Kirk-Othmer Encyclopedia of Chemical Technology.

ALKOXIDES, METAL

Metal alkoxides are compounds in which a metal is attached to one or more alkyl groups by an oxygen atom. Alkoxides are derived from alcohols by the replacement of the hydroxyl hydrogen by metal.

Sodium ethoxide was the first metal alkoxide described in 1837 (1). The alkoxides of many transition metals were developed after World War II (2–5). Today some alkoxides, including those of sodium, potassium, magnesium, aluminum, zirconium, and titanium, are commercially important. The name metal alkoxides is preferred, although metal alcoholates is also used.

Alkoxides of nonmetals are described in articles about the corresponding compounds (see Boron compounds, Boron oxides; Silicon compounds). Metal alkyls, in which the alkyl group is bound directly to the metal, are also discussed elsewhere (see Aluminum compounds).

1. Physical Properties

The metal alkoxides exhibit great differences in physical properties (Tables 1 and 2), depending primarily on the position of the metal in the periodic table, and secondarily on the alkyl group. Many alkoxides are strongly associated by intermolecular forces (3, 49, 50) which depend on the size and shape of the alkyl groups. This explains the fact that many metal methoxides are solid, nondistillable compounds, because the small methyl group has little screening effect on the metal atom. With a larger number of methyl groups and a smaller atomic radius of the metal, methoxides become sublimable and even distillable.

Table 3 (3) shows the influence of branching of the alkyl group on volatility and complexity, using titanium and zirconium amyl oxides as examples.

Many metal alkoxides are soluble in the corresponding alcohols, but magnesium alkoxides are practically insoluble. Only the distillable alkoxides, like those of aluminum, titanium, and zirconium, are soluble in weakly polar solvents. The double alkoxides are soluble in alcohol; $K[Li(OC_3H_7)_2]$, $Tl[Zr_2(OC_3H_7)_9]$, and $Na[Sn_2(OC_2H_5)_9]$ may be crystallized from alcohol. $Li[Zr_2(OC_3H_7)_9]$ may be crystallized from benzene. Several are soluble in organic solvents as indicated in Table 2; $Na[U(OC_2H_5)_6]$ is only slightly soluble.

Much work has been done on the structure of the metal alkoxides (49). The simple alkali alkoxides have an ionic lattice and a layer structure, but alkaline earth alkoxides show more covalent character. The aluminum alkoxides have been thoroughly studied and there is no doubt as to their covalent nature; the lower alkoxides are associated, even in solution and in the vapor phase. The degree of association depends on the bulkiness of the alkoxy group and can range from 2 to 4, eg, the freshly distilled isopropylate is trimeric (4):

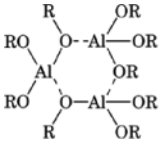


Table 1. Physical Properties of Metal Ethoxides[a]

Alkoxide	CAS Registry Number	Color and physical form	mp, °C	bp, °C/Pa[b]	Solubility in organic solvents	References
$LiOC_2H_5$	[2388-07-0]	white solid	20–24	n.d.[c]	+	(6, 8)
$NaOC_2H_5$	[141-52-6]	white solid	260 (dec)	n.d.	+	(6, 8)
KOC_2H_5	[917-58-8]	white solid	250 (dec)	n.d.	+	(6, 8)
$TlOC_2H_5$	[20398-06-5]	colorless liquid	9.5	n.d.	+	(6, 9)
$Mg(OC_2H_5)_2$	[22005-12-5]	white solid	270 (dec)	n.d.	(+)[d]	(6, 10)
$Ca(OC_2H_5)_2$	[2914-17-2]	white solid	270 (dec)	n.d.	+	(6, 9)
$Sr(OC_2H_5)_2$	[2914-18-3]	white solid	300 (dec)	n.d.	+	(6, 9)
$Ba(OC_2H_5)_2$	[2914-19-4]	white solid	270 (dec)	n.d.	+	(6, 9)
$Zn(OC_2H_5)_2$	[3851-22-7]	white solid			−	(11, 12)
$Sn(OC_2H_5)_2$	[14791-99-2]	white solid	200 (dec)		(+)	13
$Mn(OC_2H_5)_2$	[52321-91-2]	dark-brown solid			(+)	14
$Al(OC_2H_5)_3$	[555-75-9]	white solid	140	189/400	+	(6, 15)
$Ga(OC_2H_5)_3$	[2572-25-0]	white solid	144.5	180–190/150[e]	+	(16, 17)
$Cr(OC_2H_5)_3$	[7245-26-3]	light-green solid			(+)	18
$Fe(OC_2H_5)_3$	[5058-42-4]	dark-brown solid	120	155/10	+	(19, 20)
$Sb(OC_2H_5)_3$	[10433-06-4]	colorless liquid		37–38/5	+	(21, 22)
$VO(OC_2H_5)_3$	[1686-22-2]	almost colorless liquid	ca 8	91/1100	+	(22, 23)
$Ti(OC_2H_5)_4$	[3087-36-3]	white solid	ca 40	124/160	+	(24, 25)
$Zr(OC_2H_5)_4$	[18267-08-8]	white solid	172	180/13	+	(26, 27)
$Hf(OC_2H_5)_4$	[13428-80-3]	white solid	ca 180	180–200/13	(+)	28
$Th(OC_2H_5)_4$	[64653-68-5]	white solid	300 (dec)		(+)	29
$Ce(OC_2H_5)_4$	[64653-69-6]	yellow solid	200 (dec)		−	30
$V(OC_2H_5)_4$	[7637-16-3]	brown solid		100/5	+	31
$Ge(OC_2H_5)_4$	[14165-55-0]	colorless liquid	−72	54.5/670	+	(32, 33)
$Sn(OC_2H_5)_4$	[3173-69-1]	white solid	unmeltable	n.d.	+	(34, 35)
$U(OC_2H_5)_4$	[64653-70-9]	light-green liquid	dec		−	36
$Nb(OC_2H_5)_5$	[3236-82-6]	light-yellow liquid	6	156/6.6	+	37
$Ta(OC_2H_5)_5$	[6074-84-6]	colorless liquid	22	137/6.6	+	(37, 38)
$W(OC_2H_5)_5$	[26143-11-3]	red-black liquid		120/6.6	+	7
$U(OC_2H_5)_5$	[10405-34-2]	dark-brown liquid	180 (dec)	160/6.6	+	(39, 40)
$Sb(OC_2H_5)_5$	[7610-33-5]	colorless solid	46	135–145/20	+	41
$U(OC_2H_5)_6$	[64653-71-0]	dark-red liquid		72/0.13	+	42

[a] Refs. (6, 7).

