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REACTIONS AND SYNTHETIC APPLICATIONS OF METAL ALKOXIDES*

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One of the most characteristic properties of the metal alkoxides is their facile reactivity with protic reagents (e.g., water, alcohols, glycols, silanols, β-ketoesters, β-diketones, carboxylic acids, oximes, hydroxylamines, alkanolamines, β-ketoamines, Schiff bases, hydroxythiols, hydroxy carboxylic acids, amines, thiols, thio-β-diketonates, dialkyldithiophosphoric acids, etc.) to yield a variety of organic derivatives of metals and alcohols. The solubility of metal alkoxides in organic solvents offers a distinct advantage in the syntheses of derivatives of metals whose salts are susceptible to hydrolysis in aqueous media; the inertness of the side-product alcohol and its convenient removal (often azeotropically with the solvent) not only ensures a high purity of the product, but also makes it possible to synthesize mixed products in novel coordination states.

A renewed interest being focussed on the applications of metal alkoxides in organic and organometallic syntheses is revealing their fastly growing potential in directions such as syntheses of asymmetric alcohols, carbonylation reactions for esters, selective nucleophilic reagents and providing better substrates for synthesis of even simple organometallic derivatives.

Key Words : Metal Alkoxides and their Reactions

INTRODUCTION

THE early applications of aluminium isopropoxide and tertiary butoxide as catalysts in the well-known Meerwein-Verley-Pondorff and Qppenauer reaction in 1920's was followed by a period of lull in metal alkoxide chemistry for nearly the next three decades.

With the renaissance of inorganic chemistry, a vigorous interest in the chemistry of alkoxy derivatives of almost all the metals[1] has been sustained the early 1950's. The volatility and solubility of metal alkoxides in organic solvents, not only provided attractive features at a time when few inorganic compounds with such covalent characteristics were known, but these features have been of great value in their purification and applications to synthetic inorganic chemistry. Their facile interactions with a variety of protic reagents[2,3] in organic solvents often in a desired stoichiometric ratio have provided an extremely large list of

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novel organic derivatives of metals, many of which can not be prepared by any alternative route so far.

Following the far-reaching applications of metal alkoxides to synthetic inorganic chemistry, the pendulum is again appearing to shift to synthetic organic reactions. The earliest applications of aluminium alkoxides *via* Meerwein-Ponndorf-Verley reactions have been revived in a novel form to the synthesis of asymmetric alcohols.[4,5] Another direction in which notable success has been achieved is in the synthesis of organic esters by rhodium and palladium catalyzed carbonylation reactions with metal alkoxides.[6,7] Although the stabilization of earlier transition metals carbon σ-bond by the presence of alkoxy groups had been noticed quite early,[8] yet organometallic compounds such as $CH_3Ti_3(OPr^i)_3$ and $CH_3Zr(OBu)_3$ have been only recently employed[9,10] as selective nucleophilic reagents in organic synthesis.

Of the vast amount of literature now available on the reactions and synthetic applications of metal alkoxides, attention would be focussed mainly on the contributions from our own laboratories in pursuance of the indicated purpose of this invited lecture; this would be followed by a very brief account of the fastly emerging applications of metal alkoxides in organometallic and organic synthesis.

Results and Discussion

Applications of Metal Alkoxides in the Synthesis of Organic Derivatives of Metals

Basically, these synthetic uses of metal alkoxides depend on their chemical reactivity coupled with their volatility and solubility in common organic solvents. Amongst derivatives (with simpler composition) of metals, their unique and general volatility offers certainly an unparalleled asset in the ease of their purification. Solubility in common organic solvents makes them as extremely attractive synthons for preparations of a variety of novel derivatives of metals (e.g., Al, Ga, Ti, Zr, Ge, Sn, As, Sb, V, Nb, Ta, etc.), the ions of which are susceptible to hydrolysis (generally to an undefined extent) in aqueous solutions.

