RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

March 1965

ALCOHOL DERIVATIVES OF THE ALKALI AND ALKALINE EARTH METALS, MAGNESIUM, AND THALLIUM(I)

N. Ya. Turova and A. V. Novoselova

CONTENTS

I. Classification of the alcohol derivatives of the elements 161

II. Alkoxides of the alkali and alkaline earth metals, magnesium, and thallium(I) 162

A. Methods of preparation 162

B. Physical properties of alkoxides and certain structural problems 167

C. Chemical properties of alkoxides and their main applications in organic and inorganic preparations 171

1. Addition reactions 171

2. Substitution reactions 174

3. Oxidation reactions 176

4. Thermal decomposition of alkoxides 176

5. Catalytic action of alkoxides 176

III. Phenoxides of the alkali and alkaline earth metals, magnesium, and thallium(I) 177

A. Methods of preparation 177

B. Properties of phenoxides 179

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 ($K_{diss} \geq 10^{-10}$). 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 ΔH for the replacement of subsequent H atoms (thus the value shown in Fig. 1 for ΔH 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 (which are usually insoluble in ammonia[41]), the equilibrium of the ionic reaction:

$$M(NH_3)_6 + nROH \underset{}{\overset{NH_3}{\rightleftharpoons}} M(OR)_n + n/2\ H_2\ (n=1 \text{ or } 2),$$

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.

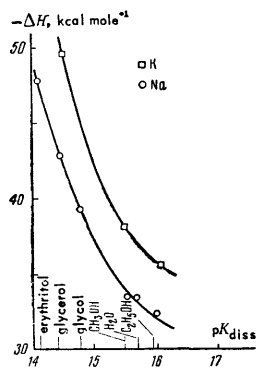


Fig. 1. Relation between the acidity function of alcohols and the heats of formation of the alkali metal alkoxides by the reaction:

$$M_{solid} + ROH_{liquid} = MOR_{solid} + \tfrac{1}{2}H_{2\ gas}.$$

The value of ΔH 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]

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 ΔH and the ΔH 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 (ΔH 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] †

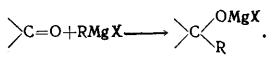
(b) Reduction of carbonyl-containing compounds. This class includes, firstly, many reduction

§ 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, $C_3H_5(OH)(ONa)_2.C_2H_5OH$.

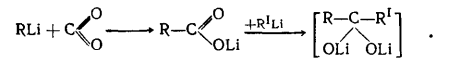
† This reference is incorrect. References to Meisenheimer's work in this area are to be found in "Grignard Reactions of Nonmetallic Substances" by M. S. Kharasch and O. Reinmuth, Constable, London, 1954, pp. 1264–1276 (Ed. of Translation).

reactions of Grignard complexes which are accompanied by the formation of alkoxymagnesium halides — derivatives of secondary and tertiary alcohols:

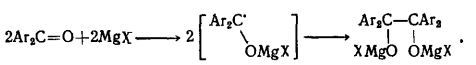


That the products of this reaction were alkoxides was finally decided only in 1941 by Nesmeyanov and Sazonova. Until then many authors had considered them to be addition compounds of RMgX and oxo-compounds [10].

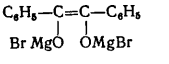
After the discovery of the Grignard synthesis, the possibility of using alkylsodium and alkyllithium compounds [105,106] as reductants for carbonyl compounds was demonstrated. The reaction of organolithium compounds with carbon dioxide, described by Gulman, must be mentioned. As a result of addition 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:



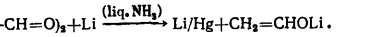
An alkoxide of a special type, an enolate of structure



was obtained in the reduction of the α-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].

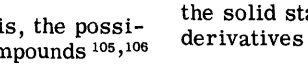
The formation of metalketyls occurs also in the action of metallic sodium or potassium on aromatic and aliphatic ketones [109,110]. The reaction of dialkyl and diaryl carbonates with sodium takes place quantitatively and serves for the production of extremely pure carbon monoxide. In this case, alkoxides 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].

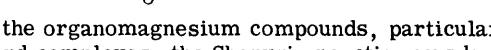
The reaction of carbon monoxide with the alkali and alkaline earth metals also belongs formally to this class of reactions. The pyrophoric "carbonyls" formed as a result have attracted the attention of chemists since the time of Liebig. Until very recently it was thought that they were salts of hexahydroxybenzene — 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] 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: $x Mg(C_6H_5)_2 + SiH_4 = HMgC_2H_5 + SiH_{4-x}(C_2H_5)_x$ — 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° = 26.43 $H_T^0 - H_0^0$ = 3374, Φ^* = — 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, β = 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 5×10^{-2} mmHg, α = 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., α = 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, α=3—5; I[139]; II[43]	NaOR, decomp. 270° I[14, 162]; II[43]; V[162]	KOR, decomp. 250° I[14, 148]; 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*[173, 173]	$(KO)_2R$[173, 174] | $(RbO)_2R$[171, 173] | $(CsO)_2R$[115, 173, 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]

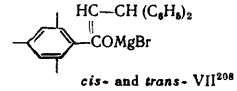
R	Solubility, moles NaOR $litre^{-1}$	R	Solubility, moles NaOR $litre^{-1}$
$n\text{-}C_3H_7$	>1	$iso\text{-}C_4H_9$	0.63
$iso\text{-}C_3H_7$	0.22	$s\text{-}C_4H_9$	0.66
$n\text{-}C_4H_9$	>1	$t\text{-}C_4H_9$	0.34(27°)

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°) $Mg(OR)_2\cdot 3ROH$, decomp. 40° $Mg(OR)_2$, decomp. 350° I[21—26]; III[57, 191, 192]	$Ca(OR)_2$, decomp. > 150° I[193, 194]; II[44, 45]; III[55, 56, 192, 195]; IV[45]; V[97]	$Sr(OR)_2$ II[44]; IV[45]; V[97]	$Ba(OR)_2$ decomp. 250° I[28]; II[44, 45]; IV[45]; V[28, 140]
C_2H_5OH	$Mg(OR)_2\cdot x ROH$ $Mg(OR)_2$, I[21, 25—31]; III[57]; VIII[125] $C_2H_5OMgOCH_3$, III[61] C_2H_5OMgX, X=H, BH_4, AlH_4 VIIc[61, 122]; X=C_2H_5, VIIa[201]	$Ca(OR)_2\cdot 2ROH$, decomp. 50° I[193, 194, 197, 31]; II[45]; III[193, 196—199]; IV[45] $Ca(OR)_2$	$Sr(OR)_2$ II[44, 45]; IV[45]	$Ba(OR)_2$ II[44, 45]; IV[45] $Ra(OR)_2$[200]
$n\text{-}C_3H_7OH$	$Mg(OR)_2$, I[19, 24]	$Ca(OR)_2$, I[193]		
$iso\text{-}C_3H_7OH$	$Mg(OR)_2$, I[30, 152]; III[57]			
$iso\text{-}C_4H_9OH$	$Mg(OR)_2$, I[19]	$Ca(OR)_2$, II[44, 45]; IV[45]		$Ba(OR^n)_2$, II[202]
$iso\text{-}C_5H_{11}OH$	$Mg(OR)_2$, 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 | CH_2OH	MgO_2R, III[57]	CaO_2R, II[45,202]; IV[45]; $Ca[OROH]_2$, IV[45]	SrO_2R II[46, 202]; IV[46]	BaO_2R, II, IV[46]
$HOCH(CH_2OH)_2$	MgO_2ROH, III[57]	CaO_2ROH, V[204]		
$HOCH_2CHOH$ | $HOCH_2CHOH$		$CaO_2R(OH)_2$, 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]	$[(C_6H_5)(BrMgO)C=]_2\cdot(C_2H_5)_2O$ VII[107]	 *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 α 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 $NaOC(C_6H_5)_3$ (μ = 1.62 D) [165] and $LiOBu^t$ (μ = 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).

