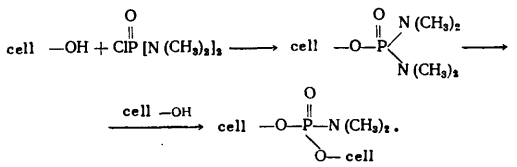
The phosphorylation of cellulose with amides and hydrazides of phosphorus is of definite value, e.g. with the corresponding polyphosphonitrilic derivatives[81,138,139]. In spite of the relatively high temperature (~ 140°) the reaction involves hardly any degradation of the polysaccharide, since no deleterious substances are evolved in the process. A reaction which develops by a mixed mechanism must also be mentioned. Thus tetramethylphosphorodiamidic chloride, on interaction with cellulose, forms its first ester link by alcoholysis of



, and the second by means of

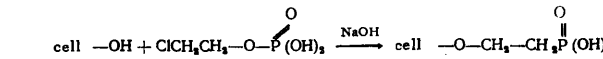


:[81]

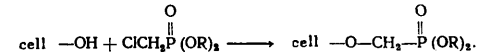


### 4. Indirect Phosphorylation

It appears that derivatives of cellulose containing phosphorus have been prepared in which hydrogen atoms of hydroxy-groups of the cellulose have not been replaced by acid radicals containing phosphorus. Treatment of cellulose with 2-chloroethyl phosphates in alkaline medium yields 2-phosphatoethylcellulose containing 1.3% of phosphorus[140]:

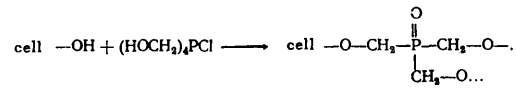


The phosphonomethylation of cellulose by the action of salts[22,25,40,45,141,142] or esters[45] of chloromethylphosphonic acid has been comparatively well studied:

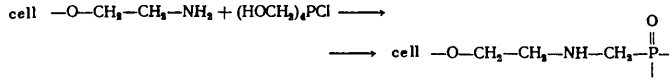


The phosphorus content of the resulting samples usually varies between 0.7% and 2%. The mechanical qualities of phosphonomethylcellulose are not very high, and it is therefore recommended that the initial material should first be treated with 1,3-dichloropropane for the partial cross-linking of the macromolecules[142].

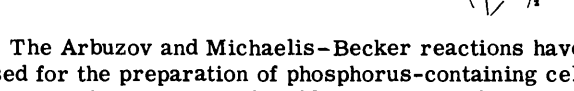
A phosphinylmethylated cellulose is formed when the polysaccharide is treated with tetrakishydroxymethylphosphonium chloride[23,24,143]:



It appears that aminoethylcellulose can be used in this reaction[144]:



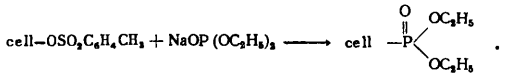
2-Phosphinylaminoethylcellulose has been obtained by the use of azirides of phosphoric or phosphorothioic acids as modifying reagents[145-147]:



The Arbuzov and Michaelis–Becker reactions have been used for the preparation of phosphorus-containing celluloses. Thus reaction of a chloroacetate with triethyl phosphite yields a product which was regarded as a phosphonoacetate[148]. In view of the results of a more detailed study of the Arbuzov reaction using $\alpha$-halogeno-carbonyl compounds[149], such a structure cannot be entirely justified for the product obtained. Quite recently a study has been made of the reaction of chlorodeoxycellulose with triethyl phosphite[77]:

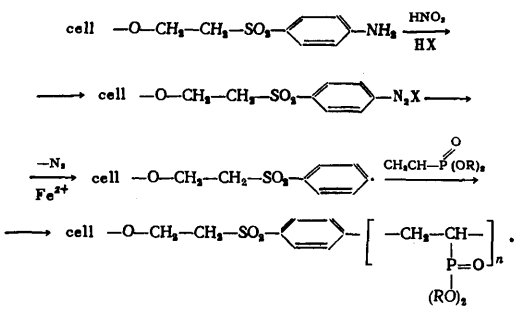


The product contains 5% of phosphorus. An analogous material is obtained by the interaction of cellulose toluene-*p*-sulphonate with sodium diethyl phosphite[13]:



Recently an original method has been developed in the Soviet Union for preparing phosphorus-containing cellulose derivatives by grafting vinylphosphonic esters to the cellulose. The principle of the method consists in introducing a small quantity of aromatic amino-groups into the macromolecule. After diazotisation of the amino-derivative in

the presence of a reducing agent, e.g. a ferrous salt, nitrogen is evolved and macroradicals are formed, which initiate the formation of graft chains on the cellulose. The 2-sulphanilylethyl ether has been used as cellulose derivative containing an aromatic amino-group [150]:



The phosphorus content of the product does not usually exceed 4–4.2%.

## III. PHOSPHITYLATION OF CELLULOSE BY DERIVATIVES OF ACIDS OF TERVALENT PHOSPHORUS

During recent years interest has grown in macromolecular compounds containing acid radicals of tervalent phosphorus. There are obviously three main reasons for this: firstly phosphitylation with acid derivatives of tervalent phosphorus is usually more efficient and occurs under milder conditions than with derivatives of quinquevalent phosphorus [64]; secondly, macromolecular phosphites and phosphonites can be readily converted by reactions of polymeric type into various derivatives of acids of quinquevalent phosphorus which it is difficult or even impossible to obtain by direct phosphorylation [151]; and thirdly, macromolecular derivatives of tervalent phosphorus acids possess specific properties which make them promising for industrial exploitation, e.g. as antioxidants and stabilisers for polymers [152,153], additives in oils [154], etc.

All this obviously applies to modified celluloses containing acid radicals of tervalent phosphorus. Since 1960, therefore, patents and scientific publications have started to appear systematically on the preparation and properties of these compounds.

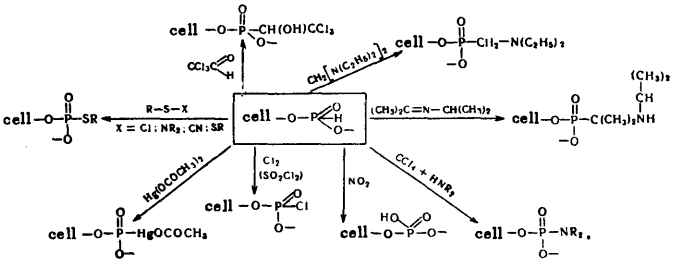
### 1. Phosphitylation by Acid Chlorides

Only one report has appeared on this topic, acetates, butyrates, and other esters of cellulose being phosphitylated with alkyl(or aryl)phosphonous dichlorides and dialkyl(or diaryl)phosphinous chlorides in the presence of tertiary amines [73]. In view of the complexity of the phosphitylation of cellulose with chlorophosphines and similar compounds, as well as the publication of a large number of papers on new methods for the mild phosphitylation of hydroxy-compounds with other reagents, little development on these lines is to be expected in the future.

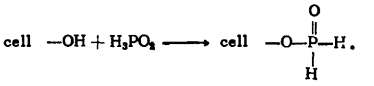
### 2. Phosphitylation by Acids

Phosphorous acid is known to be an effective phosphitylating agent [155], and its reaction with cellulose has therefore been studied. The reaction can be accomplished in several ways — by phosphitylation in an organic solvent, in molten phosphorous acid, or in an inert gas [156] — the second method enabling cellulose phosphites to be obtained containing up to 17% of phosphorus, though the product is strongly degraded. It is most convenient to modify cellulose by the third method [156], the optimum temperature being 120–130°, the duration being 3–15 h, and the phosphorus content reaching 14%.

The products obtained, which are acid phosphites, are reactive compounds which can be converted by reactions of polymeric type into cellulose derivatives containing fragments of various acids of quinquevalent phosphorus [157]:



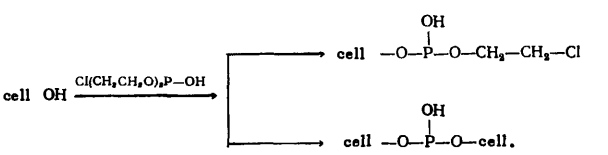
Quite recently cellulose has been phosphinylated by heating it with hypo-phosphorous (phosphinous) acid [158]:



In view of the high coordination and saturation of phosphorus in the compounds obtained, they show great promise for various chemical transformations.

### 3. Phosphitylation by Esters

As efficient phosphitylating agents, esters of tervalent acids of phosphorus are employed also for the phosphitylation of cellulose. A comparatively detailed study of this reaction has been made on mono- [157,159], di- [160–162], and tri-alkyl (or -aryl) phosphites [162,163] of various types and on acid phosphonites [160,164]. Transesterification of acid phosphonites with the reaction products gives cellulose phosphonites cell–O–P($CH_3$)–OH in which $\gamma$ = 150. The transesterification of di- and tri-alkyl (or -aryl) phosphites is a more complex process, products being formed in which one, two, or three alkoxyls (or aroxyls) have been replaced by a polysaccharide residue. The reaction can be followed by introducing a phosphite in which the alkyl radical contains a halogen atom. In the transesterification of bis-2-chloroethyl phosphite, for example, the content of phosphorus and of chlorine in the reaction product is used to establish under what conditions polyesters containing mainly alkyl glycosyl phosphite or mainly diglycosyl phosphite fragments are formed [162]:

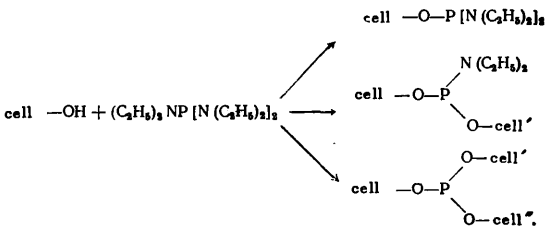


Acid phosphites of the cellulose series, especially those obtained with industrial dimethyl phosphite [161], are of

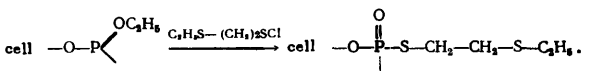
interest for the preparation of various phosphorylated celluloses. They have been converted into compounds containing fragments capable of complex formation, pesticidal activity, etc.[161]

4. Phosphitylation by Nitrogen-Containing Derivatives

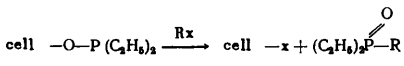
One of the most effective and convenient methods of phosphitylation is the alcoholysis of amides of tervalent acids of phosphorus[165]. This reaction has been applied also to cellulose[166]. Tetraethylphosphinous amide, ethyl tetraethylphosphorodiamidite, and phosphorus hexaethyltriamide have been studied as phosphorylating agents. In the first case a cellulose diethylphosphinite is formed (under optimum conditions the degree of phosphorylation is close to 20%); in the second and third cases, amido-esters or cross-linked esters of cellulose are obtained, e.g.