Besides many other reactions of synthetic utility, one of the most extensively exploited reactions of metal alkoxides for synthetic purposes is their facile reactivity with water and any organic compound having a hydroxy group (e.g., alcohols, silanols, glycols, acids, enolic forms of β-diketones and β-ketoesters, oximes, hydroxylamines, alkanolamines, β-ketoamines and Schiff bases, hydroxythiols, etc.). In cases of metals which tend to form rather stable M-N or M-S bonds, the reactivities of the metal alkoxides with amino-or thio-reagents also offer attractive possibilities. In addition to the above, the reactions of metal alkoxides with organic and silyl esters, hydrogen halides, halogens, acyl halides acid anhydrides, some coordinating ligands as well as unsaturated substrates can be utilized for synthetic purposes. A very brief account of these reactions will now be presented in a convenient order, beginning with alcoholysis, which has been most extensively exploited and ending with hydrolysis which appears to be overshadowing now all other uses of metal alkoxides.

Reactions of Metal Alkoxides with Alcohols

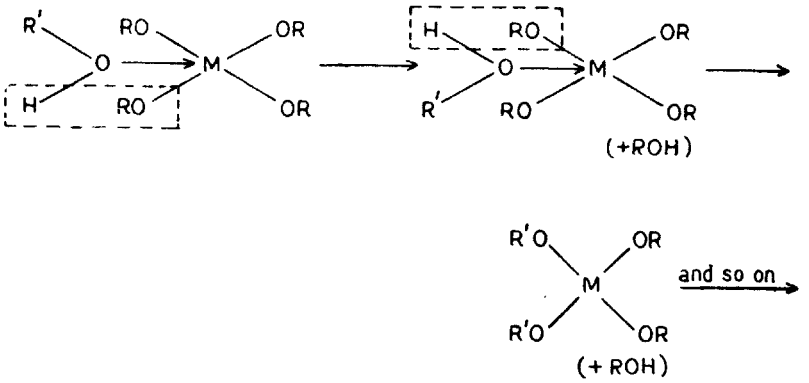
Alkoxy derivatives of the elements generally tend to react with all hydroxy compounds resulting in the replacement of their alkoxy groups. For example, the reactions of alkoxides with alcohols (and phenols), generally termed as alcoholysis or alcohol interchange reactions, can be represented by the following general equation:

$$M(OR)_n + xR'OH \rightleftharpoons M(OR)_{n-x}(OR')_x + xROH$$

The forward reaction can be promoted by fractionating out the alcohol formed if it is more volatile. In some cases a solvent like benzene which forms a low-boiling azeotrope with the liberated alcohol (e.g., ethanol or isopropanol) facilitates not only the fractionation of the liberated alcohol, but also makes it possible to carry out the reaction in any stoichiometric ratio of the reactants to yield the desired mixed alkoxides, many of which are stable entities with interesting structural features. In some cases (e.g. methoxides), the forward reaction is highly facilitated by the instantaneous separation of the insoluble methoxides on mixing the alkoxide with methanol.

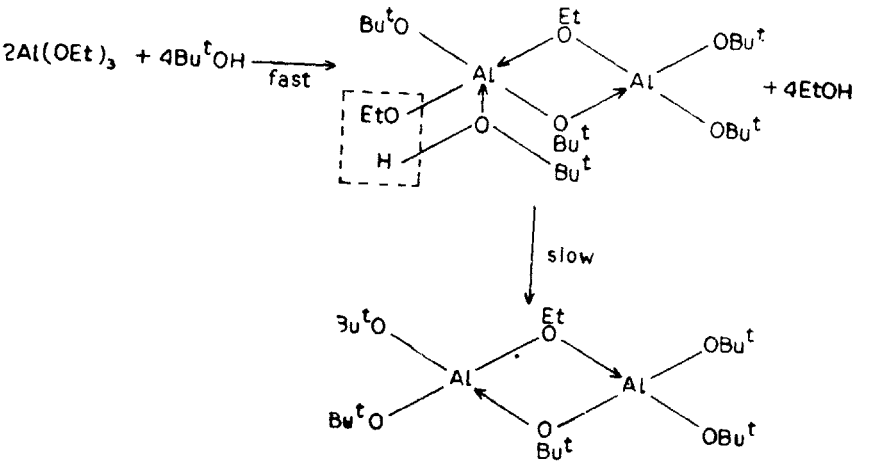
The alcoholysis reactions have been widely put to synthetic uses for alkoxy derivatives of various elements like beryllium,[11] zinc,[12] boron,[13] aluminium,[14] gallium,[15] indium,[16] germanium,[17,18] tin[19,20] titanium,[21] zirconium,[21] hafnium,[22] cerium,[23] thorium,[24] vanadium,[24] niobium,[25] tantalum,[26,27] arsenic,[28] antimony,[28] chromium,[29,30] selenium,[31] tellurium,[31] iron,[29,30] cobalt,[29,30] nickel,[29,30] copper,[29,30] lanthanides[32] and uranium.[33]