§ α 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[213]		
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[213]		
$R(OTl)_6$-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]	$C_{12}H_{18}O_7(OTl)_4$ 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 λ_∞ 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. ΔH 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	—
	$n\text{-}C_3H_7OH$	1:1	4.67	3.76	—
	$iso\text{-}C_4H_9OH$	1:1	2.71	—	—
	$iso\text{-}C_5H_{11}OH$	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 μ 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

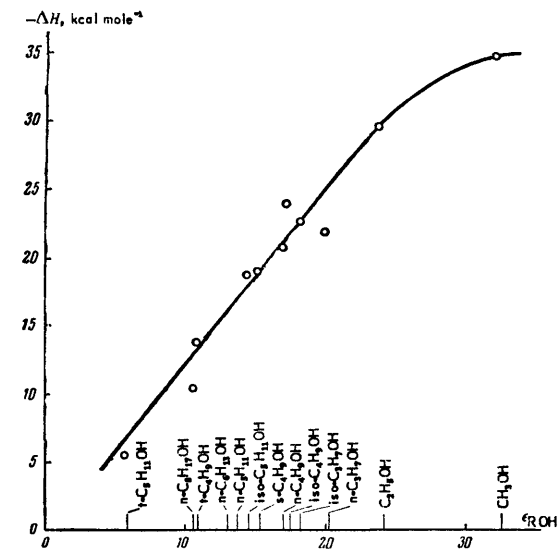


Fig. 2. Relation between the heats of formation of the alcohol addition compounds by the reaction:

$$C_2H_5OMgI + 3ROH = C_2H_5OMgI.3ROH$$

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]

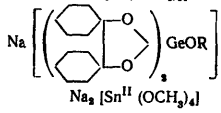
Hence their molecules, by analogy, for example, with $Al[BH_4]_3$, appear entirely covalent and it can be assumed that there is something in common between the molecular structures of "alkoxy-salts" and the corresponding double hydrides. In connection with this, there is the interesting question of the 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
$K[Li(iso\text{-}OC_3H_7)_3]$	—	—	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
$K[D(NH_2)(OCH_3)_3]$	—	—	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, 237
$M[Al(OR)_4]_2$	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
$K[Al(NH_2)(OC_2H_5)_3]$	—	—	226
$M[Al(OR)_x R'_{4-x}]_n$	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
$Na_2[Sn^{II}(OCH_3)_4]$	—	—	248
$Na[Sn_2(OC_2H_5)_5]$ (?)	—	—	226, 249, 250
$M_2[Sn(OC_2H_5)_6]$ (?)	(NaH), K, Sn^{II}	—	226, 250, 251
$KH_2[Ti(OC_4H_9)_6]_2$	—	—	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
$Na[Fe(OR)(CO)_3]$ **	—	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:

$$MOR + H_2S \rightarrow MHS \xrightarrow[(ROH)]{t^\circ} M_2S\downarrow.$$

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.nROH. 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

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 Ba(OR)(OH)·0.33ROH $Ba(OH)_2 \cdot 2ROH \cdot H_2O$[98,197,279]
C_2H_5OH		Ca(OR)(OH)·0.33ROH[197,198,280] Ca(OR)(OH)[272]		Ba(OR)(OH)·0.33ROH[197,279]

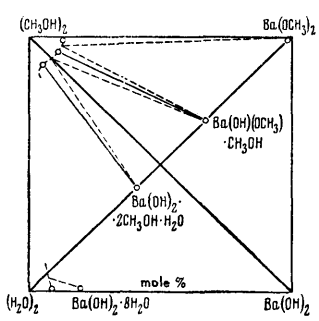


Fig. 3. Approximate solubility diagram for the $Ba(OCH_3)_2$–CH_3OH–H_2O system (20°) after Scholder and Kreutz[98].

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.

(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:

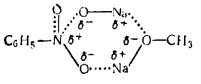
$$NaOC_2H_5+3I_2 \longrightarrow CH_2I_2+CHI_3+H_2O+NaI.$$

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]:

$$C_6H_5NO_2+CH_3ONa \longrightarrow C_6H_5-\overset{\overset{O}{|}}{N}=NC_6H_5+HCOONa+CH_2O+H_2O.$$

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 α-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:

$$M(OR)_n \rightarrow M_2O_n+C_nH_{2n}+ROH \quad (I)$$

$$M_2O_n+ROR \quad (M_2O_n) \quad (II)$$

$$C_nH_{2n+2}+C_nH_{2n}CHO+H_2\ (III) \qquad M(OH)_n+C_nH_{2n}. \quad (IV)$$

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:

$$2\ \begin{matrix}CH_2OM\\|\\CH_2OH\end{matrix} \xrightarrow{t^\circ<200^\circ} (CH_2OM)_2+(CH_2OH)_2.$$

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:

$$RCH_2CH_2\dot{O}H + H\dot{C}H-CH_2OH \xrightarrow{(-H_2O)} RCH_2CH_2-CH-CH_2OH.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad R'$$

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[314,318,319,323,324]; VI[321]; IX[322]
	Cr (o-$C_6H_4OLi)_3 \cdot 2C_4H_8O$[316]	$NaOAr \cdot 3H_2O$; m.p. 52°	
		$NaOAr \cdot NaOH \cdot 2.5H_2O$; m.p. > 100°	$CsOAr$, V[318]
		$NaOAr \cdot 0.5C_4H_8O_2$	
		$NaOAr$, m.p. 60°, decomp. 450°; [17,317]; II[147]; V[318–320]; VI[321]; IX[322]	
2-$CH_3C_6H_4OH$	$NaOAr \cdot 3ArOH$		$KOAr \cdot 3ArOH$
	$NaOAr \cdot n\ ArOH \cdot 6H_2O$ (n=1 or 2)		$KOAr$, V[318,319]
	$NaOAr \cdot H_2O$		
	$NaOAr \cdot 3NaOH \cdot 6H_2O$		
	$NaOAr$, m.p. < 0°, V[319,325]; 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° KOAr, m.p. 36°; V[319,319]
4-$CH_3C_6H_4OH$	NaOAr, m.p. 125°, decomp. 450°; I[312]; V[312,319]; VI[326]	KOAr·3ArOH, m.p. 148° KOAr, m.p. 92°, decomp. 420°; V[312,319,319,323]
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[319,323]; VI[326]	KOAr·4ArOH·5H_2O KOAr, liquid; V[319,323]
β-$C_{10}H_7OH$	LiOAr, I[218] NaOAr, m.p. 120°; I[220] V[319,323]; VI[326]	KOAr·2ArOH·5H_2O KOAr, m.p. 40° I[218]; V[319,323]
2-$CH_3OC_6H_4OH$	2NaOAr·5ArOH·2H_2O, m.p. 139° NaOAr·5ArOH, m.p. 172° NaOAr, m.p.. 120°; V[319,323]; VI[327]	KOAr·3ArOH KOAr·ArOH·1.5H_2O, m.p. 188° KOAr, m.p. 168°; 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° 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; NaOAr, V[332]	KOAr·2ArOH; 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 NaOAr, decomp. 220°; V[283]	
2,4,6-$Br_3C_6H_2OH$		KOAr·2ArOH KOAr, V[332,332]
2,4,6-$I_3C_6H_2OH$		KOAr·2C_2H_5OH KOAr, decomp. 90°; α ~ 5 (in $CHBr_3$); V[282]
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] NaOAr·H_2O; V[334,335] NaOAr, m.p. 373°	KOAr·H_2O V[336] CsOAr·ArOH V[330]
Br_5C_6OH	NaOAr; V[336]	
$C_6H_4(OH)_2$-1,2	2NaOAr (OH)·Ar $(OH)_2$·6H_2O NaOAr (OH)·Ar $(OH)_2$ $(NaO)_2$Ar; V[323,337]; VI[326]	KOAr (OH)·Ar $(OH)_2$·2H_2O KOAr (OH)·Ar $(OH)_2$·0.5H_2O V[323,337,330]
$C_6H_4(OH)_2$-1,3	NaOAr (OH) $(NaO)_2$ Ar, V[326]; VI[326]; IX[322]	KOAr (OH)·2H_2O, IX[322] KOAr (OH) $(KO)_2$Ar·4H_2O, V[314]; VI[329]
$C_6H_4(OH)_2$-1,4	NaOAr (OH)·4ArOH NaOAr (OH) $(NaO)_2$Ar, V[323]; VI[326]	KOAr (OH)·7Ar $(OH)_2$, V[323]
$C_6H_3(OH)_3$-1,2,3	NaOAr $(OH)_3$ $(NaO)_2$ Ar (OH) $(NaO)_2$ Ar, VI[340]	
	2-$NaOC_6H_3$—C_6H_5OH-2′, V[330] 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.