The normal phosphites and the phosphinites of cellulose which have been prepared are reactive compounds, being oxidised to the corresponding quinquevalent derivatives merely by the action of oxygen[166]. With sulphur they give phosphorothionates and phosphinothionates not hitherto described in the literature. With sulphenyl chlorides, cellulose phosphates are converted into phosphorothiolates. In this way it has been possible to prepare a phosphorylated cellulose containing residues of the well-known insecticide Isosystox[166]:



Dialkylphosphinites of cellulose, like simple esters of tervalent phosphorus, undergo the Arbuzov reaction, forming a deoxyhalogenocellulose:



A paper has appeared very recently on the phosphitylation of cellulose with hydrazides of phosphorous acid. Thus 1-methyltrimethylene dimethylphosphorohydrazidite acylates cellulose under milder conditions than in the corresponding preparation with amides[167].

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A large amount of research has been done on the phosphorylation of cellulose, but a certain uniformity of chemical approach to phosphorylation can be seen in most of the work. In recent years success has been achieved in developing new ways of phosphorylating cellulose by methods which have not yet become "classical". These investigations may be expected to yield new phosphorus-containing materials of interest for the national economy.

Fresh progress in the phosphorylation of cellulose will depend to a considerable extent on the attention paid to physicochemical laws in conducting these transformations of polymeric type.


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# OXIDATION–REDUCTION POLYMERS

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## 1. INTRODUCTION†

Great interest has arisen in recent years in macromolecular compounds of a new type, oxidation–reduction polymers or, as they are still called, electron exchangers. The latter term has been coined by analogy with ion exchangers, but its choice is unfortunate, since the oxidation or reduction of a polymer does not involve the

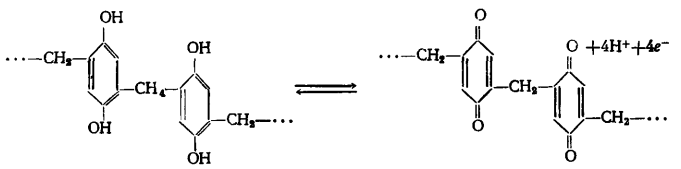
† Fresh results have been published since this paper was submitted for publication, and are collected together in the supplementary references [205–275].

exchange of electrons, as occurs with ions in the case of ion exchangers, but their absorption or donation. Nevertheless, the term has become widely used both in the Soviet and in the foreign literature. Several authors prefer the term "redox resins" or "redoxites".

The synthesis of ion-exchange resins was accomplished in 1936. It was established that the acidic or basic groups of the original monomers retain their properties in the polymeric compounds. The question naturally arose of the possibility of obtaining similar systems containing other functional groups. Much attention was paid to the synthesis of macromolecular compounds containing groups capable of reversible oxidation and reduction. Tsvet discussed the role of such a system as early as 1906 [1] in papers on the chromatographic method of investigation. Many workers have shown that redox groups maintain their oxidation–reduction functions in polymeric compounds. Numerous papers have been published on the synthesis and application of redox polymers, but they have usually been concerned with particular questions, and do not show the present-day position or the prospects for this class of compounds. The few papers and reviews [2-25,205-207] of general character do not give an all-round account of the subject. No systematic classification of redox polymers or rational nomenclature for them has yet appeared.

Redox polymers are macromolecular compounds showing limited swelling, of three-dimensional structure (sometimes linear), which differ in composition but contain groups capable of undergoing reversible oxidation–reduction reactions with substances which can undergo these reactions and are present in contact with the polymers. Their behaviour is similar to that of soluble redox systems, the main difference being that redox polymers are obtained in the form of insoluble granules, can therefore be readily separated from the solution with which they are in contact, and do not contaminate the reaction products.

The reaction resembles the redox process between quinol and quinone. The oxidation–reduction process of a redox polymer can be represented by the equation




Redox polymers are not in the nature of ion exchangers, since they do not contain fixed ions, and therefore undergo oxidation and reduction, not ion exchange, although the phenolic hydroxyls of some redox polymers behave in strongly alkaline medium as fixed ionogenic groups. Individual redox polymers obtained in recent years contain, in addition to the redox groups, fixed strongly acid groups (they are sometimes termed redox ion exchangers [25]).

Work on the synthesis of redox polymers began only comparatively recently. Prokhorov and Yankovskii [26] first obtained redox ion exchangers in the early 1940s by treating sulphonated coal with an iron(II) salt. Later Mills and Dickinson [27] prepared redox ion exchangers by treating anion exchangers with solutions of copper (or silver) salts. According to Sansoni [15] patent claims appeared in 1944 for the preparation of redox polymers by polycondensation methods.

At the end of the 1940s Cassidy and his coworkers [28,29] made extensive investigations on the synthesis and application of polymeric electron exchangers based on vinylquinol. Somewhat later Sansoni [30] published work on the preparation of redox ion exchangers based on monomeric redox systems sorbed on ion exchangers.

Manecke [31] synthesised polycondensation polymers based on benzenepolyols, and Soloway and Schwartz [32] those based on naphthaquinones. The work of Gregor and his coworkers [33,208], Overberger and Lebovits [34], Trostyanskaya [2], Berlin et al. [35-37], Davankov [38,39], Dalibor [40], etc. is also widely known.

## 2. SYNTHESIS OF REDOX POLYMERS BY POLYCONDENSATION

Attempts have been made to obtain redox polymers by the polycondensation of polyhydric phenols, aminophenols, and phenylenepolyamines with formaldehyde [15].

Redox polymers have been synthesised by the polycondensation of quinol or resorcinol with formaldehyde, and of quinol, pyrogallol, and catechol with phenol and formaldehyde [41,42]; and the synthesis and properties of monomolecular quinol–phenol–formaldehyde compounds have been described [43].

A method has been patented [44] for preparing a series of redox condensation polymers on the basis of pyrogallic acid, catechol, and resorcinol.

In order to improve the chemical stability, redox polymers have been synthesised [45,46] on the basis of polycyclic aromatic derivatives of juglone, 2-hydroxyanthraquinone, alizarin, anthrarufin, quinalizarin, chrysazin, and purpurin.

Redox polymers have been obtained also from quinol and formaldehyde, or quinol, phenol, and formaldehyde [19,47-49], or resorcinol, Methylene Blue, and formaldehyde [50], or resorcinol, various dyes, and formaldehyde [40].

Conditions for the production of resorcinol–quinol–formaldehyde polymers have been more closely specified [51].

Berlin and his coworkers [35-37,52,53] have synthesised a new class of macromolecular compounds, the polyaminoquinones, which are capable of oxidation–reduction, and have high thermal stability. These polymers have been obtained by the reaction of chloranil with benzidine (or hexamethylenediamine), quinone with diamines, and of *p*-benzoquinone with bisdiazotised *p*-phenylenediamine, benzidine, and benzidine-3,3′-dicarboxylic acid. Their enhanced thermal stability and their improved magnetic, electrical, and ion-exchange properties make them of great interest [54-56].

Polycondensation of the original monomer with formaldehyde has been used to obtain [57] redox polymers from *p*-nitrosophenol, *p*-nitrosoaniline, hydrazobenzene, arsenobenzene, indamines, indophenols, benzenepolyols, anthracenepolyols, naphthalenediols, phenanthrenepolyols, etc. [209]

A polymer possessing high redox capacity has been synthesised [32] from naphthazarin (5,8-dihydroxy-1,4-naphthaquinone) and formaldehyde.

A linear redox polymer has been obtained [58] by converting *N*-methoxymethyl-polyamides into the *N*-mercaptomethyl form, which in turn can probably be reversibly oxidised and reduced.

The polycondensation[59] of equimolecular quantities of *p*-dimethoxybenzene and 1,4-bischloromethyl-2,5-dimethoxybenzene gives poly-(2,5-dimethoxy-1,4-phenylenemethylene), which after demethylation and oxidation gives a polyquinone. Polymeric quinones are also obtained by oxidising the product of the polycondensation of quinol, phenol, and formaldehyde in the molecular proportions 1:1:3, etc.[210,211]

Polycondensation redox polymers have unsatisfactory kinetic properties[25]. This is one of the principal reasons for their limited use. The poor kinetic properties are to a considerable extent due to the low swellability of the polymers. The ability to diffuse[19,25,60,61], which in these cases determined the reaction velocity, was inadequate. The hydrocarbon skeleton of ion exchangers is hydrophobic, and only the introduction of polar groups into the skeleton confers hydrophilic properties — and hence the power of limited swelling — on the polymer. Although polar (phenolic) groups are present in the macromolecule of polycondensation redox polymers, they are little dissociated in aqueous solution, and therefore the swelling power of the polymer is low. On the other hand, redox reactions, unlike ion-exchange processes, are not ionic, and therefore occur slowly.

Redox processes in solution can be catalysed by certain substances[62,63]. The oxidation $Fe^{2+} \rightarrow Fe^{3+}$, for example, occurs more rapidly in the presence of chloride ions. It has been established[64], in an investigation of electron-exchangers, that chloride ions accelerate the reaction of cerium ions with the polymer. Manecke and his co-workers[46] did not observe this effect of chloride ions on their redox polymers, but they showed that, when monomeric quinones are added to the solution, the reaction between oxidant and polymer is more rapid and the potential of the polymer is established within a shorter time on titration (Fig. 1). The monomeric quinone is here acting as a catalyst. The quinone probably reacts with the quinol form of the polymer to form a semiquinone, the latter form of the polymer being oxidised more rapidly[46]. It is generally known[65,66] that under certain conditions a monomeric quinol can react with a monomeric quinone, and that intermediate products can be formed in the oxidation of quinol. Thus there are no grounds for completely excluding the possibility of such processes in polymeric compounds.