These reactions appear to proceed through the SN^2 type mechanism involving a four-centred cyclic transition state:



Obviously such reactions would be susceptible to steric factors. Although in general the facility for interchange of alkoxy groups increases from tertiary to secondary to primary groups (MeO > Eto > $Pr^iO \gg Bu^tO$),[34] yet even in cases where reactions are rather slow they can be driven to completion if the alcohol produced in the reaction is continuously fractionated out. For example, the interchange of aluminium ethoxide with secondary butanol is slower than that

with normal butanol, yet the former reaction also could be pushed to completion. However, in the case of tertiary butanol, the reaction becomes extremely slow after the replacement of two moles of etnanol per mole of $Al(OEt)_3$. Even if ethanol is carefully and continuosly fractionated out, it does not appear to proceed beyond the formation of a product of the comoposition, $Al_2(OEt)(OBu^t)_5$. In view of the dimeric nature of the product, $[Al(OEt)(OBu^t)_2]_2$ also, these reactions can be represented as shown below:



In order to explain the possibility of the last stage of the slow reaction, an unsymmetrical structure was suggested[14] for the product, $[Al(OEt)(OBu^t)_2]_2$, in which the Al atom on the left is sterically less hindered and may allow the coordination of another mole of tertiary butanol, leading to slow replacement. Both the aluminium atoms in the final product $Al_2(OEt)(OBu^t)_5$ are surrounded by one ethoxy and three tertiary butoxy groups, precluding the coordination of another bulky tertiary butanol at either of the two aluminium atoms. The unsymmetrical type of stucture suggested on the basis of chemical reactivity for $[Al(OEt)(OBu^t)_2]_2$, has been confirmed[35] more recently by pmr spectroscopy for the analogous $[Al(OPr^i)OBu^t)_2]_2$.

Alkoxides of earlier transition metals (Ti, Zr, Hf, Th, V, Nb, Ta) undergo facile alcoholysis reactions, in which mainly steric factors appear to be reponsible for non-completion of a few reactions, exemplified below :

$$2Zr(OMe)_4 + 6Bu^tOH \longrightarrow (Bu^tO)_3\,Zr(\mu\text{–}OMe)_2\,Zr(OBu^t)_3 + 6MeOH$$

$$Ta(OMe)_5 + 4Pr^iOH/Bu^tOH \longrightarrow Ta(OMe)(OPr^i/OBu^t)_4 + 4MeOH$$

Alkoxides of main group elements also undergo facile alcohol interchange reactions. Thus while $Te(OPr^i)_4$ is converted[31] into the corresponding tetra-alkoxides with primarily, secondary and tertiary alcohols, $(EtO)_2SeO$ undergoes partial alcoholysis only with secondary and tertiary alcohols.

Recent investigations[29] on alcoholysis reactions of alkoxides of some later '3*d*' metals have revealed some novel features, in which besides steric factors the relative stabilities of the different coordination states appear to play a dominant role. It has been observed that whereas primary alkoxides of iron[36] (III) and copper(II)[37,38] undergo facile alcoholysis reactions like earlier transition metal alkoxides, primary alkoxides of Cr(III),[39] Co(II)[40] and Ni(II)[41] do not appear to be reactive towards other alcohols at all. However, secondary and tertiary alkoxides of these three metals Cr(III), Co(II) and Ni(II) generally undergo facile exothermic alcoholysis with primary alcohols. This salient difference in the reactivity, for example in the case of nickel alkoxides, has been explained due to octahedral nature of primary alkoxides in contrast to the tetrahedral geometry of secondary and tertiary alkoxides of nickel (II).