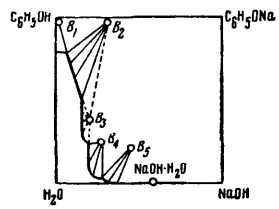


Fig. 4. Equilibrium diagram of the C_6H_5ONa–C_6H_5OH–H_2O system at 25°. [320]

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 $LiOAr\cdot 2H_2O$ $LiOH\cdot H_2O$ 25° [314]	ArOH (B_1) $NaOAr\cdot 2ArOH$ (B_2) $NaOAr\cdot ArOH\cdot 3,5H_2O$ (B_3) $NaOAr\cdot 3H_2O$ (B_4) $NaOAr\cdot NaOH\cdot 2.5H_2O$ (B_5) $NaOAr\cdot ArOH\cdot 8H_2O$ $NaOAr\cdot ArOH\cdot 7H_2O$ 0 — 50° [320]	ArOH $KOAr\cdot 3ArOH$ $KOAr\cdot 2H_2O$ $KOH\cdot 2H_2O$ 25° [314]	ArOH $Ca(OAr)_2\cdot 3\cdot H_2O$ $Ca(OH)_2$ 25° [314]	ArOH $M(OAr)_2.4H_2O$ $M(OH)_2.8H_2O$ 25° [314]
o-$CH_3C_6H_4OH$		ArOH $NaOAr\cdot 3ArOH$ $NaOAr\cdot H_2O$ $NaOAr\cdot 3NaOH\cdot 6H_2O$ $NaOAr\cdot ArOH\cdot 6H_2O$ $NaOAr\cdot 2ArOH\cdot 6H_2O$ $NaOH\cdot H_2O$ $NaOH\cdot 4H_2O$ 0 — 50° [325]			
p-$C_6H_4(OH)_2$			$Ar(OH)_2$ $KOArOH\cdot 2H_2O$ $KOArOH\cdot 4H_2O$ 30° [314]		$Ar(OH)_2$ $Ba(ArO)_2\cdot 2H_2O$ * $Ba(OH)_2\cdot 8H_2O$ 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.) $Ca(OAr)_2 \cdot 5.5H_2O$ ($< 0°$) $Ca(OAr)_2 \cdot 3H_2O$ $Ca(OAr)_2 \cdot 2H_2O$ (?), decomp. 105° $Ca(OAr)_2$; V[311, 312, 314]	$Sr(OAr)_2 \cdot 4H_2O$ V[314] $Ba(OAr)_2 \cdot 4H_2O$ $Ba(OAr)_2$, 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] $BaO_2Ar \cdot 3.5H_2O$, decomp. 240° 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° $BaO_2Ar \cdot 2H_2O$, 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° $BaO_2Ar \cdot 2H_2O$, 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]

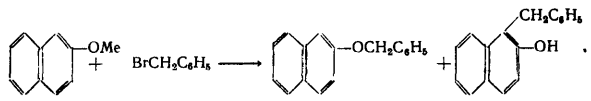
The "crystal phenolates", MOAr.*n*ArOH, are readily soluble in water, alcohol, acetone, and can be recrystallised from hot benzene. They all crystallise well and melt without decomposition.

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].

1. V. E. Tishchenko, Zhur. Russ. Fiz.-Khim. Obshch., 31, 694, 784 (1899).
2. K. A. Kocheshkov and A. N. Nesmeyanov, "Sinteticheskie Methody v Oblasti Metalloorganicheskikh Soedinenii Elementov III Gruppy" (Synthetic Methods in the Field of Organometallic Compounds of the Group III Elements), Vol. 4, 1945.
3. W. Gerrard and M. Lappert, Chem. Rev., 58, 1081 (1958).