[b] To convert Pa to mm Hg, divide by 133.3.

[c] n.d. = not distillable.

[d] Less soluble.

[e] Sublimes.

Structures are highly varied among the transition metals. The titanium atom in titanium tetraethoxide has the coordination number 6 (Fig. 1). The corresponding zirconium compound, with coordination number 8, has a different structure (Fig. 2). Metal alkoxides are colored when the corresponding metal ions are colored, otherwise they are not.

2. Chemical Properties

The most outstanding property of the metal alkoxides is ease of hydrolysis.

$$NaOC_2H_5 + H_2O \leftrightharpoons NaOH + C_2H_5OH$$

Table 2. Physical Properties of Double Alkoxides

Alkoxide[a]	CAS Registry Number	mp, °C	bp, °C/Pa[b]	Reference[c]
$K[Li(OC_3H_7)_2]$	[64653-73-2]			44
$Na[Zr_2(OC_3H_7)_9]$[d]	[24492-19-1]	168–180	260/1	45
$K[Zr_2(OC_3H_7)_6]$[d]	[64653-75-4]		subl 200/26.6	45
$Li[Zr_2(OC_3H_7)_9]$	[64653-74-3]		260/26.6	45
$Tl[Zr_2(OC_3H_7)_6]$	[64683-25-6]		subl 220/66.5	45
$Mg[Al(OC_2H_5)_4]_2$	[64653-77-6]	129	220–228/53.5	44
$Ca[Al(OC_3H_7)_4]_2$	[64653-61-8]	124	230–240/400	44
$K[Al(OC_4H_9)_4]$	[64653-62-9]	164–165		44
$Mg[Al(OC_3H_7)_4]_2$	[64653-63-0]	20	130–142/260	44
$Co[Al(OC_2H_5)_4]_2$[d,e]	[64653-64-1]			44
$Na[Sn_2(OC_2H_5)_9]$[d]	[24992-46-1]	260 (dec)		44
$Ca[U(OC_2H_5)_6]_2$[f]	[64653-65-2]		subl 200/0.13	46
$Al[U(OC_2H_5)_6]_3$[d,g]	[64653-66-3]		111–115/0.16	47
$U[Al(OC_3H_7)_4]_4$[d,h]	[64653-67-4]		95–97/0.13	48
$Na[U(OC_2H_5)_6]$[f]	[64653-58-3]	dec		47

[a] White solids unless otherwise noted.
[b] To convert Pa to mm Hg, divide by 133.3.
[c] See references 11 and 43 for double alkoxides of zinc, aluminum, gallium, and indium, respectively.
[d] Soluble in organic solvents.
[e] Violet solid.
[f] Green solid.
[g] Green liquid.
[h] Green oil.

$$2\,VO(OC_4H_9)_3 + 3\,H_2O \rightleftharpoons V_2O_5 + 6\,C_4H_9OH$$

This is used for sol-gel applications (51–54), a three step process:

(1) Partial hydrolysis of a metal alkoxide to form reactive monomers.
(2) Condensation of these monomers to form colloidlike oligomers (sol formation).
(3) Additional hydrolysis to promote polymerization and cross-linking leading to a three-dimensional matrix and gel formation.

Although outlined here in a sequential fashion, these reactions occur simultaneously at various stages of the overall process.

Uranium hexa-*tert*-butoxide is an exception and does not react with water (55). References 3 and 5 discuss chemical properties of alkoxides. In some cases hydrolysis is reversible, but usually it is not (23, 56).

The reaction of alkoxides with alcohols leads to the equilibrium

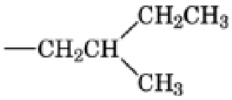
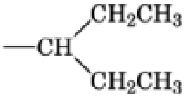
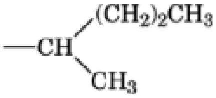
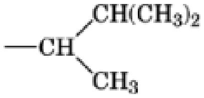
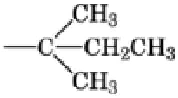
$$M(OR)_x + R'OH \leftrightharpoons M(OR)_{x-1}(OR') + ROH$$

Dihydric alcohols give normal or cyclic alkoxides.