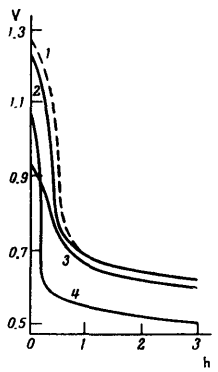



Fig. 1. Fall in potential with time during the reduction of a sulphuric-acid solution of $Ce^{4+}$ on various redox polymers[46]: 1) redox polymer from quinol, phenol, and formaldehyde; 2) redox polymer from quinol, hydroxybenzenesulphonic acid, and formaldehyde; 3) as (2) in 1 *N* KCl solution; 4) as (2) with additions of a catalyst (dimethylbenzoquinone).

It has been proposed to introduce other polar groups, mainly sulpho-groups[46,212] (Fig. 1), to improve the hydrophilic and kinetic properties of redox polymers. However, they are found to diminish the stability of the polymer, and above all do not produce sufficient effect.

The addition of oxidation and reduction catalysts does not solve the kinetic problem. The decisive factor in the reaction velocity is the diffusion of reactants into the interior of the polymer. The low swelling power of the polymer does not provide sufficiently large intramolecular pores, commensurate with the radius of the reactant ions or molecules. Therefore reaction takes place only on the surface of the polymer grains, or else inside the grain but at an extremely low rate. There is no great value in accelerating the process on the surface of the grains, since the redox capacity is insignificant in such cases. The rate-determining factor is not the reaction itself but the diffusion process.

The authors consider that it is possible to accelerate redox processes by producing a polymer of definite structure, e.g. macroporous, which would ensure ready access of the reactants to all functional groups.

An extensive literature exists on the effect of structure on ion-exchange processes[213] and on the use of ion-exchange sieves[67-96]. The use of strongly swelling polymers, possessing great intramolecular porosity, is of decisive importance for the ion exchange of substances of high molecular weight[97,98]. The synthesis has recently been developed, and the industrial manufacture organised, of macroporous ion exchangers of low swelling power. Such resins have considerable advantages over the usual strongly swelling ion-exchange resins, being characterised by improved physicochemical properties[99,214-232].

A method has been proposed[100] for the synthesis of macroporous redox polymers which permits a considerable increase and control of their moisture content, and hence of the reaction velocity. It yields polymers of high and controllable porosity, this being achieved by adding to the reaction mass sufficient of an inert diluent, which is subsequently washed out of the final product. Compounds containing hydroxyl, carboxyl, or carbonyl groups, several inorganic salts, carbohydrates, and other substances can be mixed with the initial monomers for this purpose. Isopentyl alcohol and oleic acid are the most effective; pyridine, sodium chloride, glucose, etc. are less effective. The resulting redox polymers are characterised by increased moisture-absorption and redox capacity and improved kinetic properties (Fig. 2). The amount of additive used is of great significance here.

Methods for the synthesis of phenol–formaldehyde polymers have been worked out in some detail. However, the first attempts at preparing quinol–phenol–formaldehyde redox polymers showed little success. The polymers were obtained as a powdery mass, which was hydrophobic and of low redox capacity. It was later proposed[42] that ethanol and other organic substances should be used as solvents, and this permitted considerable improvement in the properties of the resulting electron exchangers.

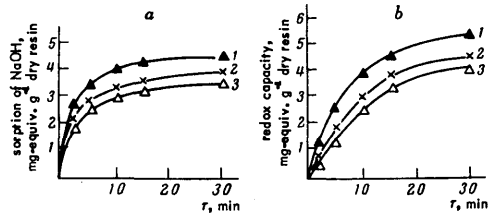



Fig. 2. Kinetic curves for macroporous redox polymers [100]: *a*) sorption of NaOH; *b*) the reduction $Fe^{3+} \rightarrow Fe^{2+}$; with the pores formed by different concentrations of isopentyl alcohol: 1) 0.55 M; 2) 0.92 M; 3) 0.

Phenol has also been used as third component in the synthesis of benzenepolyol–formaldehyde redox polymers, with the aim of (1) obtaining insoluble cross-linked polymers, and (2) avoiding the formation of semiquinones.

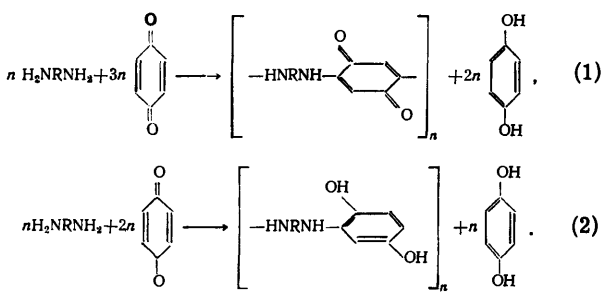
Little difference is found among methods suggested for the synthesis of this type of redox polymers. The preparation of quinol–formaldehyde polymers can be cited as a characteristic example [19,42,100]. A mixture of quinol and phenol was dissolved in ethanol, concentrated hydrochloric acid was added, and then a solution of formaldehyde was gradually introduced. The reaction mass was heated to about 60°, and maintained at this temperature first with stirring in the reaction vessel and then in a thermostat. The resulting polymer was ground up, and unchanged monomers were rinsed out and extracted with alcohol and water.

In order to obtain redox polymers based on mixtures of benzenepolyols, a solution of formaldehyde and quinol in methanol was added to the reaction vessel. After some time resorcinol and an acid catalyst were added at an elevated temperature, and an exothermic reaction began. The polymer was freed from unchanged impurities by steam-distilling off the latter [51].

Redox polymers were obtained based on resorcinol and Methylene Blue [50] and on resorcinol and various dyes [32,40].

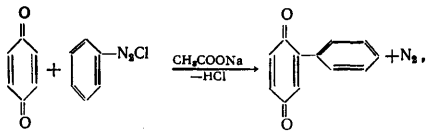
Polymers based on juglone, 2-hydroxyanthraquinone, alizarin, anthrarufin, chrysazin, quinalizarin, and purpurin have been obtained in the same way as quinol–phenol–formaldehyde polymers, in alcoholic medium but under more severe conditions, with precondensation at 100°, hardening, and aging of the gel at 100–150° for several hours. The more severe processing conditions have a deleterious effect on the redox properties of the resulting polymers [45,46].

Polyaminoquinones have been obtained by the interaction of various diamines with chloranil and *p*-benzoquinone in alcohol at elevated temperature [35,52]. The reaction of quinones with diamines can be represented by the scheme [52]



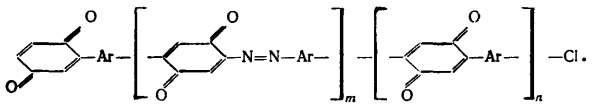

Increasing the quantity of diamine had no effect on the yield of polyaminoquinone.

The process of arylating quinones by the action of diazonium salts [101,102]

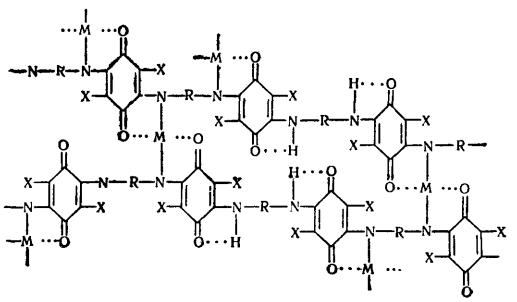



and the application of this method to the preparation of arylated quinones [103], as well as the synthesis of a diquinonylbenzene by the reaction of *p*-phenylenebisdiazonium salts with *p*-benzoquinone, have been described previously [104].

The interaction of bisdiazotised *p*-phenylenediamine, benzidine, and benzidine-3,3′-dicarboxylic acid with quinone has been used [53] to obtain hitherto undescribed polymeric azophenylenequinones of general formula




The polymers possess electron-exchange properties and appreciable electronic conductivity, are fairly thermostable, and gave narrow electron spin resonance signals having an integral intensity of the order of $10^{18}$–$10^{20}$ paramagnetic particles per gramme [53]. Polymeric aminoquinones are also able to form with metal salts insoluble and infusible complexes having roughly the structure [35]



The electron-exchange properties, reaction velocity, chemical stability, redox potential, and several other properties have been examined with many types of redox polymers. In the investigation of oxidation–reduction processes, oxidised polymers can be reduced with various reducing agents — ammoniacal sodium dithionite (10% solution in 1 *N* ammonia), a sulphuric-acid solution of titanous chloride (10% solution in 1 *N* sulphuric acid) — rate of oxidation usually being expressed by the change in potential of the polymer with time. The potentiometric titration curves obtained show that condensation products of quinol react more slowly than polymers of pyrogallol and catechol, a gradual slowing down in the redox process being observed with all specimens [31].

Polymers based on pyrogallol with a high phenol content reacted more rapidly (Fig. 3) and had lower chemical stability [31] (Table 2). The rate of oxidation of naphthaquinone (juglone) polymers was higher than that of polymers of the anthraquinone (quinalizarin) series, but lower than that of quinol polymers [45,46] (Fig. 4).

The redox capacity was most frequently determined from the number of milliequivalents of tervalent iron which could be reduced by one gramme of polymer (based on the

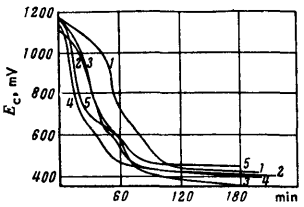



Fig. 3. Fall in potential with time in the oxidation of various redox polymers by the same quantity of oxidant[31]:
1) quinol–phenol–formaldehyde (1 : 1 : 2);
2) pyrogallol–phenol–formaldehyde (1 : 1 : 3);
3) pyrogallol–phenol–formaldehyde (1 : 0.5 : 2);
4) catechol–phenol–formaldehyde (1 : 2 : 4);
5) catechol–phenol–formaldehyde (1 : 1 : 2).