4. R. Toussaint, Rev. chim. industr., 39, 162, 226, 290, 322 (1930).
5. G. D. Byrkit and E. C. Soule, Chem. Eng. News, 22, 1903 (1944).
6. A. G. Arend, Perfumery Essent. Oil Record, 38, 372 (1947).
7. O. C. Dermer, Chem. Rev., 14, 385 (1934).
8. F. Ullmann, "Enzyklopädie der technischen Chemie", 3. Aufl. Band 3, Urban and Schwarzenberg, München, 1953, p. 280.
9. M. Sittig, "Natrii" (Sodium), Gosatomizdat, 1961, p. 253.
10. S. T. Ioffe and A. N. Nesmeyanov, "Metody Elementoorganicheskoi Khimii" (Methods of Organoelemental Chemistry), Izd. Akad. Nauk SSSR, 1963.
11. F. G. A. Stone and W. A. G. Graham (Editors), "Inorganic Polymers", Academic Press, New York, 1962, p. 413.
12. D. C. Bradley, Prog. Inorg. Chem., 2, 303 (1960).
13. G. Thomas, Ann. Chim. (France), [12], 6, 367 (1951); translated into Russian in "Tsezii" (Caesium), Inostr. Lit., 1956.
14. I. W. Brühl, Ber., 37, 2066 (1904).
15. F. Adickes, W. Simson, and P. P. Peckelhoff, Ber., 67, 1436 (1934).
16. A. Meuwsen, Ber., 68, 124 (1935).
17. N. Fisher and S. M. MacElvain, J. Amer. Chem. Soc., 56, 1768 (1934).
18. S. Mamedov, Trudy Azerbaidzhan. Filiala Akad. Nauk SSSR, 55, 187 (1938); Chem. Abs., 35, 1381 (1941).
19. A. P. Terent'ev, Bull. Soc. chim. France [4], 35, 1150 (1924); "Primenenie Magniya v Organicheskoi Khimii" (Use of Magnesium in Organic Chemistry), Moscow, 1925; Memuary Khim. Otdel., Obshch. Lyubitelei Estestvoznanie, Antropologii i Etnografii.
20. U. S. P. 2 336 045 (1943); Chem. Abs., 38, 3097 (1944); U. S. P. 2 437 272 (1944); Chem. Abs., 42, 4194 (1948).
21. L. Menier, Compt. rend., 134, 472 (1902).
22. T. Evans and H. S. Fry, J. Amer. Chem. Soc., 26, 1168 (1904).
23. L. Tissier and V. Grignard, Compt. rend., 132, 836 (1901).
24. V. Cerchez, Bull. Soc. chim. France, [4], 43, 767 (1928).
25. M. Quinet, Bull. Soc. chim. France, [5], 2, 1201 (1935).
26. U. S. P. 2 570 058 (1951); Chem. Abs., 46, 1670 (1952).
27. H. S. Fry, J. Amer. Chem. Soc., 28, 796 (1906).
28. L. I. Smyth and P. E. Wiley, J. Amer. Chem. Soc., 68, 889 (1946).
29. H. Meerwein and R. Schmidt, Annalen, 444, 221 (1925).
30. U. S. P. 2 287 088 (1939); Chem. Abs., 37, 141 (1943).
31. F. J. Villani and F. F. Nord, J. Amer. Chem. Soc., 69, 2605 (1947).
32. German P 973 323 (1960); Chem. Zentr. 13 521 (1960).
33. J. D. McMahon and L. E. Russell, Chem. Ind., 57, 462 (1945).
34. V. D. Bogatskii, Trudy Odess. Univ., Khemiya, 1936, p. 25.
35. R. Forcrand, Compt. rend., 104, 116 (1887); Chem. Zentr., 211 (1887).
36. R. Forcrand, Compt. rend., 110, 859 (1890); Chem. Zentr., I, 956 (1890).
37. R. Forcrand, Compt. rend., 103, 1263 (1886); Chem. Zentr., I, 81 (1887); Compt. rend., 104, 169 (1887); Chem. Zentr., 267 (1887).
38. F. A. Long and P. Billinger, in "Electrolytes: An International Symposium" (Edited by B. Pesce), Pergamon, Oxford, 1962, p. 152.
39. M. E. Spaght, S. B. Thomas, and E. S. Parks, J. Phys. Chem., 36, 884 (1932).
40. R. Forcrand, Compt. rend., 106, 746 (1888).
41. C. A. Kraus and G. F. White, J. Amer. Chem. Soc., 45, 768 (1923).
42. E. Chablay, Compt. rend., 140, 1343 (1905); Chem. Zentr., II, 113 (1905).
43. E. Chablay, Ann. Chim. (France), [9], 8, 145 (1917).
44. E. Chablay, Compt. rend., 153, 819, 953 (1911); Chem. Zentr., I, 16 (1912).
45. E. Chablay, Ann. Chim. (France), [9], 8, 167, 179, 185 (1917).
46. E. Chablay, Compt. rend., 154, 1507 (1912); Chem. Zentr., II, 233 (1912).
47. G. F. White, A. B. Morrison, and E. G. Anderson, J. Amer. Chem. Soc., 46, 961 (1924).
48. L. Schmid and B. Becker, Ber., 58, 1966 (1925).
49. L. Schmid, A. Waschkau, and E. Ludwig, Monatsh., 49, 107 (1928).
50. P. P. Shorygin and N. N. Makarova-Zemlyanskaya, Zhur. Obshch. Khim., 7, 283 (1937).
51. S. N. Ushakov and E. M. Lavrent'eva, Zhur. Prikl. Khim., 26, 960 (1953).
52. U. S. P. 2 267 733 (1941); Chem. Abs., 36, 2567 (1942).
53. B. P. 552 739 (1943); Chem. Abs., 38, 4269 (1944).
54. U. S. P. 2 278 550 (1942); Chem. Abs., 36, 4830 (1942).
55. A. Contardi and B. Ciocca, Rend. Ist. Lombardo Sci. Lettere, [2], 68, 127 (1935); Chem. Zentr. II, 3085 (1935).
56. Canad. P. 473 611 (1951); Chem. Zentr., 3082 (1952).
57. U. S. P. 2 510 550 (1950); Chem. Abs., 44, 9977 (1950).
58. F. W. Bergstrom and W. C. Fernelius, Chem. Rev., 12, 99 (1933).
59. F. V. Tserevitinov, Izv. Moskov. Kommerch. Inst., 4 (1917).
60. N. Gaylord, "Reduction by Complex Metal Hydrides" (Translated into Russian), Inostr. Lit., 1959.
61. R. Bauer, Z. Naturforsch, 17B, 626 (1962).
62. J. H. Jones and J. S. Thomas, J. Chem. Soc., 123, 3289 (1923).
63. R. C. Menzies, J. Chem. Soc., 1571 (1930); 1131 (1934).
64. R. K. Abbott, Iowa State Coll. J. Sci., 18, 3 (1943); Chem. Abs., 38, 61 (1944).
65. U. S. P. 2 451 945 (1945); Chem. Abs., 43, 2218 (1949).
66. U. S. P. 3 053 906 (1962); Chem. Abs., 58, 2174 (1963).
67. G. Jander and K. Wickert, Z. phys. Chem., 178A, 66 (1936/37).
68. V. I. Mikheeva, Uspekhi Khim., 23, 837 (1954).
69. E. Wiberg and R. Hartwimmer, Z. Naturforsch, 10b, 290, 291 (1955); German P. 961 706 (1957); Chem. Zentr., 7864 (1958).
70. German P. 164 297 (1905); Chem. Zentr., II, 1747 (1905).
71. USSR P. 40 344 (1934); Chem. Zentr., I, 642 (1936).
72. USSR P. 148 392 (1962); Byul. Izobret., Nos. 13 and 14 (1962).
73. U. S. P. 1 910 331 (1931); Chem. Zentr., II, 2723 (1932); German P. 628 023 (1934); Fortschr. TheerfarbFabr., 22, 53 (?); French P. 680 794 (1929); see Ref. 4.
74. German P 505 474 (1928); Chem. Zentr., II, 3080 (1930).
75. U. S. P. 2 405 712 (1946); Chem. Zentr., 1151 (1947).
76. U. S. P. 1 978 647 (1931); Chem. Zentr., I, 2085 (1935).
77. German P. 513 677 (1926); Fortschr. TheerfarbFabr., 17, 176 (1932); B. P. 255 880; Chem. Zentr., I, 2207 (1928).
78. C. F. Cross and J. M. Jacobs, J. Soc. Chem. Ind., 45, 320 (1926); Chem. Zentr., II, 2155 (1926).
79. R. Forcrand, Compt. rend., 112, 484, 1006 (1891); Chem. Zentr., I, 654, 1053 (1891).
80. U. S. P. 2 796 443 (1957); Chem. Zentr., 7959 (1959).
81. German P. 968 903 (1958); Chem. Zentr., 12 530 (1958).
82. R. Forcrand, Compt. rend., 182, 609, 1191 (1926); Chem. Zentr., I, 3038; II, 1382 (1926).
83. N. V. Sidgwick and L. E. Sutton, J. Chem. Soc., 1461 (1930).
84. S. Sugden, J. Chem. Soc., 326 (1929).
85. B. Reuter and A. Goegel, Z. anorg. Chem., 268, 101 (1952).
86. K. Freudenberg and G. Uthemann, Ber., 52, 1509 (1919).
87. G. Brauer (Editor), "Handbuch der präparativen anorganischen Chemie" (Translated into Russian), Inostr. Lit., 1956, p. 413.
88. L. F. Dahl, G. L. Davis, and D. L. Wampler, J. Inorg. Nuclear Chem., 24, 357 (1962).
89. A. F. Wells "Structural Inorganic Chemistry" (Translated into Russian), Inostr. Lit., 1948, p. 594.
90. J. Bailar and J. Busch (Editors), "The Chemistry of the Coordination Compounds" (Translated into Russian), Inostr.