Amino alcohols react similarly (57):

$$Ti(OR)_4 + HOC_2H_4NH_2 \longrightarrow Ti(OR)_3(OC_2H_4NH_2) + ROH$$

Table 3. Boiling Points and Molecular Complexities of Amyloxides of Titanium and of Zirconium

	Titanium alkoxide			Zirconium alkoxide		
R in $M(OR)_4$	CAS Registry Number	bp, °C/Pa[a]	Molecular complexity	CAS Registry Number	bp, °C/Pa[a]	Molecular complexity
$-(CH_2)_4CH_3$	[1058-24-1]	175/80	1.4	[64653-49-2]	256/1	3.2
$-(CH_2)_2CH(CH_3)_2$	[19480-47-8]	148/10	1.2	[64653-50-5]	247/10	3.3
 $-CH_2CH(CH_2CH_3)(CH_3)$	[64653-51-6]	154/50	1.1	[64653-52-7]	238/10	3.7
$-CH_2C(CH_3)_3$	[35061-92-8]	105/5	1.3	[26159-00-2]	188/20	2.4
 $-CH(CH_2CH_3)(CH_2CH_3)$	[64653-53-8]	112/5	1.0	[64653-54-9]	178/5	2.0
 $-CH((CH_2)_2CH_3)(CH_3)$	[53973-00-5]	135/100	1.0	[64653-55-0]	175/5	2.0
 $-CH(CH(CH_3)_2)(CH_3)$	[64653-56-1]	131/50	1.0	[64653-57-2]	156/1	2.0
 $-C(CH_3)(CH_2CH_3)(CH_3)$	[10585-26-9]	98/10	1.0	[24675-20-5]	95/10	1.0

[a] To convert Pa to mm Hg, divide by 133.3.

Metal alkoxides and carboxylic acids give salts (58):

$$\mathrm{Al(OR)_3 + 3\,R'COOH \longrightarrow Al\left(R'COO\right)_3 + 3\,ROH}$$

Titanium tetraalkoxides react with only three equivalents of acid (59):

$$\mathrm{Ti(OR)_4 + 3\,R'COOH \longrightarrow Ti(OR)\ \left(R'COO\right)_3 + 3\,ROH}$$

In some cases the mixed salts are unstable and eliminate an ester (60):

$$\mathrm{Zr(OR)\ (R'COO)_3 \xrightarrow{30^{\circ}C} ZrO(R'COO)_2 + R'COOR}$$

Metal alkoxides and phenol usually form phenolates smoothly (61).

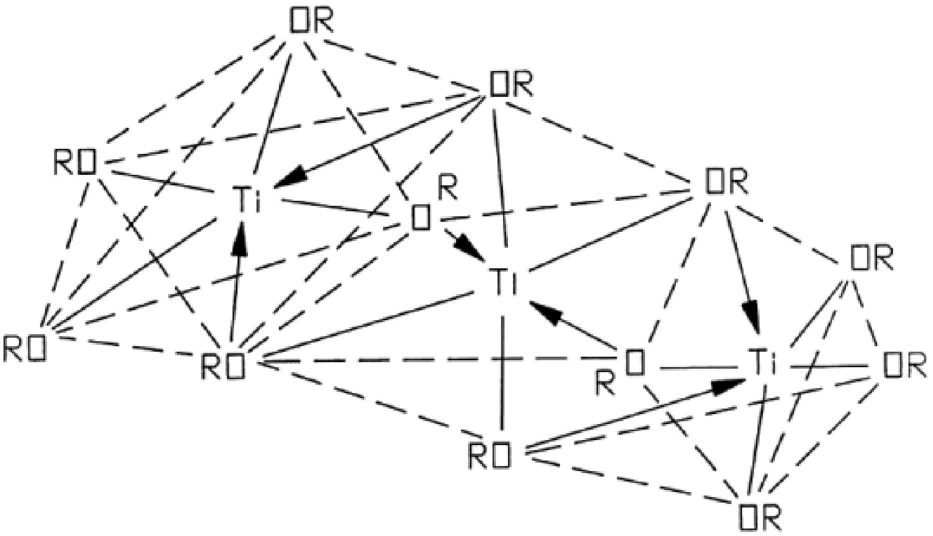


Fig. 1. Structure of $Ti_3(OR)_{12}$.

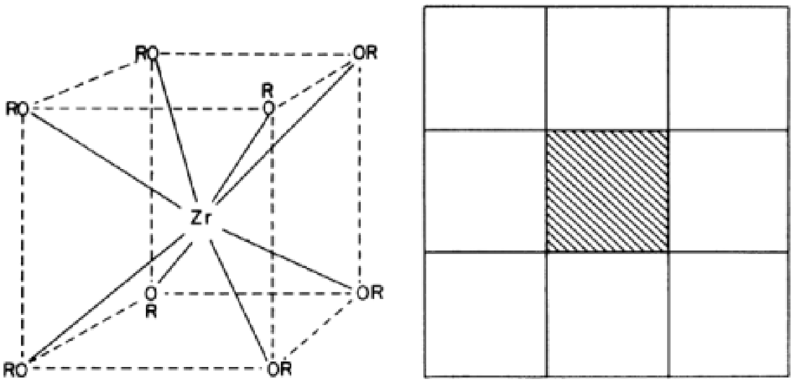


Fig. 2. Structure of $Zr(OR)_8$. Left, unit **A**; right, plane view, eight of unit **A**.

Enols and alkoxides give chelates with elimination of alcohol. For example, in the reaction of the enol form of acetylacetone [123-54-6] all four alkoxide groups attached to zirconium can be replaced, but only two of the four attached to titanium (Fig. 3). Acetoacetic esters react similarly.

Metal alkoxides catalyze the Tishchenko condensation of aldehydes (62), the transesterification of carboxylic esters, the Meerwein-Ponndorf reaction (63), and other enolization and condensation reactions.

$$2\ \mathrm{RCHO} \xrightarrow{\mathrm{NaOR}} \mathrm{RCOOCH_2R}$$

$$\mathrm{RCOOR' + R''OH} \xrightarrow{\mathrm{NaOR}} \mathrm{RCOOR'' + R'OH}$$

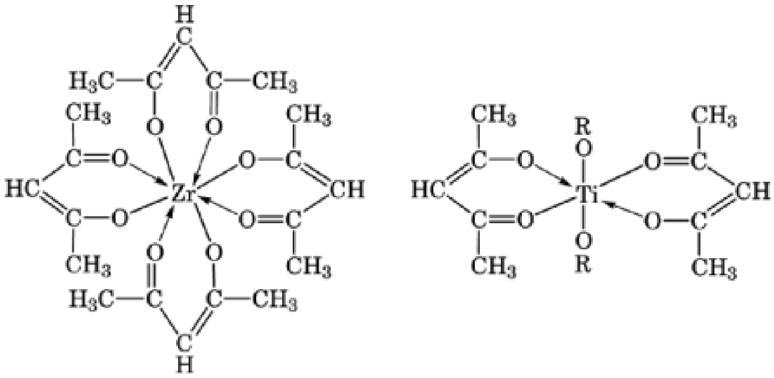


Fig. 3. Products of the reaction of $M(OR)_4$ with $CH_3{-}\overset{OH}{\overset{|}{C}}{=}CH{-}\overset{O}{\overset{\|}{C}}{-}CH_3$ where $M{=}Zr$, coordination number 8, or Ti, coordination number 6.