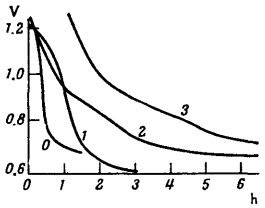



Fig. 4. Fall in potential with time in the reduction of a sulphuric-acid solution of $Ce^{4+}$ on various redox polymers[46]:
0) quinol–phenol–formaldehyde (1 : 1 : 3);
1) juglone–phenol–formaldehyde (1 : 1 : 3);
2) quinalizarin–phenol–formaldehyde (1 : 1 : 4);
3) quinalizarin–phenol–formaldehyde (1 : 2 : 3).

TABLE 1. Redox capacity of naphthaquinone and anthraquinone polymers[46].

| Component reactants | Molecular proportions | Redox capacity, mg-equiv. $g^{-1}$ |
|---|---|---|
| Juglone–phenol–formaldehyde | 1:1:3 | 4.5 |
| 2-Hydroxyanthraquinone–phenol–formaldehyde | 1:1:2 | 1.1 |
| Alizarin–phenol–formaldehyde | 1:1:3 | 0.5 |
| Anthrarufin–phenol–formaldehyde | 1:1:2 | 1.4 |
| Ditto | 1:1:3 | 1.3 |
| » | 1:1:4 | 2.1 |
| » | 1:2:3 | 1.1 |
| Chrysazin–phenol–formaldehyde | 1:1:2 | 1.5 |
| Ditto | 1:1:3 | 1.5 |
| » | 1:1:4 | 2.5 |
| » | 1:2:3 | 1.5 |
| Purpurin–phenol–formaldehyde | 1:1:3 | 0.7 |
| Quinalizarin–phenol–formaldehyde | 1:1:2 | 1.7 |
| Ditto | 1:1:3 | 1.7 |
| » | 1:1:4 | 2.5 |
| » | 1:2:3 | 1.4 |

TABLE 2. Fall in redox capacity of certain polymers[31].

| Component reactants | Molecular proportions | Redox capacity, mg-equiv. $g^{-1}$ | | Fall in capacity, % |
|---|---|---|---|---|
| | | 1st determination | 2nd determination | |
| Quinol–phenol–formaldehyde | 1:1:2 | 6.4 | 6.4 | 0.0 |
| Ditto | 1:1:2.5 | 7.0 | 6.9 | 1.4 |
| » | 1:1:3 | 6.8 | 6.7 | 1.5 |
| » | 1:0.5:2 | 9.9 | 9.2 | 7.1 |
| » | 1:0:1 | 14.7 | 12.6 | 14.3 |
| Pyrogallol–phenol–formaldehyde | 1:1:2 | 5.9 | 5.3 | 10.2 |
| Ditto | 1:1:3 | 5.5 | 5.1 | 7.3 |
| » | 1:1:4 | 5.3 | 4.6 | 13.2 |
| » | 1:1:2.5 | 3.9 | 3.3 | 15.4 |
| » | 1:2:3 | 4.2 | 3.6 | 14.3 |
| » | 1:2:4 | 4.0 | 3.6 | 10.0 |
| » | 1:0.5:1.5 | 7.5 | 6.3 | 16.0 |
| » | 1:0.5:2 | 7.7 | 6.5 | 15.6 |
| » | 1:0.5:2.5 | 7.7 | 6.5 | 15.6 |
| Catechol–phenol–formaldehyde | 1:1:2 | 7.3 | 5.8 | 20.6 |
| Ditto | 1:1:3 | 7.1 | 5.7 | 19.7 |
| » | 1:0.5:1.5 | 9.4 | 7.5 | 17.6 |
| » | 1:0.5:2 | 9.5 | 7.4 | 22.1 |

dry material) under equilibrium conditions[233]. Values representing the redox capacity of several polymers are given in Tables 1 and 2.

Chemical stability has usually been determined by repeating oxidation–reduction cycles, the redox capacity being determined after each cycle and the stability of the polymer being assessed from the change therein. Polymer samples obtained from dihydric phenols showed inadequate stability: their capacity fell somewhat after many alternations of oxidation–reduction cycles (Table 2)[19,31]. The stability fell also under the action of solutions of oxidising agents and of alkalis. Polymers obtained by treating sulphonated phenol-formaldehyde resins with potassium hydrogen fluoride or with diazotised sulphanilic acid and then reducing with sodium dithionite solution were also unstable[47].

The fall in redox capacity might be a consequence of — (1) gradual elution of components of low molecular weight containing active groups, (2) irreversible oxidation of hydroxybenzenes in the polymer to quinone methides[31,105], and (3) degradative processes.

Polymers based on chloranil and benzidine were black in colour, did not melt, and did not dissolve in the usual organic solvents, being soluble only in concentrated sulphuric acid and partly in formic acid and dimethylformamide; whereas polymers of chloranil and hexamethylenediamine were infusible pinkish grey powders, insoluble in the usual organic solvents but soluble in concentrated sulphuric acid[35,37]. Their disadvantage is the difficulty of quantitative reduction of active groups. Polyaminoquinones are more difficult to reduce[52] than polyvinylquinols[28,29], being similar in this respect to aromatic polyquinones[106] containing systems of conjugated bonds.

The ability of polyquinones in oxidised and reduced states to swell has been examined[107,234]. The infrared spectra have shown that, after a few oxidation and reduction cycles, polyquinones acquire a very small number of carboxy-groups.

The physical and mechanical properties, the chemical stability, and the static and dynamic redox capacity of resorcinol–quinol–formaldehyde polymers have been examined[51] as functions of the hydrogen-ion concentration, the rate of filtration, and the concentration of reducible iron ion; the reproducibility of the static redox capacity has also been determined. After seven oxidation–reduction cycles, the capacity has fallen from 4.4. to 3.6 mg-equiv. × × $g^{-1}$, the mean decrease per cycle being 2.6% (Fig. 5). The apparent redox potential was determined by potentiometric titration, and a technique worked out for regenerating the oxidised polymer. Tin(II) chloride, sodium sulphite, sodium dithionite, hydroxylamine, and other substances were used as reductants, the most successful reducing agent for this polymer being sodium dithionite. The physical and mechanical properties and the chemical stability of the resulting polymers are listed in Table 3.

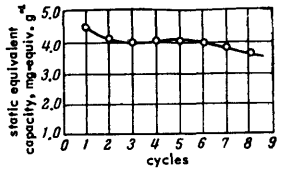



Fig. 5. Reproducibility of static redox capacity of resorcinol–quinol–formaldehyde polymer with respect to the iron ion [51].

TABLE 3. Physical and mechanical properties and chemical stability of quinol–resorcinol–formaldehyde polymers [51] (determined by methods described in monograph [108]).

| Conditions | Solvent | Loss in wt., % |
|---|---|---|
| Thermal stability 150° | Methanol | 20.45 |
| Comminution 93.2% | Ethanol | 17.4 |
| Grinding 102.7% | Acetone | 19.7 |
| Bulk density of air-dry polymer 0.686 t $m^{-3}$ | Benzene | 2.5 |
| Bulk density of moist polymer 0.588 t $m^{-3}$ | Hydrogenated kerosene | 2.0 |
| Swellability, 11.66% | 3.5 *N* nitric acid | 4.2 |
| | 3.5 *N* hydrochloric acid | 0.2 |
| | 6.0 *N* sulphuric acid | 1.5 |
| | 2.5 *N* caustic soda | 6.1 |

It was concluded from an analysis of the potentiometric titration curves that a semiquinone is formed during the redox titration of a polymer based on quinol, resorcinol, and formaldehyde, or on quinol, phenol, and formaldehyde [41,109]. An equation suggested earlier [110] was used to calculate the equilibrium constant for oxidised and reduced forms of the condensation products, which in the second case (molecular proportions 1 : 1 : 2) was 43. [41]

The standard redox potential $E_0$ of these polymers has been determined. For the first group of polymers $E_0$ = = 0.68 V, [51] whereas the values for the second group are 0.605 V at pH 1.67, [41] and 0.70 V at pH 0.2. [31]

Measurement of the redox potential of an electron--exchange polymer by potentiometric titration consists in mixing the insoluble polymer with a soluble compound possessing a redox function, in which it is easy to measure the redox potential [23,41,111]. When equilibrium is established, the redox potential of the polymer $E_{pol}$ is equal to the potential of the solution $E_{soln}$. By means of the auxiliary system in solution, therefore, the equilibrium potential of the solid redox polymer can be measured at the same time.

If the concentration of oxidised substances is represented [23] by [Ox], and that of reduced substances by [Red], we obtain for the solution

$$E_{soln} = E_{0\,soln} + \frac{RT}{nF} \ln \frac{[Ox]_{soln}}{[Red]_{soln}}, \quad (1)$$

and for the polymer

$$E_{pol} = E_{0\,pol} + \frac{RT}{nF} \ln \frac{[Ox]_{pol}}{[Red]_{pol}}, \quad (2)$$

where $E_0$ is the standard redox potential (in V), $n$ the number of electrons involved in the reaction, $F$ Faraday's constant (96 500 C), $R$ the gas constant (8.31 J $deg^{-1}$ $mole^{-1}$), and $T$ the absolute temperature (°K). When equilibrium is established, we have

$$E_{0\,soln} + \frac{RT}{nF} \ln \frac{[Ox]_{soln}}{[Red]_{soln}} = E_{0\,pol} + \frac{RT}{nF} \ln \frac{[Ox]_{pol}}{[Red]_{pol}}, \quad (3)$$

which can be written

$$E_{0\,pol} = E_{0\,soln} + \frac{RT}{nF} \ln \frac{[Ox]_{soln}}{[Red]_{soln}} - \frac{RT}{nF} \ln \frac{[Ox]_{pol}}{[Red]_{pol}}. \quad (4)$$

Substitution for the difference in potential from Eqn. (1) in Eqn. (4) yields for the redox potential of the polymer finally

$$E_{0\,pol} = E_{soln} - \frac{RT}{nF} \ln \frac{[Ox]_{pol}}{[Red]_{pol}}. \quad (5)$$