Lit., 1960.
91. R. Wegscheider, Monatsh, 39, 201 (1918).
92. F. Adickes, Ber., 63, 2753 (1930).
93. D. Williams and R. W. Bost, J. Chem. Phys., 4, 251 (1936).
94. E. F. Caldin and G. Long, J. Chem. Soc., 3737 (1954).
95. J. Murto, Suomen Kem., 35, No. 9, 157B (1962); Ref. Zhur. Khim., 11B, 493 (1963).
96. A. S. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jnr., "Organic Solvents: Physical Properties and Methods of Purification" (Translated into Russian), Inostr. Lit., Moscow, 1958.
97. E. Berner, Ber., 71, 2015 (1938); Arch. Math. Natur., 45, 123 (1942); Chem. Zentr., I, 1361 (1943).
98. R. Scholder and M. Kreutz, Annalen, 653, 1 (1962).
99. J. C. Jungers and K. Wirtz, Bull. Soc. chim. belges, 45, 679 (1936).
100. H. Lund and J. Bjerrum, Ber., 64, 210 (1931).
101. R. Forcrand, Compt. rend., 106, 665 (1888); Chem. Zentr., 515 (1888).
102. E. Geiger and H. Nobs, Helv. Chim. Acta, 41, 1295 (1958).
103. E. Müller and T. Töpel, Ber., 72, 273 (1939).
104. V. M. Tolstopyatov, Zhur. Obshch. Khim., 2, 105 (1932); 5, 73, 83 (1935); 9, 1148 (1939); 15, 565 (1945).
105. P. P. Shorygin, "Uspekhi Organicheskoi Khimii" (Progress in Organic Chemistry), Gosizdat, 1928.
106. H. Gulman, Rec. Trav. chim., 50, 1052 (1931); J. Amer. Chem. Soc., 55, 1265 (1933).
107. M. Gomberg and W. E. Bachmann, J. Amer. Chem. Soc., 49, 236, 2584 (1927).
108. M. Gomberg and W. E. Bachmann, J. Amer. Chem. Soc., 52, 4967 (1930).
109. O. A. Reutov, "Teoreticheskie Problemy Organicheskoi Khimii" (Theoretical Problems of Organic Chemistry), Izd. Moskov. Gos. Univ., Moscow, 1956, p. 228.
110. H. Staudinger and A. Binkert, Helv. Chim. Acta, 5, 703 (1922).
111. S. T. Bowden and T. John, J. Chem. Soc., 213 (1940).
112. A. N. Nesmeyanov, I. F. Lutsenko, and R. M. Khomutov, Dokl. Akad. Nauk SSSR, 120, 1049 (1958).
113. A. N. Nesmeyanov, L. A. Kazitsyna, I. F. Lutsenko, and G. A. Rudenko, Dokl. Akad. Nauk SSSR, 127, 115 (1959).
114. B. V. Nekrasov, "Kurs Obshchei Khimii" (Course of Organic Chemistry), Goskhimizdat, 1948.
115. L. Hackspill and L. A. van Altnea, Compt. rend., 206, 1818 (1938).
116. E. Weiss and W. Büchner, Helv. Chim. Acta, 46, 1121 (1963).
117. E. Weiss and W. Büchner, Z. anorg. Chem., 330, 251 (1964).
118. G. Wittig, F. Meyer, and G. Lange, Annalen, 571, 167 (1951).
119. H. Gilman, A. H. Haubein, and H. Herzfeld, J. Org. Chem., 19, 1034 (1954).
120. H. Gilman and S. D. Rosenberg, J. Org. Chem., 18, 1554 (1953).
121. E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds" (Translated into Russian), Inostr. Lit., 1963.
122. R. Bauer, Z. Naturforsch, 17b, 201 (1962).
123. R. C. Huston, J. Org. Chem., 6, 125 (1941); 12, 90 (1947); 13, 331 (1948).
124. I. Ribas and E. Tapia, Anales real Soc. españ. Fís. Quím., 28, 636 (1932); 30, 778 (1932); Chem. Zentr., II, 3862 (1932); I, 2078 (1933).
125. B. Szilard, Z. Elektrochem., 12, 393 (1906).
126. P. Brun, Compt. rend., 203, 315 (1936); Chem. Zentr., I, 59 (1937).
127. U. S. P. 2438963 (1948); Chem. Abs., 42, 5045 (1948).
128. M. Quinet, Bull. Soc. chim. France, [5], 5, 1569 (1938).
129. C. Charmetant and R. Paris, Compt. rend., 220, 314 (1945); Chem. Abs., 40, 3686 (1946).
130. J. U. Nef, Annalen, 318, 177 (1901).
131. D. Bryce-Smith and B. J. Wakefield, Proc. Chem. Soc., 376 (1963).
132. B. P. 526662 (1939); Chem. Abs., 35, 6979 (1941); U. S. P. 2185247 (1938); Chem. Abs., 34, 2865 (1940).
133. P. J. Wheatley, J. Chem. Soc., 4270 (1960).
134. H. Dunken and J. Krausse, Z. anorg. Chem., I, 27 (1961).
135. E. Weiss, Helv. Chim. Acta., 46, 2051 (1963).
136. J. D. Hanawalt, H. W. Rinn, and L. K. Frevel, Ind. Eng. Chem., Analyt., 10, 477 (1938).
137. D. C. Bradley and M. M. Faktor, Nature, 184, 55 (1959).
138. R. Forcrand, Compt. rend., 101, 161 (1885); Chem. Zentr., 660 (1885).
139. A. P. Simonov, D. N. Shigorin, T. V. Talalaeva, and K. A. Kocheshkov, Dokl. Akad. Nauk SSSR, 136, 634; 141, 665 (1961); Optika i Spektrosk., 17, 848 (1964).
140. J. F. Durand, Compt. rend., 172, 504, 1505 (1921); Chem. Zentr., III, 872 (1921).
141. G. Grenier and F. F. Westrem, J. Amer. Chem. Soc., 79, 1802 (1957).
142. O. Frölich, Annalen, 202, 290 (1880).
143. R. Forcrand, Compt. rend., 100, 1500 (1885); Chem. Zentr., 551 (1885).
144. F. Fichter, P. Girard, and H. Erlenmeyer, Helv. Chim. Acta., 13, 1232 (1930).
145. H. C. Brown and H. I. Schlesinger, J. Amer. Chem. Soc., 75, 205 (1953).
146. M. Engel, Compt. rend., 103, 156 (1886).
147. F. H. Seubold, J. Org. Chem., 21, 156 (1956).
148. R. Forcrand, Compt. rend., 104, 68 (1887); Chem. Zentr., I, 136 (1887).
149. T. V. Talalaeva, G. V. Tsareva, A. P. Simonov, and K. A. Kocheshkov, Izv. Akad. Nauk SSSR, Ser. Khim., 638 (1964).
150. R. Forcrand, Compt. rend., 114, 301 (1892).
151. C. A. Bischoff, Ber., 32, 1763 (1899).
152. Y. Ishii and S. Sekiguchi, J. Chem. Soc. Japan, 62, 1051 (1959); 64, 1497 (1961).
153. B. P. 875162; Chem. Abs., 56, 13096 (1962); U. S. P. 3021311–4; Chem. Abs., 57, 12719 (1962).
154. E. Reboul, Compt. rend., 108, 39 (1889); Chem. Zentr., 1, 186 (1889).
155. B. M. Mikhailov and P. M. Aronovich, Dokl. Akad. Nauk SSSR, 98, 791 (1954).
156. F. Asinger, B. Fell, and G. Collin, Chem. Ber., 96, 716 (1963).
157. I. B. Golovanov, A. P. Simonov, A. K. Piskunov, T. V. Talalaeva, G. V. Tsareva, and K. A. Kocheshkov, Dokl. Akad. Nauk SSSR, 149, 835 (1963).
158. H. Pines and L. Schaap, J. Amer. Chem. Soc., 79, 2956 (1957).
159. B. B. Graves and B. F. Vincent, Chem. Ind., 2137 (1962).
160. J. C. Gjaldbaek, Acta Chem. Scand., 2, 687 (1948).
161. U. S. P. 2938017 (1960); Chem. Zentr., 18148 (1961); Belg. P. 612398 (1962); Chem. Abs., 58, 1559 (1963).
162. L. Ya. Bryusova and F. A. Ogorodnikova, "Sintezy Dushistykh Veshchestv: Sbornik Statei" (Preparation of Perfumes: Collected Papers), 1939, p. 85.
163. C. A. Bischoff, Ber., 36, 159 (1903).
164. C. A. Kraus and P. B. Bien, J. Amer. Chem. Soc., 55, 3609 (1933).
165. L. M. Nazarova, Zhur. Fiz. Khim., 28, 36 (1954).
166. R. Forcrand, Compt. rend., 107, 1160 (1889); Chem. Zentr., I, 148 (1889).
167. R. Forcrand, Compt. rend., 108, 240 (1889); Chem. Zentr., I, 314 (1889).
168. R. Forcrand, Compt. rend., 107, 343 (1888); Chem. Zentr., 1232 (1888).