Mixed chloride alkoxides are prepared by reaction with acyl chlorides, metal chlorides, hydrogen chloride, or chlorine (64).

$$M\,(OR)_4 + 2\ R'COCl \longrightarrow M\,(OR)_2\,Cl_2 + 2\ R'COOR$$

$$M\,(OR)_4 + MCl_4 \longrightarrow 2\ M\,(OR)_2\,Cl_2$$

$$M\,(OR)_4 + 2\ HCl \longrightarrow M\,(OR)_2\,Cl_2 + 2\ ROH$$

Bromine compounds are prepared similarly. These reactions are best carried out in an inert solvent.

Alkoxides often react to give double alkoxides (44):

$$NaOC_2H_5 + Al\,(OC_2H_5)_3 \longrightarrow NaAl\,(OC_2H_5)_4$$

In the presence of alcohol, another type of double alkoxide also forms (44):

$$NaOC_2H_5 + C_2H_5OH + Zr\,(OC_2H_5)_4 \longrightarrow NaHZr\,(OC_2H_5)_6$$

Other double alkoxides are more covalent, distillable, and often more soluble in organic solvents.

Alkaline earth metal alkoxides decompose to carbonates, olefins, hydrogen, and methane; calcium alkoxides give ketones (65). For aluminum alkoxides, thermal stability decreases as follows: primary > secondary > tertiary; the respective decomposition temperatures are ca 320°C, 250°C, and 140°C. Decomposition products are ethers, alcohols, and olefins.

Zirconium alkoxides behave similarly in regard to thermal stability. The series zirconium methoxide [28469-78-5], zirconium ethoxide [18267-08-8], zirconium isopropoxide [2171-98-4], zirconium *tert*-butoxide [2081-12-1] shows decreasing thermal stability.

Many metal alkoxides decompose at higher temperatures to lower valency compounds, in some cases to metal.

3. Preparation

3.1. From Metals and Alcohol

Alkali metals, alkaline earth metals, and aluminum react with alcohols to give metal alkoxides (2, 3, 65):

$$M + ROH \longrightarrow MOR + \frac{1}{2} H_2$$

The speed of the reaction depends both on the metal and on the alcohol, increasing as electropositivity increases and decreasing with length and branching of the chain. Thus sodium reacts strongly with ethanol, but slowly with tertiary butyl alcohol. The reaction with alkali metals is sometimes carried out in ether, benzene, or xylene. Some processes use the metal amalgam or hydride instead of the free metal. Alkaline earth metals and aluminum are often covered with an oxide film which hinders the reaction.

3.2. From Metal Oxides and Hydroxides

This reaction is usually an equilibrium in which the water must be removed by physical or chemical means (23, 56, 66):

$$NaOH + C_2H_5OH \rightleftharpoons NaOC_2H_5 + H_2O \,(\text{also with K, Tl; not with Li});$$

$$V_2O_5 + 6\ ROH \rightleftharpoons 2\ VO(OR)_3 + 3\ H_2O \ (\text{also with } Sb_2O_3);$$

$$MoO_3{\cdot}2\ H_2O + 2\ CH_3OH \longrightarrow MoO_2(OCH_3)_2 + 3\ H_2O$$

3.3. From Metal Halides

The reaction of metal chlorides with alcohols can give metal chloride alkoxides (67–69), eg

$$2\ ZrCl_4 + 5\ C_2H_5OH \longrightarrow ZrCl_3(OC_2H_5){\cdot}C_2H_5OH + ZrCl_2(OC_2H_5)_2{\cdot}C_2H_5OH + 3\ HCl$$

The HCl formed can lead to secondary reactions, especially with unsaturated or tertiary alcohols.

Metal alkoxides may achieve complete replacement of halogen.

$$MCl_x + x NaOR \longrightarrow M(OR)_x + x NaCl$$

Ammonia and alcohol may be used instead of sodium alkoxides to manufacture alkoxides of titanium and other metals such as zirconium, hafnium, germanium, niobium, tantalum, aluminum, and tin.

$$\mathrm{TiCl_4 + 4\ ROH + NH_3 \longrightarrow Ti\,(OR)_4 + 4\ NH_4Cl}$$

3.4. From Alcoholysis and Transesterification

Metal alkoxides of higher, unsaturated, or branched alcohols are difficult to prepare directly and are usually made from lower metal alkoxides by means of alcoholysis:

$$\mathrm{M\,(OR)}_n + n\mathrm{R'OH} \rightleftharpoons \mathrm{M\left(OR'\right)}_n + n\mathrm{ROH}$$

The reaction is driven to completion by distilling the lower boiling alcohol. Metal methoxides are frequently insoluble and cannot be employed as starting materials in this reaction; by the same token, they can be conveniently prepared from solutions of higher alkoxides by precipitation with methanol. Alcoholysis also gives mixed metal alkoxides:

$$\mathrm{M\,(OR)}_{2n} + n\mathrm{R'OH} \rightleftharpoons \mathrm{M\,(OR)}_n\left(\mathrm{OR'}\right)_n + n\mathrm{ROH}$$