If $[Ox]_{pol}/[Red]_{pol}$ is known, $E_{0\,pol}$ can be calculated. When 50% of the reactive groups in the polymer have been oxidised, we obtain

$$\frac{[Ox]_{pol}}{[Red]_{pol}} = 1 \quad \text{and} \quad \frac{RT}{nF} \ln \frac{[Ox]_{pol}}{[Red]_{pol}} = 0, \quad (6)$$

i.e.

$$E_{0\,pol} = E_{soln}. \quad (7)$$

The equilibrium constant can be calculated in the way described by Manecke [112]. Reaction of the redox polymer in the reduced form $H_2R$ with oxygen, for example, can be represented schematically by the equation

$$2H_2R + O_2 \rightleftarrows 2R + 2H_2O.$$

The equilibrium constant $k$ for this reaction is computed from the difference between the potential of oxygen $E_{0\,O_2}$ and that of the polymer $E_{0\,pol}$:

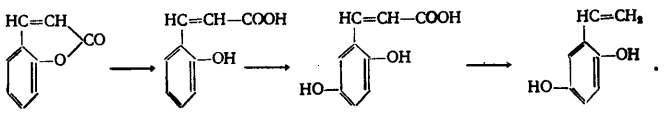
$$E_{0\,O_2} - E_{0\,pol} = \frac{RT}{4F} \ln \frac{a_R^2 \, a_{H_2O}^2}{a_{H_2R}^2 \, P_{O_2}} = \frac{RT}{4F} \ln k, \quad (8)$$

$$\ln k = \frac{4R}{RT} (E_{0O_2} - E_{0\,pol}). \quad (9)$$

Putting $E_{0\,O_2}$ = 1.23 V and $E_{0\,pol}$ = 0.7 V, [31,41,42] we obtain $k = 3 \times 10^{36}$.

## 3. SYNTHESIS OF REDOX POLYMERS BY POLYMERISATION

In 1949 macromolecular compounds capable of oxidation and reduction were obtained by the polymerisation of vinylquinol [28,29]. The vinylquinol starting material was prepared by the scheme [28,29,113,114]

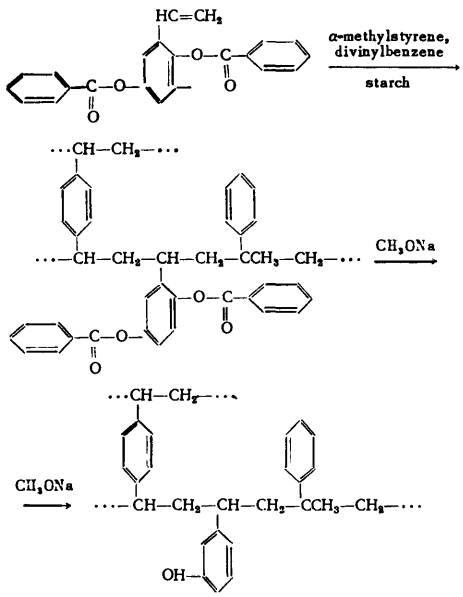



It can also be prepared by another method [115,116], which consists of several stages and its very laborious. The final yield of vinylquinol is low as in the previous case.

The polymerisation of vinylquinol was conducted, without a catalyst, in sealed tubes at 125°. After cooling, the polymer was extracted with hot benzene to remove unchanged monomer. The polymer was a brittle solid mass, pale amber in colour, soluble in polar organic solvents but insoluble in benzene. In the presence of water the polymer became soft and tacky. It was not a success: although all the active groups were reduced, the polymer gradually lost its activity with repeated oxidation–reduction cycles [28,29].

It was established later[117,118] that these polymers consisted predominantly of dimers and trimers of vinylquinol. It is difficult to obtain macromolecular compounds because quinol itself inhibits polymerisation[119].

When the hydroxy-groups in vinylquinol were protected by conversion into dibenzoates or diacetates, polymers could be obtained of molecular weight of the order of 70 000.[117,121] The dibenzoate or the diacetate was copolymerised also with styrene, α-methylstyrene, vinylpyridine, methyl methacrylate, methyl acrylate, or divinylbenzene in the presence of an initiator (benzoyl peroxide, azoisobutyronitrile) and a protective colloid (starch) at an elevated temperature (58–90°) in sealed tubes which had first been evacuated and then filled with nitrogen. The polymerisation was conducted in toluene (styrene and α-methylstyrene), chloroform (4-vinylpyridine), or benzene (methyl methacrylate and methyl acrylate). The duration of polymerisation was 30 minutes, and the degree of conversion <10%.[121-125]




The linear polymers were precipitated with hexane[124]. Linear benzoylated polymers dissolved better in toluene than in acetic acid; whereas the solubility of acetylated polymers was greater in acetic acid.

Polymers of different composition were obtained[126] by copolymerising vinylquinol with acrylic or maleic acid.

In order to improve the kinetic properties[64,122-123,127], cross-linked polymers and copolymers of the above dibenzoates or diacetates were sulphonated, and the ion-exchange and electron-exchange properties investigated. Oxidation and reduction of the sulphonated polymers were extremely slow, but completely reversible over the range $8.5 > pH > 4.7$. Outside these pH limits, partial decomposition of the polymers and irreversible oxidation were observed, and under certain conditions the cation-exchange capacity decreased. The stability of the polymers could be increased by replacing vinylquinol by its methylated derivatives, and divinylbenzene by other cross-linking agents. The polymerisation of 2,5-dimethoxy-3,4,6-trimethylstyrene and 2,5-dimethoxy-3,6-dimethylstyrene gave[128] new methylated vinylquinol polymers — polyvinyl-3,4,6-trimethylquinol and polyvinyl-3,6-dimethylquinol — possessing redox properties. Polymerisation was conducted in the presence of the boron trifluoride–ether complex at a low temperature (-20°) for 36 h. The resulting polymer was treated with hydrobromic acid in glacial acetic acid. The former dissolved in organic solvents, whereas the latter was an insoluble rubberlike substance.

The chemical shifts in the nuclear magnetic resonance signals of several methylated quinols and their derivatives have been measured[129], and the behaviour of dimethyl ethers of quinol and that of methylated quinols on oxidation, etc. have been studied[120,130,235,236].

It has been proposed[127] to obtain redox polymers also by the copolymerisation of vinylquinol with monomers of general formula $CH_2 : CAlkAr$, where the alkyl group contains 1–8 C atoms, and Ar represents phenyl, biphenylyl, naphthyl, or their derivatives. Sometimes other components have been added to the initial reaction mixture.

Reaction with carbonyl chloride of a suspension of 2,5-diacetoxyphenylalanine hydrochloride[131] in dioxan gave 4-(2,5-diacetoxybenzyl)-2,5-dioxooxazolidine, polymerisation of which in dioxan in the presence of alcoholic alkali yielded poly-β-(2,5-diacetoxyphenyl)-DL-alanine of molecular weight 11 000, which could be hydrolysed by alkali and by concentrated hydrochloric acid to poly-β-(2,5-dihydroxyphenyl)-DL-alanine. These methods can be used to obtain new redox polymers of polypeptide character.

A general method has been worked out[132] for obtaining hydroxylated polystyrenes possessing electron-exchange properties and high redox potentials, and methods have been improved for the synthesis of polyvinylquinol. Poly-3-vinylcatechol and poly-3-vinylbiphenyl-4,4′-diol have been prepared from the bismethoxymethyl ethers of the 3-vinyl derivatives of respectively quinol, catechol, and biphenyl-4,4′-diol. The structure of the ethers was established by hydrolysis and reduction to ethyl derivatives of phenols, and also by infrared and ultraviolet spectroscopy. Polymerisation of the resulting monomers was conducted in toluene in the presence of benzoyl peroxide.

Sulphonated derivatives of dicyclopentadienyliron (ferrocene) have also been obtained[133], but were unstable to oxidants. They deposited iron. Potentiometric titration of ferrocene and several of its derivatives has been undertaken. Titration of the diammonium disulphonate gave no positive results, since the reversible transition of iron from the ferrous to the ferric form was accompanied by side-reactions.

Redox potentials have been determined[64,134], ultraviolet spectra of polymers and copolymers of vinylquinol have been recorded, and the effects of pH, salt concentration, and sulphonation on the absorption spectra have been studied. The apparent standard redox potential has been found to depend on the degree of reduction and to be independent of molecular weight when the latter is large. The polymers proved to have higher potentials than the monomers. The potential of a polymer is established slowly on titration at a platinum electrode.

Methods have been described[135] for obtaining 2-vinylanthraquinone from 2-methylanthraquinone. Macromolecular compounds having electron-exchange properties have been prepared by the polymerisation of 2-vinylanthraquinone or by its copolymerisation with styrene, α-methylstyrene, or maleic anhydride in the presence of azoisobutyronitrile, benzoyl peroxide, titanous chloride, or metallic sodium.

Anthraquinone redox polymers have been obtained[136] by the polymerisation of 2-vinylanthraquinone, the reaction of anthraquinone-2-aldehyde and anthraquinon-2--ylmethyl toluene-*p*-sulphonate with poly(vinyl aclohol), and also the polycondensation of ethyl anthraquinon-2--ylmethylenemalonate with ethylene glycol, butane-1,4--diol, diethylene glycol, glycerol, etc.[237].

2,3,5-Trimethyl-6-vinylbenzene-1,4-diol[137], 2-methyl--3-vinyl-1,4-naphthaquinone[138], 1(and 2)-vinylanthraquinone[139], 2,3-dimethyl-5-vinyl-1,4-phenylene diacetate, and 2,3,5-trimethyl-6-vinyl-1,4-phenylene diacetate[140] have been synthesised, among other monomers[238-248], for the preparation of redox polymers.

Soluble and cross-linked poly-*m*-aminostyrene has formed the basis[141,142] for the synthesis of poly-6-vinylisatin, poly-6-vinylindirubin, and poly-6-vinylindol-3-benzothien-2′-ylindigo, and the redox capacity, apparent standard redox potential, and other properties have been examined. Porous indigoid resins have been obtained from porous poly-*m*-aminostyrene.