169. R. Forcrand, Compt. rend., 96, 1728 (1883); Chem. Zentr., 530 (1883).
170. V. E. Tishchenko and A. F. Kosternaya, Zhur. Obshch. Khim., 7, 1369 (1937).
171. T. G. Pearson, Nature, 131, 166 (1933).
172. W. Büchner, Helv. Chim. Acta, 46, 2111 (1963).
173. A. Joannis, Compt. rend., 116, 1518 (1893); 158, 874 (1914).
174. W. F. Sager, A. Fatiadi, and P. C. Parks, J. Inorg. Nuclear Chem., 25, 187 (1963).
175. R. Setton, Compt. rend., 238, 2323 (1954).
176. H. Hibbert, Canad. J. Res., 14, 77 (1936); Chem. Zentr., II, 3674 (1936); J. Amer. Chem. Soc., 61, 1908 (1939).
177. E. A. Letts, Ber., 5, 159 (1872).
178. R. Forcrand, Compt. rend., 104, 361 (1887); Chem. Zentr., 297 (1887).
179. W. F. Löbisch and A. Loos, Monatsh., 2, 842 (1881).
180. R. Forcrand, Compt. rend., 107, 346 (1888); Chem. Zentr., 1154 (1888).
181. R. Forcrand, Compt. rend., 110, 904 (1890); Chem. Zentr., I, 988 (1890).
182. R. Forcrand, Compt. rend., 114, 226 (1892).
183. A. P. Simonov, D. N. Shigorin, T. V. Talalaeva, and K. A. Kocheshkov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1126 (1962).
184. D. C. Bradley, J. Chem. Soc., 4780 (1958).
185. W. K. McEwen, J. Amer. Chem. Soc., 58, 1129 (1936).
186. N. Bjerrum and L. Zechmeister, Ber., 56, 894 (1923).
187. G. E. M. Jones and O. L. Hughes, J. Chem. Soc., 1202 (1934).
188. A. G. Ogston, Trans. Faraday Soc., 32, 1683 (1936).
189. M. Barak and H. Hartley, Z. phys. Chem., 165A, 283 (1933).
190. E. Masdupuy and F. Gallais, Compt. rend., 225, 128 (1947).
191. E. Szarwasy, Ber., 30, 305, 808, 1836 (1897).
192. R. J. Williams and R. W. Truesdail, J. Amer. Chem. Soc., 45, 1348 (1923).
193. F. M. Perkin and L. Pratt, J. Chem. Soc., 95, 159 (1909).
194. R. L. Robinson and W. E. Scott, J. Chem. Soc., 704 (1931).
195. U. S. P. 3009964 (1961); Ref. Zhur. Khim., 20L49 (1962).
196. G. Doby, Z. anorg. Chem., 35, 93 (1903).
197. R. Forcrand, Compt. rend., 153, 1441 (1911); Ann. Chim. (France), [8], 26, 216 (1912); Chem. Zentr., I, 557; II, 321 (1912).
198. H. Moissan, Compt. rend., 127, 499 (1898); Bull Soc. chim. France, [3], 21, 883 (1899).
199. P. Breteau, Bull. Soc. chim. France, [4], 9, 585 (1911).
200. N. Richl and G. Wirths, Z. phys. Chem., 194, 108 (1944).
201. W. H. Birnkraut, Inorg. Chem., 2, 1074 (1963).
202. U. S. P. 3031439 (1962); Chem. Abs., 57, 2434 (1962).
203. H. Meerwein, J. prakt. Chem., [2], 147, 215 (1936).
204. N. A. Toropov, A. I. Borisenko, and P. V. Shirokova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 65 (1953).
205. G. Roederer, Bull. Soc. chim. France, [3], 35, 715 (1906).
206. A. Gunz and Mentrel, Bull. Soc. chim. France, [3], 29, 585 (1903).
207. V. V. Chelintsev, "Organicheskie Katalizatory" (Organic Catalysts), Izd. Akad. Nauk SSSR, 1939.
208. A. N. Nesmeyanov, V. A. Sazanova, and E. V. Landor, Dokl. Akad. Nauk SSSR, 63, 395 (1948).
209. Lamy, Compt. rend., 55, 836 (1862); 59, 780 (1868).
210. R. Forcrand, Compt. rend., 176, 20 (1923); Chem. Zentr., III, 125 (1923).
211. W. A. Kahlbaum, K. Roth, and P. Stedler, Z. anorg. Chem., 29, 223 (1902).
212. R. C. Menzies, J. Chem. Soc., 1382 (1947).
213. R. C. Menzies and M. E. Kieser, J. Chem. Soc., 186 (1928).
214. S. S. Nametkin and N. I. Mel'nikov, Zhur. Obshch. Khim., 5, 371 (1935).
215. G. H. Christie and R. C. Menzies, J. Chem. Soc., 127, 2369 (1925).
216. L. Rosenthaler, Pharm. Acta Helv., 17, 195 (1942); Chem. Abs., 37, 2722 (1943).
217. L. P. McHatton and M. I. Soulal, J. Chem. Soc., 2771 (1952); 4095 (1953).
218. V. A. Zagorevskii, Zhur. Obshch. Khim., 27, 3055 (1957).
219. R. C. Menzies and E. M. Wilkins, J. Chem. Soc., 125, 1148 (1924).
220. R. Forcrand, Compt. rend., 103, 596 (1886); Chem. Zentr., 833 (1886); Compt. rend., 104, 291 (1887); Chem. Zentr., 267 (1887).
221. R. Forcrand, Compt. rend., 97, 108 (1883); Chem. Zentr., 581 (1883).
222. Z. Kęcki and J. Witanowski, Roczniki Chem., 37, 881 (1963).
223. G. Giacomello, Gazzetta, 66, 350 (1936); Chem. Zentr., II, 2330 (1936).
224. A. I. Shatenshtein and E. A. Yakovleva, Zhur. Obshch. Khim., 28, 1713 (1958); Dokl. Akad. Nauk SSSR, 136, 882 (1961).
225. L. Cambi, Atti R. Acad. Lincei, [5], 23, 1, 244 (1914); Chem. Zentr., I, 1412 (1914).
226. H. Meerwein and T. Bersin, Annalen, 476, 113 (1929).
227. H. C. Brown and E. J. Mead, J. Amer. Chem. Soc., 78, 3614 (1956).
228. H. A. Lehmann and D. Tiess, Z. anorg. Chem., 304, 89 (1960).
229. U. S. P. 2999653 (1961); 2785098 (1957); Ref. Zhur. Khim., 20L45 (1962); 12485 (1959).
230. G. Hesse and M. Maurer, Annalen, 658, 21 (1962).
231. R. E. Davis and J. A. Gottbrath, J. Amer. Chem. Soc., 84, 895 (1962).
232. H. C. Brown, E. J. Mead, and C. J. Shoaf, J. Amer. Chem. Soc., 78, 3616 (1956).
233. H. Meerwein and W. Pannwitz, J. prakt. Chem., [2], 141, 143 (1934).
234. L. A. O'Leary and H. H. Wenzke, J. Amer. Chem. Soc., 55, 2117 (1933).
235. K. Ziegler and H. Hoberg, Angew. Chem., 73, 577 (1961); German P. 1127900 (1962); Chem. Abs., 57, 11235 (1962).
236. O. Schmitz-DuMont, Angew Chem., 63, 489 (1951).
237. H. C. Brown and R. F. McFarlin, J. Amer. Chem. Soc., 80, 5372, 5377 (1958).
238. M. S. Kulpinsky and F. F. Nord, J. Org. Chem., 8, 256 (1943).
239. H. Meerwein, German P. 482870 (1925); Fortschr. Theer-farbFabr., 16, 138 (1931).
240. O. Schmitz-DuMont and V. Habernickel, Naturwiss, 39, 20 (1952).
241. O. Schmitz-DuMont and G. Bungard, Chem. Ber., 92, 2399 (1959).
242. H. C. Brown and K. F. McFarlin, J. Amer. Chem. Soc., 78, 252 (1956).
243. F. W. Frey, P. Kobetz, G. C. Robinson, and F. O. Sistrunk, J. Org. Chem., 26, 2950 (1961).
244. H. Lehmkuhl and W. Eisenbach, Angew. Chem., 74, 779 (1962).
245. U. S. P. 3060216 (1962); Chem. Abs., 58, 3125 (1963).
246. O. Schmitz-DuMont, D. Merten, and D. Eiding, Z. anorg. Chem., 319, 362 (1963).
247. R. Müller and L. Heinrich, Chem. Ber., 95, 2276 (1962).
248. E. Amberger and M. R. Kula, Chem. Ber., 96, 2562 (1963).
249. D. C. Bradley, E. V. Caldwell, and W. Wardlaw, J. Chem. Soc., 4775 (1957).
250. J. C. Maire, Ann. Chim. (France), [13], 6, 969 (1961); "Thèses", Masson, Paris, 1961.
251. H. Meerwein and E. Geschke, J. prakt. Chem., [2], 147, 207 (1936).
252. W. G. Bartley and W. Wardlaw, J. Chem. Soc., 422 (1958).
253. O. Schmitz-DuMont, "Inorganic Polymers" (Translated into Russian), Inostr. Lit., 1961, p. 81.
254. K. Dostàl and L. Zbořilova, Z. anorg. Chem., 316, 335 (1962).