Transesterification with carboxylic acid esters is also useful (70):

$$\mathrm{M\,(OR)}_n + n\mathrm{R''COOR'} \rightleftharpoons \mathrm{M\left(OR'\right)}_n + n\mathrm{R''COOR}$$

3.5. From Metal Amides

Dimethyl and diethyl amides of some metals react smoothly to give good yields of certain metal alkoxides that are otherwise difficult to obtain (71, 72).

$$\mathrm{M\left(NR'_2\right)_4 + 4\ ROH \longrightarrow M\,(OR)_4 + 4\ R'_2NH \text{ where } M = V, Cr, \text{ or } Nb \text{ and } R' = CH_3 \text{ or } C_2H_5}$$

3.6. Mixed Halide Alkoxides

Metal chlorides, hydrogen chloride, and carboxylic acid chlorides convert metal alkoxides to metal chloride alkoxides.

3.7. Double Alkoxides

Complex double alkoxides are formed when a solution of an alkali or alkaline earth metal alkoxide is added to a solution of an alkoxide of aluminum, titanium, or zirconium and a series of such compounds have been prepared (44).

3.8. Other Methods

Other methods have only specialized significance. These include alcoholysis of organometallic compounds (73), sulfides (74), and carbides (75),

$$\mathrm{CuCH_3 + ROH \longrightarrow CuOR + CH_4}$$

$$TiS_2 + 4\,ROH \longrightarrow Ti\,(OR)_4 + 2\,H_2S$$

$$CaC_2 + 2\,ROH \longrightarrow Ca\,(OR)_2 + C_2H_2$$

and oxidation of organometallic compounds (76):

$$AlR_3 + 1\,\frac{1}{2}\,O_2 \longrightarrow Al\,(OR)_3$$

This reaction is important in the manufacture of long-chain alcohols by means of hydrolysis of the aluminum alkoxide.

Examples of oxidation of metal alkoxides (40, 42) include:

$$U\,(OC_2H_5)_4 + \frac{1}{2}\,Br_2 \longrightarrow UBr\,(OC_2H_5)_4$$

$$5\,U\,(OC_2H_5)_4 + O_2 \longrightarrow 4\,U\,(OC_2H_5)_5 + UO_2$$

$$Nb(OR)_4 + ROH \longrightarrow Nb(OR)_5 + \frac{1}{2}\,H_2$$

The Meerwein-Ponndorf reaction may be exemplified by (77):

$$Ti\left[OCH\,(CH_3)_2\right]_4 + 4\,CCl_3CHO \longrightarrow Ti\,(OCH_2CCl_3)_4 + 4\,CH_3COCH_3$$

4. Commercial Alkoxides

Table 4 lists the manufacturers of some metal alkoxides, and the individual materials are described in the following. Some other properties of metal ethoxides are summarized in Table 1.

4.1. Alkali Metal Alkoxides

4.1.1. Sodium Methylate

Sodium methoxide [124-41-4] $NaOCH_3$, mol wt 54.0, is a white, caustic, hygroscopic powder; self-ignition at 70–80°C; purity 97–99%; density, $d_4^{20} = 0.45$ g/mL; powder density after loose shaking, 0.45 g/mL; apparent density (packing weight), 0.60 g/mL; medium grain size, 0.07 mm; soluble in methanol (33% at 20°C), insoluble in hydrocarbons and most common organic solvents.

Manufacture is either by reaction of molten sodium with methyl alcohol or by the reaction of methyl alcohol with sodium amalgam obtained from the electrolysis of brine in a Castner mercury cell (78). Both these methods produce a solution of sodium methylate in methanol and the product is offered in two forms: a 30% solution in methanol, and a solid, which is a dry, free-flowing white powder obtained by evaporating the methanol. The direct production of dry sodium methylate has been carried out by the introduction of methanol

Table 4. Manufacturers of Metal Alkoxides

Product	Producer	Country
sodium methylate, solid	Amspec Chemical Corp.	USA
	Badische Anilin und Sodafabrik A.G.	Germany
	Hüls A.G.	Germany
	Nippon Soda	Japan
	Olin Corp.	USA
solution	Amspec Chemical Corp.	USA
	Badische Anilin und Sodafabrick A.G.	Germany
	Hüls A.G.	Germany
	Occidental Chemical Corp.	USA
	Olin Corp.	USA
sodium ethylate	Amspec Chemical Corp.	USA
	Hüls A.G.	Germany
	Mitsubishi Chemical	Japan
	Nippon Soda	Japan
sodium *t*-butylate	Amspec Chemical Corp.	USA
	Callery Chemical Co. Div. of MSA	USA
sodium isopropylate	Amspec Chemical Corp.	USA
potassium methylate, solid	Hüls A.G.	Germany
potassium ethylate, solid	Hüls A.G.	Germany
potassium *t*-butylate, solid	Hüls A.G.	Germany
	Callery Chemical Co. Div. of MSA	USA
magnesium ethylate	Hüls A.G.	Germany
	Nippon Soda	Japan
	Mitsubishi Chemical	Japan
magnesium *n*-propylate	Hüls A.G.	Germany
magnesium alkoxides (other)	Specialty Organics Inc.	USA
	Hüls A.G.	Germany
calcium ethoxide	Mitsubishi Chemical	Japan
aluminum isopropylate	Chattem Chemical Co.	USA
	Deutsche Texaco A.G.	Germany
	Mitsubishi Chemical	Japan
	Nippon Soda	Japan
aluminum *sec*-butylate	Deutsche Texaco A.G.	Germany
aluminum alkoxides (other)	Ethyl Corp.	USA
	Hexcel Chemical Co.	USA
	Joseph Ayers	USA
	Nippon Soda	Japan
	Vista Chemical Co.	USA
titanium alkoxides	AKZO	USA
	Black Uhler Chemical Co., Inc.	USA
	E. I. du Pont de Nemours & Co., Inc.	USA
	Hüls A.G./Hüls America, Inc.	Germany/USA
	Kenrich Petrochems. Inc.	USA
	Kronos-Titan G.m.b.H.	Germany
	Nippon Soda	Japan
	Rhone-Poulenc S.A.	France
	Tioxide Chemicals, Ltd.	UK
vanadium alkoxides	Mitsubishi Chemical	Japan
germanium alkoxides	Nippon Soda	Japan
	Mitsubishi Chemical	Japan
zirconium alkoxides	Hüls A.G.	Germany
	Nippon Soda	Japan
	Mitsubishi Chemical	Japan
	Tioxide Chemicals, Ltd.	UK
tantalum ethoxide	Nippon Soda	Japan
	Mitsubishi Chemical	Japan