The inertness of Cr(III) primary alkoxides to alkoxides to alcoholysis may also be ascribed to the special stability of octahedral chromium(III) (with three singly occupied lower energy t_{2g} levels). The Jahn-Teller effect does not appear to be able to disturb the regularity of this octahedral species, which is consequently unable to react both by dissociative as well as associative mechanism. $Cr(OBu^t)_4$, a tetrahedral species stabilized by two singly occupied lower energy e_g levels in a tetrahedral ligand field, is readily converted into the corresponding Cr(III) alkoxide on treatment with methanol, ethanol or isopropanol, which is understable on the basis of the greater stability and insolubility of the octahedral species.

Although simple alkoxides of later transition metals show some unique features in their alcoholysis reactions, their bimetallic alkoxides, e.g.,

$[Cr\ Al(OPr^i)_4]_3$,[42] $Mn\ [Al(OPr^i)_4]_2$,[29]

$[Fe\{Al(OPr^i)_4\}_{2or3}]$,[43] $Co\ [Al(OPr^i)_4]_2$,[44]

$Ni\ [Al(OPr^i)_4]_2$,[45] $Ni\ [Ga(OPr^i)_4]_2$,[46] $Ni\ [Nb(OPr^i)_6]_2$,[47]

$[Ni\ [Ta\ [OPr^i)_6]_2$,[47] $Ni\ [Zr_2(OPr^i)_9]_2$[46] and $Cu\ [Al(OPr^i)_4]_2$[38]

exhibit alcohol interchangeability similar to non-transition or earlier transition metals, which is understable as the SN^2 reaction in these cases may be occurring on the Al, Ga, Nb, Ta or Zr atom.

Similar to alcohols, silanols have been found to react with metal alkoxides to form the corresponding metal silyloxide :

$$M(OR)_n + xR_3'\ SiOH \rightleftharpoons M(OSiR_3')_x\ (OR)_{n-x} + x ROH$$

Zeitler and Brown[48] isolated $Ti(OSiPh_3)_4$ and $Ti\{O_5Si_4(C_6H_5)_8\}_2$ by the reactions of $Ti(OBu)_4$ with Ph_3SiOH and $Ph_2Si(OH)_2$ respectively. Bradley and Thomas[49] prepared $Ta(OSiMe_3)_5$ and $\{(Me_3SiO)_4\ Nb\}_2\ O$ by the reactions of $Ta(OEt)_5$ and $Nb(OEt)_5$ with $Me_3\ SioH$. The reaction of $Al(OPr^i)_3$ with $Bu^t_3\ SiOH$ in 1 : 2 molar ratio yields[50] $[Al(OPr^i)\ (OSiBu^t_3)_2]_2$, but attempts to synthesize the *tris*-product were unsuccessful probably due to steric reasons.[14]

A complicating factor affecting the above reactions of involving silanols appears to be the condensation tendency of the silanols themselves :

$$2R_3SiOH \longrightarrow (R_3Si)_2\,O + H_2O$$

This side reaction not only reduces the amount of silanol actually available for the reaction, but the water produced therein tends to hydrolyze the reactants as well as the products. Bradley, Kapoor and Smith[51] attempted the addition of Me_3SiOH gradually through a side inlet in the reaction vessel and were successful in synthesizing $U(OSiMe_3)_5$ and $U(OSiMe_3)_6$.

Reactions of Metal Alkoxides with Organic Esters and Silyl Esters

Following an earlier observation by Baker,[52] the transesterification reactions of metal alkoxides were extensively explored by Mehrotra *et al.* for the synthesis of alkoxy (particulary tertiary) derivatives of various metals (Al,[53] GA,[54] Fe,[36] V,[24] Ti,[53] Zr,[53] Hf,[53] Nb,[55] Ta,[55] Ln[56])

$$M(OR)_n + x CH_3COOR' \rightleftharpoons M(OR)_{n-x}(OR')_x + x CH_3COOR$$

The transesterification reactions in general appear to be less prone to steric factors then the alcoholysis reactions. Further transesterification reactions have a distinct advantage over the alcoholysis reactions when tertiary butoxides are being synthesized from the isopropoxide due to the large (~9°) boiling point difference between tertiary butyl and isopropyl acetates compared to only ~0.2° difference between the corresponding alcohols. The utility of the transesterification reactions has been extended considerably by the use of an inert solvent like cyclohexane (b.p. 80.8 °C) which forms a convenient azeotrope with ethyl acetate (b.p. 72.8 °C as well as isopropyl acetate (b.p. 78.9 °C). The technique has, therefore, been extended for the preparation of alkoxides/mixed alkoxides of a number of metals.