255. R. G. Jones, E. Bindschadler, and H. Gilman, J. Amer. Chem. Soc., 78, 6027 (1956).
256. F. Feigl and P. Krumholz, Monatsh., 59, 314 (1932).
257. R. Criegee, B Marchand, and H. Wannowius, Annalen, 550, 99 (1942).
258. N. Ya. Turova, A. V. Novoselova, and K. N. Semenenko, Zhur. Neorg. Khim., 4, 997 (1959) [Russ. J. Inorg. Chem., 453 (1959)].
259. U. S. P. 3065049 (1962); Chem. Abs., 58, 3126 (1963).
260. W. S. Luder and S. Zuffanti, "The Electronic Theory of Acids and Bases" (Translated into Russian), Inostr. Lit., 1960.
261. M. S. Kulpinski and F. F. Nord, Nature, 151, 363 (1943).
262. S. Sujishi and J. N. Keith, J. Amer. Chem. Soc., 80, 4138 (1958).
263. H. C. Brown, E. J. Mead, and P. A. Tierney, J. Amer. Chem. Soc., 79, 5400 (1957).
264. M. Quinet, Bull. Soc. chim. France, [5], 3, 1824 (1936).
265. A. C. Cope, J. Amer. Chem. Soc., 56, 1344 (1934).
266. D. L. Yabroff and C. W. Porter, J. Amer. Chem. Soc., 54, 2454 (1932).
267. W. A. Fessler and R. L. Shriner, J. Amer. Chem. Soc., 58, 1385 (1936).
268. R. E. Dessy, J. Amer. Chem. Soc., 80, 5824 (1958).
269. A. Rosenheim and O. Libknecht, Ber., 30, 1838 (1897).
270. F. Beilstein, Annalen, 112, 124 (1859).
271. J. Dumas and E. Peligot, Annalen, 35, 284 (1840).
272. A. Destrem, Ann. Chim. (France), [5], 27, 20 (1882); Chem. Zentr., 392 (1880).
273. J. A. Christiansen and J. C. Gialdbaek, Kgl. danske Videnskab. Selskab, Mat.-fys. Medd., 20, No. 3, 22 (1942); Chem. Zentr., I, 599 (1943).
274. H. Remy, "Lehrbuch der anorganishchen Chemie", Vol. II, Akademie Verlag, Leipzig, 1960, p. 243.
275. L. Wöhler, Z. anorg. Chem., 213, 129 (1933).
276. A. Rule, J. Chem. Soc., 99, 560 (1911); 103, 873 (1913).
277. A. P. Kreshkov and A. N. Chivikova, Zhur. Prikl. Khim., 27, 1128 (1954).
278. R. Forcrand, Compt. rend., 102, 1397 (1886); Chem. Zentr., 692 (1886).
279. R. Forcrand, Compt. rend., 120, 737 (1895); Chem. Zentr., 998 (1895).
280. R. Forcrand, Compt. rend., 119, 1266 (1895); Chem. Zentr., 423 (1895).
281. N. V. Sidgwick and F. M. Brewer, J. Chem. Soc., 127, 2379 (1925).
282. W. H. Hunter, J. Amer. Chem. Soc., 43, 145, 154 (1921); Zhur. Obshch. Khim., 7, 2202, 2206 (1937).
283. M. S. Newman and F. J. Evans, J. Amer. Chem. Soc., 76, 4187 (1954).
284. E. M. Trautner and J. B. Polya, Austral. Chem. Inst. J. and Proc., 52 (1948); Chem. Abs., 42, 5848 (1948).
285. M. Lebl, Z. anorg. Chem., 314, 156 (1962).
286. K. Rossmanith and H. Macalka, Monatsh., 94, 295 (1963).
287. A. Le Berre, Bull. Soc. chim. France, 1198, 1543 (1961); 1682 (1962).
288. A. M. Butlerov, Annalen, 107, 110 (1858).
289. Y. Ogata and J. Mibae, J. Org. Chem., 27, 2048 (1962).
290. A. I. Shatenshtein, "Izotopnyi Obmen i Zameshchenie Vodoroda v Organicheskikh Soedineniyakh" (Isotopic Exchange and Replacement of Hydrogen in Organic Compounds), Izv. Akad. Nauk SSSR, 1960, p. 318.
291. H. Tropsch and A. Philippovich, Abhdl. Kenntnis Kohle, 7, 78 (1925); Chem. Zentr., II, 1482 (1926).
292. I. L. Knunyants, Yu. A. Cheburkov, and Yu. V. Makarov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1471 (1961).
293. H. D. Zook, J. March, and D. F. Smith, J. Amer. Chem. Soc., 81, 1617 (1959).
294. S. Berkman, J. C. Morrel, and G. Egloff, "Catalysis, Inorganic and Organic" (Translated into Russian), Gostoptekhizdat, 1949.
295. L. P. Laukkanen, Suomen. Kem. 30B, 139 (1957); 31, 134 (1958); 34, 175 (1961); Ref. Zhur. Khim., 17831, 53786 (1958); Chem. Abs., 58, 11227 (1963).
296. H. Aspelung and L. Lindh, Chem. Abs., 37, 5028 (1943).
297. "Organic Reactions" (Translated into Russian), Collection 2, Inostr. Lit., 1950, p. 196.
298. M. F. Grundon and H. B. Henbest, J. Chem. Soc., 1855 (1963).
299. G. A. Kon, J. Chem. Soc., 251 (1931).
300. G. Gee and W. C. E. Higginson, J Chem. Soc., 1338, 1345, (1959); 4298 (1961).
301. Y. Yamashita and T. Ito, J. Chem. Soc. Japan, 63, 1746 (1960).
302. R. Schulz and W. Passmann, Makromol. Chem., 60, 139 (1963).
303. J. Ugelstad and O. A. Rokstad, Acta. Chem. Scand., 17, 208 (1963).
304. A. Ben Feit and A. Zilkha, J. Appl. Polymer Sci., 7, 287 (1963).
305. A. A. Morton, J. Amer. Chem. Soc., 69, 950, 1675 (1947); 71, 481 (1949).
306. L. W. Covert, R. Connor, and H. Adkins, J. Amer. Chem. Soc., 54, 1656 (1932).
307. U. S. P. 2256625 (1942); Chem. Abs., 36, 193 (1942).
308. U. S. P. 2834662-3 (1958); Chem. Zentr., 11875, 4719 (1960).
309. U. S. P. 3066048, 3067078 (1962); Chem. Abs., 58, 4283, 4706 (1963); B. P. 814201; Chem. Zentr., 9438 (1960).
310. N. A. Il'in, P. Hofman, N. N. Mel'nikov, and A. M. Avetisyan, Arch. Int. Pharmacodynam, 58, 371 (1938); Chem. Zentr., II, 156 (1939).
311. F. F. Selivanov, Zhur. Russ. Fiz.-Khim. Obshch., 45, 1535 (1913).
312. F. Fischer and U. Ehrhardt, Abhdl. Kenntnis Kohle, 4, 259 (1921); Chem. Zentr., I, 762 (1921).
313. G. Krüger, Z. phys. Chem. (Leipzig), 208, 249 (1958).
314. G. J. van Meurs, Z. phys. Chem., 91, 328 (1916).
315. F. Wessely, K. Benedikt, and H. Benger, Monatsh., 81, 1071 (1950).
316. F. Hein, R. Weiss, and B. Hein, Monatsber. deut. Akad. Wiss, Berlin, 1, 541 (1959).
317. R. Forcrand, Compt. rend., 116, 586 (1893).
318. German P. 156761, 157616 (1903); Chem. Zentr., I, 313 (1905).
319. A. N. Meldrum and M. M. Patel, J. Indian Chem. Soc., 5, 91 (1928); Chem. Zentr., I, 2388 (1928).
320. H. J. Lichtenstein, E. Leibnitz, W. Lewna, and J. Mothes, J. prakt. Chem., 7, 241 (1959).
321. R. Forcrand, Compt. rend., 114, 1010 (1892); Chem. Zentr., II, 28 (1892).
322. P. Karrer, "Lehrbuch der organischen Chemie" (Translated into Russian), Goskhimizdat, 1960, p. 537.
323. H. Meyer, Z. analyt. Chem., 64, 77 (1924).
324. H. Erlenmeyer, Helv. Chim. Acta, 9, 648 (1926).
325. E. Leibnitz, W. Lewna, H. J. Lichtenstein, and J. Mothes, J. prakt. Chem., 10, 6 (1960).
326. C. A. Bischoff, Ber., 33, 1249, 1261, 1386 (1903).
327. C. A. Bischoff, Ber., 33, 1269, 1392 (1900).
328. L. Schäffer, Annalen, 152, 286 (1869).
329. S. Tijmstra and N. G. Eggink, Ber., 39, 14 (1906).
330. D. Hadži, A. Novak, and I. E. Gordon, J. Phys. Chem., 67 1118 (1963).
331. L. Varnholt, J. prakt. Chem., [2], 36, 18 (1887).
332. German P. 247410 (1911); Chem. Zentr., II, 165 (1912).
333. F. Fischer, Ann. Spl., 7, 180 (1870).
334. H. Biltz and W. Griese, Ber., 37, 4013 (1904).