vapors to molten sodium in a heavy duty agitating reactor. The solid is supplied in polyethylene bags contained in airtight drums filled in a nitrogen atmosphere.

Typical specifications of the powder are as follows: sodium methylate, 97.5%; sodium hydroxide, 0.5%; sodium carbonate, 0.4%; sodium formate, 0.3%; and free methanol, 0.5%.

The 30% solution in methanol has the following specifications: sodium methylate content, 29–30%; density at 20°C, 0.972; viscosity at 30°C, $_{4.5\text{Pa}\cdot\text{s}}$ (45 P); flash point, 11°C; crystallization temperature, 7°C; miscible in alcohols; inmiscible in hydrocarbons.

4.1.2. Sodium Ethylate

Sodium ethoxide [141-52-6], $NaOC_2H_5$, mol wt 68.1, is a fine yellowish-white, free-flowing, strongly caustic, hygroscopic powder; self-ignition at 30–50°C; purity 94–97%; density at 20°C, 0.25 g/mL; powder density after loose shaking, 0.20 g/mL; apparent density (packing weight), 0.30 g/mL; medium grain size, 0.01–0.03 mm; easily soluble in ethanol (28%), insoluble in hydrocarbons and most other organic solvents.

4.1.3. Sodium tert-Butylate

Sodium *tert*-butoxide [865-48-5], $(CH_3)_3CONa$, mol wt 96.1, is a pale yellow, free-flowing, caustic, hygroscopic powder; purity 95–99%; bulk density 0.3–0.4 g/mL; fairly soluble in alcohols, sparingly soluble in ether and hydrocarbons.

4.1.4. Sodium tert-Amylate

Sodium *tert*-amylate [14593-46-5], $C_2H_5(CH_3)_2CONa$, mol wt 110.1, is a white to pale yellow, free-flowing, caustic, hygroscopic powder; purity 95–99%; bulk density 0.3–0.4 g/mL; fairly soluble in hydrocarbons.

4.1.5. Potassium Methylate

Potassium methoxide [865-33-8], $KOCH_3$, mol wt 70.13, is a fine, free-flowing, yellowish-white, caustic, hygroscopic powder; purity 96.5–99%; powder density after loose shaking, 0.75 g/mL; apparent density (packing weight), 1.00 g/mL; medium grain size, 0.05–0.8 mm; easily soluble in alcohols (33% in methanol at 20°C), insoluble in hydrocarbons.

4.1.6. Potassium Ethylate

Potassium ethoxide [917-58-8], KOC_2H_5, mol wt 84.16, is a fine, yellowish-white, free-flowing, strongly caustic, hygroscopic powder; purity 95–97%; powder density after loose shaking, 0.65 g/mL; apparent density (packing weight), 0.83 g/mL; medium grain size: 0.15–0.80 mm; easily soluble in alcohols (28% in ethanol or ether at 20°C), insoluble in hydrocarbons; under certain circumstances, self-igniting at room temperature and should therefore be handled under nitrogen.

4.1.7. Potassium tert-Butylate

Potassium *tert*-butoxide [865-47-4], $(CH_3)_3COK$, mol wt 112.2, is a fine, white, caustic, free-flowing, hygroscopic powder; purity 95–99%; density, $d_4^{20} = 0.50$ g/mL; powder density after loose shaking, 0.50 g/mL; apparent density (packing weight), 0.70 g/mL; medium grain size, 0.25–0.30 mm; soluble in alcohols (20% in *tert*-butyl alcohol at 20°C) and THF, sparingly soluble in ether and hydrocarbons. In contrast to potassium alkoxides with α-hydrogens, it is more resistant to ignition and oxidation.

4.2. Alkaline Earth Metal Alkoxides

4.2.1. Magnesium Methylate

Magnesium methoxide [109-88-6], $Mg(OCH_3)_2$, mol wt, 86.3, is an almost white powder; powder density 0.5 g/mL; grain spectrum, >500 μm (ca 10%), 200–500 μm (ca 20%), <200 μm (ca 70%); sparingly soluble in methanol, ethanol, and cyclohexane; nearly insoluble in butanol, butyl acetate, and DMF; completely insoluble in ether and hydrocarbons.

Magnesium methylate is sensitive to air and moisture, decomposing to magnesium hydroxide, carbonate, and methanol. It can be stored for one year in polyethylene bags under nitrogen or argon.

Magnesium methylate is used as a drying agent for alcohols and other organic solvents and as an intermediate in various manufacturing processes, eg, for organomagnesium compounds (79), orthocarbonic esters (80), and for oxide coatings.