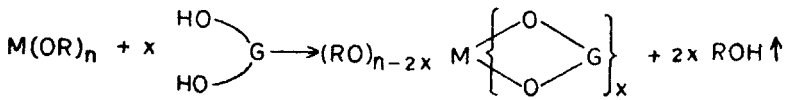
The method has been extended by Bradley and Thomas[39] for the preparation of trialkylsilyloxides of titanium, zirconium and other metals. The use of trialkylsilyl acetate is much more convenient as it does not suffer from the disadvantage of trialkylsilanols which tend to condense giving water as a side-product.

An interesting application of this technique is the reported syntheses[57] of $Al(OPr^i)_x(OSiMe_3)_{3-x}$ (where $x = 0$, 1 or 2) by the reaction of $Al(OPr^i)_3$ with $CH_3COOSiMe_3$.

The potential of metal silyloxide derivatives as sources for metal-siloxane polymers does not appear to have been fully exploited so far.

Reactions with Glycols

Metal alkoxides have been found to react readily with glycols to yield the glycolate (chelated/bridged) or mixed alkoxide glycolate derivatives, which are often shown to be interesting polymeric materials less prone to hydrolysis, etc.



A number of volatile glycol derivatives of boron, (*R*O) $B(O_2G)$; (GO_2) B(OGO) $B(O_2G)/B(OGO)_3B$ have been synthesized by the reactions of boron alkoxides with glycols in 1 : 1 and 2 : 3 molar ratios.

Glycolate derivatives of a number of metals (Al,[49*] Si,[50*,51] Ge,[52*,53*,54*] Sn, Bu_2 Sn,[55*–57*] Se,[58] Te,[58] Sb,[59] Fe,[60] Ti,[54*,61], Zr,[62] Nb,[63] Ta,[64] U,[65] Pr, Nd, Gd and Er[32]).

An interesting general feature of glycoxy derivatives of various elements is that following the miscibility of hexylene glycol and pinacol with organic solvents, their metal derivatives also tend to show greater tendency of dissolution in hydrocarbon solvents.

Reactions with Organic Acids and Anhydrides

Metal alkoxides react conveniently with organic acids and anhydrides to form the metal acylates and alcohols or esters :

$$M(OR)_n + xR'COOH \longrightarrow M(OR)_{n-x}(OOCR')_x + x\text{ROH}$$

$$M(OR)_n + x(R'CO)_2O \longrightarrow M(OR)_{n-x}(OOCR')_x + xROOCR'$$

The first attempt to prepare a metal acylate from the alkoxide and an organic acid appears to have been made in case of aluminium in 1932 by McBain and Mc Latchie[66] who reported the preparation of the dipalmitate by the reaction of aluminium ethoxide with palmitic acid. The above and other failures[67–70] in the preparation of aluminium tricarboxylates led to serious doubts[71] about their very existence. On the contrary, Lawrence[72] had reported that—

"Mehrotra [73] reported the preparation of aluminium tri-soaps by the following simple reactions:

$$Al(OPr^i)_3 + 2RCOOH \xrightarrow{C_6H_6} Al(OPr^i)(OOCR)_2 + 2Pr^iOH$$

$$Al(OPr^i)(OOCR) + RCOOH \xrightarrow[\text{slow}]{} Al(OOCR)_3 + Pr^iOH.\text{"}$$

The existence of trisoaps of aluminium was confirmed by several workers.[74–77] Mono-, di- and tri-lactates and mandelates of aluminium were synthesized by similar methods,[78] but tri-salicylate could not be prepared by this method. The reactions of gallium alkoxides with fatty acids follow[79] the same pattern as those of aluminium analogoues. On the other hand, the reactions of titanium ethoxide with fatty acids are straightforward upto 1 : 2 molar ratio, but further reactions lead to side decompositions with the elimination of organic esters[80–81] :

$$Ti(OC_2H_5)_4 + 2RCOOH \longrightarrow Ti(OC_2H_5)_2(OOCR)_2 + 2C_2H_5OH$$

$$Ti(OC_2H_5)_2(OOCR)_2 + RCOOH \longrightarrow Ti(OC_2H_5)(OOCR)_3 + C_2H_5OH \text{ etc.}$$