335. L. Jambon, Bull. Soc. chim. France, [3], 23, 825 (1900).
336. H. J. Lucas and A. R. Kemp, J. Amer. Chem. Soc., 43, 1663 (1921).
337. German P. 164 666 (1905); Chem. Zentr., II, 1702 (1905).
338. R. Forcrand, Compt. rend., 114, 1370, 1434 (1892); Chem. Zentr., II, 148, 200 (1892); Ann. Chim. (France), [6], 30, 66 (1893).
339. W. S. Hinegardner and T. B. Jonson, J. Amer. Chem. Soc., 51, 1507 (1929).
340. R. Forcrand, Compt. rend., 115, 46 (1892); Chem. Zentr., II, 348 (1892).
341. R. Forcrand, Compt. rend., 116, 192, 437 (1893); Chem. Zentr., I, 562, 643 (1893).
342. R. Schmidt, J. prakt. Chem., 31, 405 (1885).
343. Kh. Kimura and T. Takueti, Chem. Eng. (Japan), 27, 2 (1963); Ref. Zhur. Khim., 20B, 388 (1963).
344. C. Schall, J. prakt. Chem., 48, 241 (1893).
345. A. A. Morton and R. L. Letsinger, J. Amer. Chem. Soc., 67, 1537 (1945).
346. H. Niederhäusern, Ber., 15, 1119 (1882).
347. C. Böttinger, Chem.-Ztg., 19, 23 (1895).
348. H. Pauly, K. Schübel, and K. Lockemann, Annalen, 383, 288 (1911).
349. B. Elsner, Monatsh., 40, 361 (1919).
350. A. Purgotti, Gazzetta, 16, 527 (1886); Chem. Zentr., I, 335 (1887).

Lomonosov Moscow University

U.D.C. 541.515

CHEMISTRY OF UNSTABLE OXYGEN--CONTAINING RADICALS

L. M. Terman

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:

$$ROOCOOR \rightarrow ROOCO^{\cdot} + RO^{\cdot} \rightarrow ROO^{\cdot} + CO_2 + RO^{\cdot},$$

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.