A significant use is as a catalyst in a multitude of reactions, such as the formation of acrylic and methacrylic acid amides from fatty acid amides (81); of cyclic ketones such as 4-phenylcyclopentane-1,2-dione and 2,5-dihydroxy-*p*-benzoquinone from benzaldehyde diethyl acetal and 2,4-dioxo-5,5-dimethoxy-hexanoic acid methyl ester (82); of dimer aldehydes from propane (83); and for the polymerization of epoxy compounds (84).

4.2.2. Magnesium Ethylate

Magnesium ethoxide [2414-98-4], $Mg(OC_2H_5)_2$, mol wt 114.4, is an almost white hygroscopic powder; density, $d_4^{20} = 0.48$ g/mL; powder density, 0.48 g/mL; grain spectrum, $<500\ \mu m$, (ca 24%), 200–500 μm (ca 70%), $<200\ \mu m$ (ca 6%); soluble in methanol, ethanol, and DMF, insoluble in ethers and hydrocarbons. It should not be stored longer than one year. It is packaged in polyethylene bags under nitrogen or argon.

Magnesium ethylate is used as a drying agent for organic solvents, as an intermediate for the manufacture of organomagnesium and other organic products, as catalyst in the Tishchenko (85) and other reactions (86–91), in the condensation of esters (92), in alkylation reactions, and in polymerizations (84, 91).

4.2.3. Calcium Methylate Ethylate and Ethylate

Calcium methoxide [2556-53-8] and ethoxide [2914-17-2], $Ca(OCH_3)_2$ and $Ca(OC_2H_5)_2$, are white powders soluble in the corresponding alcohol (max concentration 1%). They are packaged and stored like the magnesium alkoxides.

4.3. Aluminum Alkoxides

4.3.1. Aluminum Isopropylate

In Group 3 aluminum isopropoxide [555-31-7], $Al(OCH(CH_3)_2)_3$ mol wt 204.25, is a white solid; density, $d_4^{20} = 1.0346$ g/mL; flash point, 26°C; melting point, 118.5°C; boiling point, 140.5°C at 1060 Pa (8 mm Hg); $\Delta H = 82$ J/mol (19.6 cal/mol); easily soluble in alcohols. It is supplied in blocks in 25-kg canisters or as powder in 20-kg tin cans.

The usual method of manufacturing is by direct reaction of aluminum and isopropyl alcohol. In one procedure, aluminum ingots are dissolved in excess isopropyl alcohol, using mercuric chloride or iodine as catalyst; the excess isopropyl alcohol is stripped and the remaining aluminum isopropoxide distilled. In another process (93), the reaction is controlled, requires no catalyst, and gives nearly quantitative yields. The aluminum is contained in a tower above the isopropyl alcohol and the alcohol refluxes through the column, continually washing the product into the stillpot until 100% concentration is reached. The product is then drawn off and distilled under vacuum. The stillpot is recharged with alcohol and the process is repeated. This process also lends itself to continuous production by continually drawing off product and feeding in alcohol and aluminum. Aluminum isopropoxide can also be produced by the addition of excess isopropyl alcohol to a benzene solution of aluminum chloride, followed by passage of dry ammonia which precipitates ammonium chloride. The ammonium chloride is filtered and the isopropoxide is separated by distillation.

4.3.2. Aluminum sec-Butylate

Aluminum *sec*-butoxide [2269-22-9], mol wt 246.3, $Al(OCH(CH_3)C_2H_5)_3$ is miscible with aromatic hydrocarbons; density, $d_4^{20} = 0.9671$ g/mL; flash point, 26°C; bp, 180°C at 53 Pa (0.4 mm Hg); $\Delta H = 90$ J/mol (21.5 cal/mol); degree of association, 2.4.

Aluminum alkoxides are easily soluble in hydrocarbons and in chlorinated hydrocarbons, but sparingly soluble in alcohols. They are sensitive to moisture and dry storage is essential. Aluminum alkoxides are used extensively as intermediates, for example, in the Meerwein-Ponndorf reaction (94).

4.4. Transition Metal Alkoxides

4.4.1. Titanium Alkoxides

Titanium alkoxides are made from titanium tetrachloride and the corresponding alcohols in the presence of ammonia. Higher titanium alkoxides are manufactured from lower alkoxides by alcoholysis. Titanium isopropoxide and *n*-butoxide are commercially available in barrels. Annual production of titanium alkoxides is estimated at 3000–4000 metric tons at an average price of about $4/kg.

Titanium alkoxides are used for the hardening and cross-linking of epoxy, silicon, urea, melamine, and terephthalate resins; in the manufacture of noncorrodable, high temperature lacquers; in the sol-gel process; as water repellents and adhesive agents (especially with foils); to improve glass surfaces; as catalyst in olefin polymerization, and for condensation and esterification.

Tetraisopropyl Titanate. Some properties of the ethoxide are noted in Table 1. Titanium tetraisopropoxide [546-68-9], $Ti[OCH(CH_3)_2]_4$, mol wt 284.3, is an almost colorless to light-yellowish fluid, fumes in moist air, soluble in organic solvents; density, $d_4^{20} = 0.97$ g/mL; mp, 15–19°C; bp, 232°C (49°C at 10 Pa or 0.075 mm Hg); flammable, flash point 50–60°C; $\Delta H = 76$ J/mol (18.2 cal/mol); degree of association, 1.4.

4.4.1.1. Tetrabutyl Titanate. Titanium tetra-*n*-butoxide [5593-70-4], $Ti(OC_4H_9)_4$, mol wt 340.5, is an almost colorless to light yellow viscous fluid which hydrolyzes in moist air, and is soluble in organic solvents; density, $d_4^{20} = 1.00$ g/mL; solidification point, $-50 - 80$°C; bp, ca 300°C (142°C at 10 Pa); flammable, flash point 50–60°C; $\Delta H = 113$ J/mol (27 cal/mol); degree of association, 3.4.