$$O{=}Ti(OOCR)_2 + C_2H_5OOCR$$

In the case of zirconium, for example, the reactions appear to follow the course :

$$Zr(OPr^i)_4 \ Pr^iOH + 3RCOOH \xrightarrow[\text{fast}]{} Zr(OPr^i)(OOCR)_3 + 4Pr^iOH$$

$$Zr(OPr^i)(OOCR)_3 + RCOOH \xrightarrow[\text{slow}]{} Zr(OOCR)_4 \ Pr^iOH$$

$$Zr(OPr^i)(OOCR)_3 + Zr(OOCR)_4 \longrightarrow Zr_2O(OOCR)_6 + RCOOPr$$

The reactions of zirconium isopropoxide with mendelic and salicylic acids also have been investigated by Kapoor and Mehrotra.[82] The reactions of alkoxides of Nb, Ta and V(V) also with fatty acids have been investigated by Kapoor and coworkers.[83]

More recently reactions of alkoxides of nickel[84] and chromium[85] have been investigated with carboxylic acids, yielding derivatives such as $Ni(OR)(OOCR')$, $Ni(OOCR)_2$ and $Cr(OR)_x(OOCR')_{3-x}$ (where $R = CH_3$, C_2H_5 and $R' = C_7H_{15}$, $C_{13}H_{27}$, $C_{15}H_{31}$ and $C_{21}H_{43}$).

Reactions with β-Diketones and β-Ketoesters

The enolic form of a β-diketone or B-ketoester contains a hydroxyl group and these, therefore, react readily with metal alkoxides

$$M(OR)_n + xR'COH_2COR'' \longrightarrow M(OR)_{n-x}(R'COCHCOR'')_2 + xROH$$

$$M(OR)_n + xR'COCH_2COOR'' \rightarrow M(OR)_{n-x}(R'COCHCOOR'')_x + xROH$$

(where M = Al[86], Ca[87], Sn[88], RSn[89], R_2Sn[90], Ti[91], Zr[92], Ta[93], Sb[94], Ln[95], etc.)

A special mention may be made of the facile synthesis of lanthanide *tris*-β-diketonate products by this route, as the hydrated derivatives obtained from aqueous media tend to decompose[96] when attempts are made to strip the last H_2O molecule of addition from these.

Although alkoxides of later transition metals like Cr[97] and Ni[98] do not often undergo alcoholysis reactions with simple alcohols, then reactions with β-diketones yield products with interesting coordination states :

$$Cr(OR)_3 + x\beta\text{-}dkH \xrightarrow{C_6H_6} Cr(OR)_{3-x}(\beta\text{-}dk)_x + xROH$$

$$Ni(OR)_2 + x\beta\text{-}dkH \xrightarrow{C_6H_6} Ni(OR)_{2-x}(\beta\text{-}dk)_x + xROH$$

A brief account of the reactions of metal alkoxides with β-diketones and β-ketoesters was included in the Presidential address[99] of the Indian Chemical Society in 1977.

An interesting aspect of the reactions of tetraisopropoxy-aluminates of various melats like Cu,[38] Cr,[42] Co[44] and Ni[45] with β-diketonates (β-*dk*H) is that the replacement of only terminal isopropoxy groups in derivatives of the type, $M[\mu\text{-}(OPr^i)_2 Al(OPr^i)_2]_2$ leads to volatile and monomeric products like $M[\mu\text{-}(OPr^i)_2 Al(OPr^i)(\beta\text{-}dk)]_2$ and $M[\mu\text{-}OPr^i)_2 Al(\beta\text{-}dk)_2]_2$, whereas further replacement of bridging

isopropoxy by β-diketonate groups led to separation of β-diketonate products of the two metals.