2-Methyl-3-vinyl-1,4-naphthaquinone and 2-vinylanthraquinone have been used to obtain redox polymers of more ordered structure[143,144,249] and improve chemical properties. Naphthaquinone derivatives did not polymerise, and their diacetates polymerised with great difficulty. Therefore only copolymers of 2-vinylanthraquinone with styrene and with divinylbenzene possessing redox properties were obtained. The copolymerisation was conducted in dimethyl sulphoxide at 140°. Replacement of part of the latter by n-butyl acetate and lowering the temperature of copolymerisation to 100° yielded redox polymers of spongy structure. The copolymer was sulphonated to improve its kinetic properties. The rate of the redox reaction was sufficiently high if not more than 70–80% of the total redox capacity was used. Other parameters are given in Table 4.

2,5-Bistetrahydropyran-2′-yloxyphenyl *p*-vinylphenyl sulphone, 2-tetrahydropyranyl *p*-vinylphenyl sulphide, and 4-methyl-2,5-bistetrahydropyran-2′-yloxyphenyl *p*-vinylphenyl sulphone have been synthesised[145,146,250], and converted into redox polymers. Continuous titration and a method of periodic titration with bromine in 80% acetic acid gave the standard redox potentials $E_0$ of the linear redox polymers as 0.753 ± 0.005 V for poly-*p*-vinylphenylsulphonylquinol, 0.718–0.721 V for poly-2-methyl-5-*p*--vinylphenylsulphonylquinol, and also other values for intermediate and model compounds. It was established that substituents in an unoxidised benzenoid ring have no significant influence of $E_0$, whereas the value of the latter is appreciably affected by the nature of a substituent in a quinonoid ring. Addition of an $RC_6H_4SO_2$ group to quinones increased $E_0$ by 44–66 mV in the case of quinol derivatives, and by 77–88 mV in the case of methylquinol.

Macromolecular redox systems can be obtained which are based on compounds of the polyvinylformal type[147].

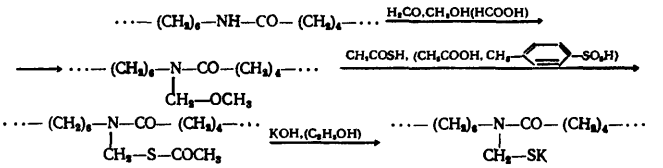
TABLE 4. Composition, ion-exchange capacity, and redox capacity of sulphonated 2-vinylanthraquinone polymers[144].

| Specimen | Molar ratio of 2-vinylanthraquinone to sum of comonomers | Divinylbenzene in polymer, mole % | Ion-exchange capacity, mg-equiv. $g^{-1}$ | Redox capacity, mg-equiv. $g^{-1}$ |
|---|---|---|---|---|
| 1 | 1:10 spongy | 12.5 | 4.375 | 1.26 |
| 2 | 1:10 | 12.5 | 4.491 | 1.01 |
| 3 | 1:3 | 6.0 | 3.563 | 2.60 |
| 4 | 1:2 | 6.0 | 3.080 | 3.24 |
| 5 | 1:1 | 8.0 | 2.021 | 4.76 |
| 6 | 1:1 | 6.0 | 2.042 | 4.61 |
| 7 | 1:1 | 4.0 | 2.084 | 4.46 |

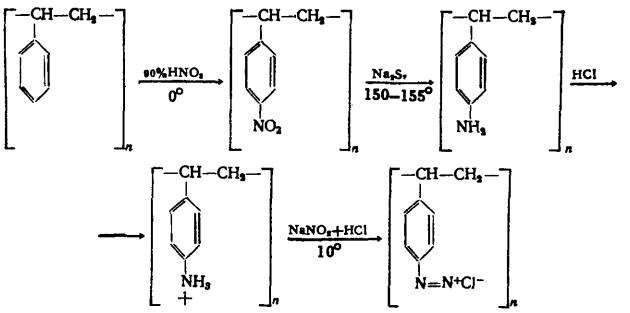
## 4. SYNTHESIS OF REDOX POLYMERS BY THE INTRODUCTION OF REACTIVE GROUPS INTO AN INERT POLYMER

Inert macromolecular compounds, containing no redox groups, have been used to obtain redox polymers.

The introduction of mercapto-groups into polyamides (nylon) yields electron-exchange polymers[25]:



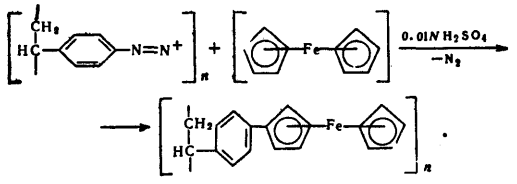
Sansoni[15] nitrated[148] cross-linked polystyrene, reduced the resulting poly-*p*-nitrostyrene to poly-*p*-aminostyrene, and diazotised the product:



He obtained[15,21] the redox polymers KVPAS, MVPAS, PFPAS, WBPAS, MBPAS, and CHPAS by coupling the diazotised poly-*p*-aminostyrene with Crystal Violet, Methyl Violet, Parafuchsine, tetramethyl-*p*-phenylenediamine, Methylene Blue, and *p*-benzoquinone respectively. These polymers showed different colours in oxidised and reduced forms. The most successful product was obtained by coupling with Methylene Blue.

The coupling of diazotised poly-*p*-aminostyrene[251] with *p*-benzoquinone, 1,4-naphthaquinone, naphthaquinone oxide, anthraquinone, and 1-chloroanthraquinone gives polymers having electron-exchange properties[23]. When quinol is used, polymers of the polyphenylbenzoquinone type are obtained[149].

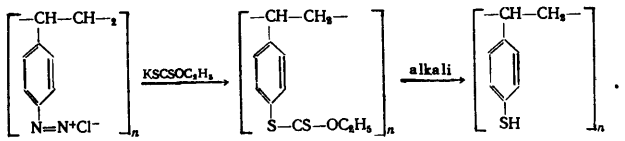
Polyferrocenestyrene redox resins have been obtained from diazotised poly-*p*-aminostyrene and ferrocene[150,207]:



Their apparent redox potentials (415 ± 10 mV) and their redox capacity with respect to the $Fe^{3+}$ ion (5.4 mg-equiv.$g^{-1}$) were determined. After twelve oxidation–reduction cycles the redox capacity had fallen from 5.4 to 2.4 mg-equiv. $g^{-1}$.

A similar method for obtaining redox polymers has been described by other authors[151,152,252].

Redox polymers of benzenethiol type have been obtained in a similar way[33,153]. Diazotised polyaminostyrene was converted by the action of potassium xanthate into poly-(vinylphenyl xanthate), which was hydrolysed to the corresponding thiol:

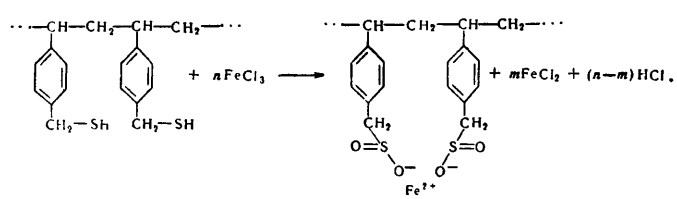



The redox capacity of the resulting polymer was 6.6 mg-equiv. $g^{-1}$. The same polymer has been synthesised from *p*-aminoacetophenone[34].

It has been proposed[154] to obtain redox polymers by introducing mercapto-groups and others[253,254] into copolymers of styrene and divinylbenzene.

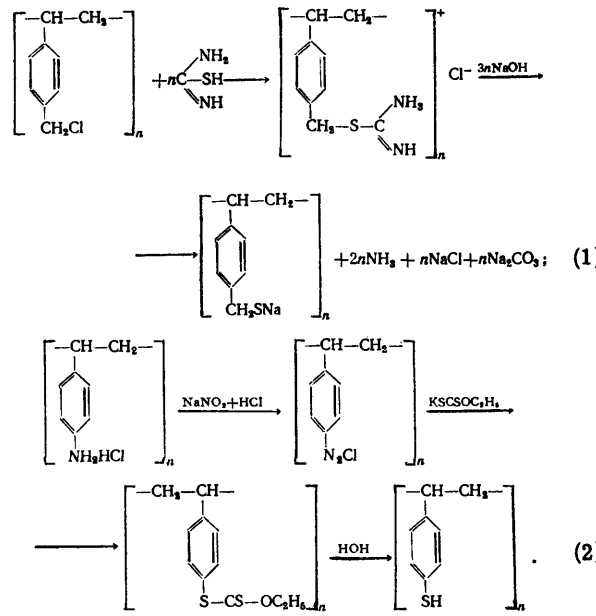
Trostyanskaya and Tevlina[155] tested methods for preparing styrene–divinylbenzene copolymers containing mercapto-groups, and found the optimum conditions for the synthesis. Copolymers of styrene with divinylbenzene or diallyl maleate, obtained by copolymerisation in suspension, were chloromethylated by the action of paraformaldehyde and hydrogen chloride in the presence of zinc chloride[156]. The chlorine atoms in the copolymers were replaced by mercapto-groups by the action of sodium sulphide or thiourea followed by hydrolysis.

The thio-copolymers showed high redox power, which remained unchanged during 8–10 cycles. The exchange capacity for the sodium ion was 2.9 mg-equiv. $g^{-1}$ at pH > 10, and 1.9 mg-equiv. $g^{-1}$ at pH 7, while the electron-exchange capacity with respect to the $Fe^{3+}$ ion was 0.4 mg-equiv. $g^{-1}$. It was pointed out that most of the mercapto-groups could be oxidised to the sulphinic acid, and take part in ion-exchange with reduced iron cations:




Mercapto-copolymers of styrene and divinylbenzene have been used for the reduction of bivalent copper ions from $CuCl_2$ solution to univalent copper, and of silver ions to metallic silver.

The synthesis[38] and properties have been described of polymers of two types containing thiol groups, a chloromethylated styrene-divinylbenzene copolymer being treated with a solution of thiourea (scheme 1) or an aminated copolymer being diazotised, xanthated, and hydrolysed (scheme 2):




The polymers possessed both electron-exchange and ion-exchange properties. The dynamic exchange capacity with respect to the $Ag^+$ ion from 0.1 *N* silver nitrate solution was 2.7–2.8 and 2.13 mg-equiv. $g^{-1}$ for (1) and (2) respectively.