4.4.2. Zirconium Alkoxides

Like the corresponding titanium compounds, the zirconium alkoxides are manufactured from solid zirconium tetrachloride and the respective alcohol in the presence of ammonia. Higher alkoxides are manufactured by alcoholysis. Zirconium *n*-propoxide and *n*-butoxide are commercially available in barrels at about $14/kg.

Zirconium alkoxides are used for cross-linking and hardening of isocyanate, epoxy, silicon, urea, melamine, and terephthalate resins; in the sol-gel process; as catalysts in condensation; and as water repellents. Zirconium alkoxides hydrolyze in moist air, but more slowly than titanium alkoxides.

4.4.2.1. Zirconium Tetra-n-propylate. Zirconium tetra-*n*-propoxide [23519-77-9], $Zr(OC_3H_7)_4$ mol wt 327.6, is a colorless solid, melting point, 214°C (95). The commercial product contains about 28% ZrO_2 and propanol; it is a yellow-brown liquid, density, $d_4^{20} = 1.05$ g/mL; solidification point below -70°C; flammable, flash point below 21°C, soluble in hydrocarbons.

4.4.2.2. Zirconium Tetra-n-butylate. Zirconium tetra-*n*-butoxide [1071-76-7] $Zr(OC_4H_9)_4$ mol wt 383.7, is a colorless solid, melting point, 134°C (95). The commercial product contains about 28% ZrO_2 and butanol; it is a yellow-brown liquid, density (apparent), $d_4^{20} = 1.07$ g/mL; solidification point below -70°C; bp, 260°C at 10 Pa (0.075 mm Hg); flammable, flash point 21°C; soluble in hydrocarbons.

4.4.3. Vanadium Alkoxides

Except for the solid methoxide, the lower vanadium alkoxides are slightly colored, yellow, or yellow-brown liquids. They are easily hydrolyzed and decompose on heating; above 100°C they darken. They are made from V_2O_5 or $VOCl_3$.

Vanadium alkoxides are used mostly in olefin polymerization as catalysts; also as hardeners and for coatings.

Of importance, besides the ethoxide and the isopropoxide, is vanadium n-butoxide [1801-76-9] (vanadyl butylate), mol wt 286.3, a yellow liquid; bp, 135°C; density, $d_4^{20} = 1.03$ g/mL. For further information about vanadium alkoxides, see references (22, 23, 96, 97).

4.5. Antimony Trialkoxides

With the exception of the solid methoxide [19727-40-3], the lower antimony trialkoxides are colorless or slightly colored distillable liquids, easily hydrolyzed. Thermally these alkoxides are rather stable. The lower antimony trialkoxides are manufactured from antimony trichloride, the higher from antimony trioxide, both on a small scale. They are used in polyester manufacture, in fireproofing, as catalysts, and for coatings. For further information about antimony trialkoxides, see references (21, 65, 98).

5. Handling, Shipment, and Toxicology

Metal alkoxides are strongly caustic and are decomposed by the humidity of the air or moisture of the skin, requiring the use of protective glasses and gloves.

The heat of hydrolysis, $\mathrm{MOR} + \mathrm{HOH} \longrightarrow \mathrm{MOH} + \mathrm{ROH}$ (exothermic), is capable of igniting alkali alkoxides, especially potassium alkoxides, on exposure to air. Such fires must be extinguished with sand or foam but not with water.

Alkoxides should be stored under cool, dry conditions. The solids are packed in polyethylene bags under nitrogen or argon that are shipped in drums with foam rubber gaskets. For the liquid alkoxides steel drums are used, usually with a polyethylene liner.

The health hazard presented by metal alkoxides reflects the toxicity of the metals they contain and the metallic hydroxides and alcohols they form on hydrolysis.

6. Analytical Methods

The ease of hydrolysis of metal alkoxides makes metal analysis a comparatively simple task. In many cases, the metal may be estimated by hydrolysis of a sample in a crucible, and ignition to the metal oxide. Alternatively, the metal ion may be brought into solution by hydrolysis of a sample with dilute acid, followed by a standard analytical procedure for a solution of that particular metal. If the alcohol liberated during the hydrolysis is likely to cause interference, it may be distilled from the solution by boiling.

The estimation of alkoxy groups is not such a simple task. One method (26, 68) involves hydrolysis and oxidation of the liberated alcohol with excess standard potassium dichromate solution. The excess may then be estimated iodometrically. This method is suitable only for methoxides, ethoxides, and isopropoxides; quantitative conversion to carbon dioxide, acetic acid, and acetone, respectively, takes place. An alternative method for ethoxides is oxidation followed by distillation, and titration of the liberated acetic acid.

For the higher alkoxy groups, standard carbon and hydrogen analysis may be used, although careful sample preparation is required because of the ease of hydrolysis. Quantitative vapor-phase chromatography of alcohol liberated during hydrolysis may also be used, but care must be taken in this case to ensure that hydrolysis is complete before the estimation is carried out.

7. Applications

Metal alkoxides are used for a great variety of purposes (99). They are useful for putting a metal into an organic solution, for instance in a homogeneously catalyzed reaction. When a metal must be fixed onto an organic or inorganic surface, it may be done by reaction of a suitable alkoxide with active groups of the surface.

They compete with other inorganic metal compounds, such as metal carboxylates, and have advantages because of their catalytic properties, ease of hydrolysis, solubility in organic solvents, and distillability. They are mainly used as catalysts (in Ziegler-Natta polymerization, transesterifications, and condensations), with partial or complete hydrolysis, alcoholysis, transesterification in coatings for plastics, textiles, glass, and metals, and in additives for adhesives and paints, for sol-gel applications (51–54), for synthesis of minerals capable of safely enclosing radioactive nuclear waste (54, 100–103) and for the cross-linking or hardening of natural and synthetic materials. Alkali metal alkoxides find their principal use in organic synthesis where they act as strong bases.

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