A simplified method has been developed[157–159] for obtaining electron-exchange polymers of thiol type based on styrene–divinylbenzene copolymers, by treating the swollen copolymer with a solution of elementary sulphur in carbon tetrachloride in the presence of aluminium chloride with heating. The duration of the reaction at 75–78° was 8–9 h. The redox capacity of such a polymer is lower than 1.6 mg-equiv. $g^{-1}$.

Conditions have been studied[160,161] for the interaction of sulphur and polystyrene in dichloroethane and nitrobenzene in the presence of Friedel–Crafts catalysts. The products possessed little redox ability.

Redox polymers have been prepared by the reaction of anthraquinone-2-aldehyde with poly(vinyl acetate) and poly-(vinyl alcohol)[162,255], the reduction of sulphonyl chlorides of styrene-divinylbenzene copolymer with polysulphides[163], and the treatment of polymers of 2-vinylpyridine with chloromethane or bromomethane[164] or of polymers and copolymers of vinyl monochloroacetate with alkali or alkaline-earth metal hydrosulphides[165], etc.[166] Treatment of poly(vinyl chloride) with hydrogen sulphide under pressure gives polychloroethylenethiol[167]. Poly(methyl α-mercaptoacrylate) has been obtained by the reaction of poly-(methyl α-bromoacrylate) with potassium hydrosulphide.

Reaction of a solution of poly(vinyl alcohol) with thiourea in the presence of hydrogen bromide gives a thiouronium salt[168–179], which is hydrolysed by alkali to polyethylenethiol.

Macromolecular compounds possessing redox properties have been obtained by the reaction[171] of styrene–maleic anhydride copolymers with 1-aminoanthraquinone,

7-amino-3-oxophenothiazine, and *p*-amino-*p'p"*-bisdimethylaminotriphenylmethane.

It has been claimed[172] that thermostable polymers having electron-exchange properties can be obtained by adding an alcoholic solution of a diamine and/or a polyamine rapidly with stirring to a hot alcoholic solution of *p*-benzoquinone. The mixture is boiled for about 40 minutes, and the polymer separated after a few hours.

Redox polymers have been obtained by using the reaction of a polymeric primary or secondary amine with the lactone of β-2,5-dihydroxyphenylpropionic acid[173].

Electron-exchange polymers have been obtained by treating polychlorotrifluoroethylene (Kel-F) powder with a solution of tetrachloroquinol in ether[174]. The redox capacity was 1.6 mg-equiv. $g^{-1}$ based on the dry polymer. These redox polymers were unstable: after a few oxidation-reduction cycles, a fall was observed in the already low redox capacity (perhaps owing to the elution of active components of low molecular weight).

## 5. REDOX ION EXCHANGERS

Ion-exchange materials, which form the framework, can be used as starting materials for the preparation of redox ion exchangers. Additional functional groups are attached to them by subsequent treatment with monomeric compounds possessing redox properties. These monomers either react with the resin or are adsorbed on it.

Prokhorov and Yankovskii[26] suggested a method for removing dissolved oxygen from water by passing the latter through a layer of sulphonated coal previously treated with a solution of a ferrous salt. This for the first time opened up a path to the preparation of redox ion exchangers.

Redox ion-exchange resins have been obtained also by treating anion exchangers with solutions of copper or silver salts[27], which formed complex compounds with the amino-groups of the anion-exchange resin:

$$4R{-}NH_2 + CuSO_4 \longrightarrow [Cu\,(R{-}NH_2)_4]SO_4.$$

Reducing properties were conferred on them by subsequent treatment with alkaline sodium dithionite solution. This reduced the copper (or silver) to a finely divided metallic state, in which the corresponding oxidation readily occurred, and the reaction products could again be reduced. The cycle could be repeated many times. On passage of water through a layer of such an ion exchanger, however, small amounts of copper (or silver) ions passed into the filtrate as a result of dissociation of the complex compounds on the surface of the anion-exchange resin. In order to retain the ions, it was proposed to use a cation-exchange resin in the sodium form, or an anion-exchange resin in the hydroxide form.

Redox ion exchangers have been obtained[15,30,175] by treating the water-swollen cation-exchange resins Wofatit F, Amberlite IR 120, and Dowex 50 with solutions of salts of iron, tin, cerium, titanium, Fuchsine, Methyl Violet, Crystal Violet, Tolusafranine, Rosinduline, Capri Blue, or Methylene Blue; and the anion-exchange resins Wofatit M and Amberlite IRA 400 with solutions of quinol, anthraquinol, tetrachloroquinol, and dihydroindigodisulphonic acid.

In the same way[175-178] strongly basic anion-exchange resins have been used as the basis for the preparation of redox ion-exchangers with inorganic anions — $H_3PO_2^-$, $S_2O_3^{2-}$, $SO_3^{2-}$, $S_2O_4^{2-}$, $NH_2NHCSO_2^-$, and $BH_4^-$ — their redox capacities and redox potentials being given in Table 5.

Redox ion-exchange resins (Table 6) have been obtained also by treating the strongly basic anion-exchange resin Dowex 2 with solutions of Alizarin, thymolphthalein, indigotetrasulphonate, indigodisulphonate, or Thymol Blue; the weakly basic anion-exchange resin Dowex 3 with a solution of thymolphthalein; or the cation-exchange resins Dowex 50 and Amberlite IRC 50 with solutions of Methylene Blue or Crystal Violet[180] (see also Ref. 256).

Redox ion-exchangers have been prepared in an analogous manner using Fuchsine and other active substances[19,257,258].

Dalibor[40,259] prepared redox ion exchangers by treating the strongly acidic KPS and the weakly acidic CP cation-exchange resins with solutions of dyes (Capri Blue, Thionine, Methylene Blue, Nile Blue, Neutral Red, etc.) and inorganic salts ($TiCl_3$, $CrCl_2$, $CuCl_2$, $Na_2S_2O_4$), and also by saturating the anion-exchange resin L 150 with solutions of mercaptoacetic or α-mercaptopropionic acid. This resulted in ionogenic bonding of the dye or inorganic salt with the resin. The interaction of Methylene Blue and of titanous chloride with the cation-exchange resin can be represented by the schemes

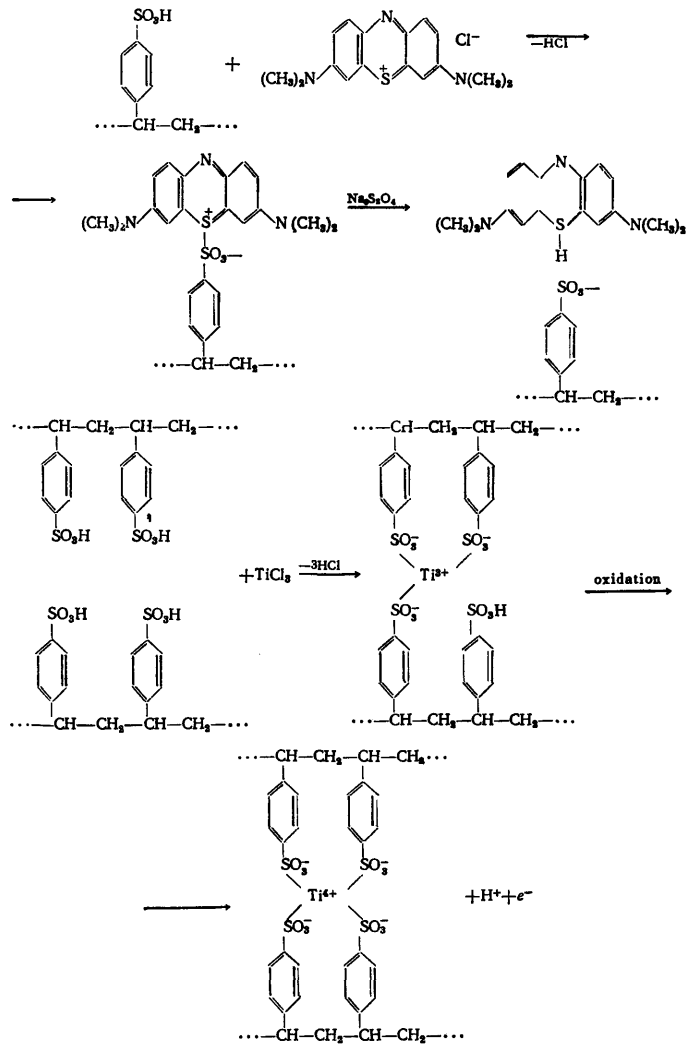


TABLE 5. Properties of some redox ion exchangers [176].

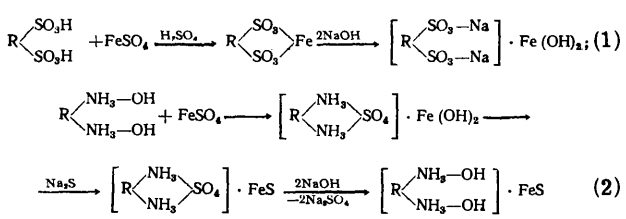
| Bound anion | Redox capacity, mg-equiv. $g^{-1}$ | time, min, to reach 50% | time, min, to reach 100% | Standard redox potential of free anion (Ref. 179) |
|---|---|---|---|---|
| $SO_3^{2-}$ | 0.83 | 5.0 | 20 | −0.17 |
| $S_2O_3^{2-}$ | 2.14 | 8.7 | 35 | −0.08 |
| $H_3PO_2^-$ | 0.37 | 8.3 | 30 | +0.50 |
| $S_2O_4^{2-}$ | 1.99 | 3.3 | 25 | +1.12 |
| $NH_2NHCSO_2^-$ | 2.13 | 5.4 | 60 | |
| $BH_4^-$ | 8.4 | — | — | |

TABLE 6. Quantities of dyes adsorbed in various ion exchangers [180].

| Dye | Ion-exchanger | Bound dye, mg/2 g ion-exchanger |
|---|---|---|
| Thymol Blue | Dowex 2 (strongly basic) | 58.0 |
| Indigodisulphonate | ditto | 100.0 |
| Indigotetrasulphonate | » | 100.0 |
| Thymolphthalein | » | 40.0 |
| Alizarin | » | 99.8 |
| Thymol Blue | Dowex 3 (weakly basic) | 8.0 |
| Thymolphthalein | ditto | 10.0 |
| Methylene Blue | Dowex 50 (strongly acidic) | 98.2 |
| Crystal Violet | ditto | 99.2 |
| Crystal Violet | Amberlite IRC 50 (weakly acidic) | 99.4 |

The quantity of dye which is bonded, but not of titanium, depends on the degree of cross-linking and the porosity of the ion-exchanger (Table 7). This can be explained by the fact that the pores in the cation-exchange resin are smaller than the radius of the dye molecule but comparable with the radius of the titanium ion.

Vol'f and his coworkers [181-184] obtained redox ion exchangers by successively treating (1) cation exchangers and (2) anion exchangers with solutions of iron(II) sulphate, alkali, and sodium sulphide (see also Refs. 260 and 261):



Redox ion-exchange resins have been obtained also by saturating a weakly basic anion-exchange resin with $CuSO_4$ solution and then reducing with alkaline sodium dithionite solution, a strongly basic anion-exchange resin with sodium sulphite solution, and a polystyrene cation-exchange resin with iron(II) sulphate solution [49].

According to available information, the Chemical Process Co. of California has placed on the market in the U.S.A. the redox ion exchanger Dualite S-10, obtained by treating the anion-exchange resin Dualite A-3 with a solution of a copper salt [16,19,22,185].

A redox anion exchanger has been obtained by saturating [186] an anion-exchange resin containing strongly and feebly basic functional groups (in the proportions 1 : 1) with an ammoniacal solution of sodium dithionite, and has been used to remove dissolved oxygen from desalinated water.

TABLE 7. Quantities of dye or titanium bound on cation exchanger [40].

| Dye or titanium | Cation-exchanger and its degree of cross-linking, % | | Bound dye or Ti, mg |
|---|---|---|---|
| Methylene Blue | KPS (strongly acidic) | 3 | 557 |
| Ditto | ditto | 6 | 204 |
| » | » | 8 | 292 |
| » | CP (weakly acidic) | 3 | 162 |
| » | ditto | 5 | 144 |
| Neutral Red | KPS (strongly acidic) | 3 | 276 |
| Ditto | ditto | 6 | 176 |
| » | » | 8 | 200 |
| » | CP (weakly acidic) | 3 | 201 |
| » | ditto | 5 | 137 |
| Janus Green | KPS (strongly acidic) | 3 | 332 |
| Ditto | ditto | 6 | 80 |
| » | » | 8 | 112 |
| » | CP (weakly acidic) | 3 | 156 |
| » | ditto | 5 | 98 |
| Capri Blue | KPS (strongly acidic) | 3 | 540 |
| Ditto | ditto | 6 | 318 |
| » | » | 8 | 403 |
| » | CP (weakly acidic) | 3 | 22 |
| » | ditto | 5 | 28 |
| Titanium | KPS (strongly acidic) | 3 | 51.0 |
| » | ditto | 6 | 49.8 |
| » | » | 8 | 48.0 |

The anion-exchange resin used was a product of the condensation of phenoxyethyl chloride with tetraethylenepentamine.

The method of preparing redox ion exchangers is fairly simple. The water-swollen cation-exchange resin in the hydrogen form, or the anion-exchange resin in the hydroxide form, is stirred for a definite time in a solution of the appropriate dye or inorganic salt, and then carefully washed with water and alcohol to remove unchanged dye or salt. The compounds mentioned above are used as reducing agents.

Redox ion exchangers have not yet found wide practical application. As already mentioned, this is due mainly to their instability, low redox capacity and gradual decrease therein, and sometimes to unsatisfactory kinetic properties. Redox ion exchangers are therefore less promising than redox polymers.

Another class of compounds containing metals of variable valency must be mentioned, in particular derivatives of chlorophyll and haemin, which possess redox functions [187]. They are of no practical value owing to their insignificant redox capacity, but they are of some interest as models of enzymes [187-193]. Natural compounds of this type play an important part in biological processes [187].

## 6. INORGANIC ELECTRON EXCHANGERS

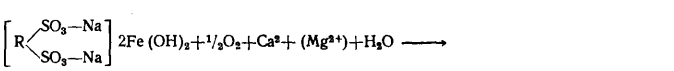
Several inorganic redox electron exchangers are known. The redox capacity of the mineral nontronite is 0.16 mg-equiv. $g^{-1}$, which corresponds to one-third of the total iron content [194]. The exchange capacity of the reduced form is aproximately 0.005 and 0.085 mg-equiv. $g^{-1}$ with respect to the $Cl^-$ and the $^{60}Co^{2+}$ ion respectively. Other inorganic electron exchangers — sodium polyvanadate, hydroxyphenyl silicate, etc. — also exist. The advantages of inorganic electron exchangers over redox polymers are absence of irreversible oxidation, relatively high rate of oxidation, and great stability to high temperatures and radiation; their disadvantages are very low capacity and instability in strongly acid and strongly alkaline media.

## 7. APPLICATIONS OF REDOX POLYMERS

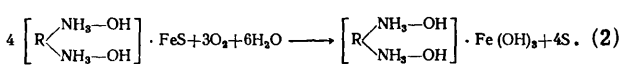
Redox polymers can be used to reduce the ions $Fe^{3+}$, $Cr^{6+}$, $V^{5+}$, $Ce^{4+}$, $Ti^{4+}$, $Ag^{+}$, $Pu^{2+}$, etc.[2,48,100,174,175,195]; to separate cations by selective reduction[15]; for the selective reduction of aldehydes to alcohols[164]; for the oxidation of copper, tin, chromium, bromide, and iodide ions[100,155]; for the oxidation of aldehydes to acids[164]; for the dehydrogenation of hydrazobenzene, cysteine, ascorbic acid, tetrahydronaphthalene, etc.[112,196]; and also for the preparation of hydrogen peroxide[17,19,100,197,198]. They can be employed to remove peroxides or readily reducible substances from lubricating and transformer oils, to remove sulphur from refined petroleum fractions[164], and to free acetylene from oxygen[19] (see also Refs. 261-265).

By means of redox polymers it is also possible to remove dissolved oxygen from water, which is very important in the struggle against corrosion[17,19,42,186,199,261,266-269].

Redox ion exchangers can be employed for the simultaneous deoxygenation and softening of water[183,184]:

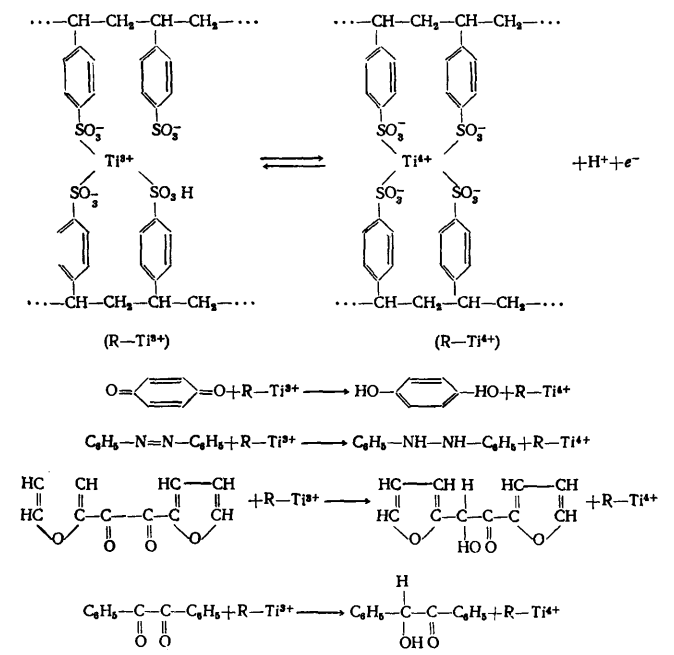


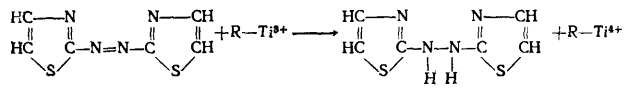
(1)



(2)

Redox ion exchangers based on Methylene Blue, Thionine, Capri Blue, Nile Blue, Neutral Red, and some other compounds have been used for the reduction of indigotetrasulphonate, indigodisulphonate, and Rosinduline GG. Redox ion exchangers prepared with $Ti^{3+}$ and $Cr^{2+}$ are employed for the reduction of *p*-benzoquinone, 1,4-naphthaquinone, benzil, furil, azobenzene, 2,2'-azothiazole, ammonium metavanadate, etc.[40]:





Redox ion-exchangers prepared by treating the anion-exchange resin L 150 with sodium dithionite solution have been used for the reduction of triphenyltetrazolium chloride and some other substances. The reduction of sodium tellurite and 2,2'-*p*-(di-*o*-methoxy)diphenylene-3,3',5,5'-tetraphenylditetrazole bromide by the anion-exchanger L 150 on which mercaptoacetic or $\alpha$-mercaptopropionic acid has been adsorbed was accelerated by light[40].

Paper impregnated with a solution — or coated with an insoluble powder — of a redox polymer can be used in radial chromatography[121] and as an indicator for the detection of small traces of oxygen, chlorine, and other oxidising agents[50,201].

Redox polymers can be employed as electrodes for the measurement of solution pH[202] and as catalysts for oxidation or reduction[17,19,100,164] and other reactions[203].

The application of redox polymers in medicine for therapeutic purposes[163], mainly for protection from radiation[204], will evidently acquire great importance[270-275].

Redox polymers have not hitherto become widespread in industry. The reasons are the unsatisfactory kinetic properties, the instability of the capacity values, and the high cost of the initial components.

The immediate task is to develop methods for the synthesis of redox polymers which will ensure a high reaction velocity and chemical stability of the polymers.

The kinetics of redox processes can be improved by producing redox polymers of macroporous structure. The chemical stability can probably be increased by using very pure vinyl monomers and producing polymers of more regular structure.

The development of effective methods, involving few stages, of the synthesis of the initial monomers may appreciably lower the cost of redox polymers.


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