Reactions with β-ketoamines and Schiff Bases

Reactions of β-ketoamines have been studied with alkoxides of boron,[100] aluminium,[101] and lanthanons,[102] these are similar to those with β-diketones except that in the cases of lanthanon isopropoxide, the final product appears to be a *bis*-derivative, $Ln(OPr^i)(OCMeCH{:}CMeNR)_2$. The investigations have been extended to the reactions of a variety of Schiff bases, which also have the characteristic $>C=N-$ group in addition to functional groups like OH, SH and COOH present in the ortho position. With a variety of mono-functional bidentate, bifunctional tridentate and other polydentate Schiff bases, a large number of derivatives with metals (B[100], Al[101,103], Ln[102], Ti[103], Zr[103], Nb[103] and Ta[103]) in novel coordination states have been synthesized. The reactions of Schiff bases have been extended to alkoxides of trialkyltin(IV)[104] and triorganoantimony(V)[105] moieties.

Detailed N-15, C-13 and Sn-119 nmr and other spectroscopic studies[109,107] have been carried out on oxinates of organotin moieties.

Reactions with Alkanolamines

Reactions of alkanolamines, $HOR'NH_2$, dialkanolamines, $(HOR')_2N$ and trialkanolamines, $(HOR')_3N$ with a number of metal alkoxides has heen studied. These reactions can be in general divided into two broad categories, i.e., (*i*) in which only the hydroxy group is reacting and (*ii*) in which the NH_2 or NHR group also shows simultaneous reactivity. For example, the reactions of $Al(OPr^i)_3$ are of the former category and can be represented by the following equations:[108]

$$Al(OPr^i)_3 + nHOCH_2NH_2 \rightarrow Al(OPr^i)_{3-x}(OCH_2CH_2NH_2)_n + nPr^iOH$$

$$Al(OPr^i)_3 + (HOCH_2CH_2)_2NH \rightarrow Al(OPr^i)(OCH_2CH_2)_2NH + 2Pr^iOH$$

$$2Al(OPr^i)_3 + 3(HOCH_2CH_2)_2NH \rightarrow Al_2\{(OCH_2CH_2)_2NH\}_3 + 6Pr^iOH$$

$$Al(OPr^i)_3 + (HOCH_2CH_2)_3N \rightarrow Al\{(OCH_2CH_2)_3N\} + 3Pr^iOH$$

The reactions of alkoxides of boron,[109] gallium,[79] silicon,[110] iron,[111] vanadium,[112] titanium,[113] zirconium,[114] niobium,[115] tantalum[116] and lanthanons[117,118] with ethanolamines resemble those with aluminium in the reactivity of hydroxyl group only.

On the other hand, the amino group also exhibits reactivity in the reactions of alkanolamines and their N-substituted derivatives with alkoxides of germanium,[119] tin and organotin moieties.[120]

Although primary alkoxides of nickel do not undergo alcoholysis reactions with simple alcohols, they do so with alkanolamine[121] in which only the hydroxyl group depicts reactivity.

Reactions with Oximes and Hydroxylamines

The reactions of metal alkoxides with oximes and hydroxylamines have provided a number of unique routes for the synthesis of a variety of interesting

derivatives of boron,[122] aluminium,[123] silicon,[124,125] germanium,[122] tin,[125] titanium,[127] zirconium,[128] antimony,[129] arsenic,[130] niobium[131] and tantalum.[132]

Reactions with Unsaturated Substrates

The insertion reactions which a number of metal alkoxides across the M–O bonds undergo with some unsaturated substrates like isocyanates, isothiocyanates, aldehydes, ketones, ketenes, carbon dioxide, carbon disulphide, sulphur dioxide are of considerable interest both from theoretical points of view as well as their potential applications in synthetic processes. In our laboratories, the insertion reactions of phenyl isocyanate with alkoxides of titanium,[133] zirconium,[134] tantalum, niobium,[135] chromium[136] and nickel[137] have been shown to proceed as illustrated below :

$$Zr(OR)_4 + n\text{PhN}=C=O \rightarrow (RO)_{4-n}Zr(N(Ph)—C(O)—OR)_n$$

A very interesting series of insertion reactions of NO, CO_2, CO etc. with alkoxides of molybdenum and tungsten has been carried by Chisholm and coworkers during the last 6–7 years.[138]

Reactions of Metal Alkoxides with Thiols and Other Sulphur Ligands

Reaction of metal alkoxides with thiols show that whereas alkoxides of metals like aluminium, silicon, titanium and zirconium do not react with thiols, alkoxides of metalloids and metals like germanium,[139] tin,[140] and antimony[141] and their organometallic moieties undergo quite facile interchange reactions :

$$M(OR)_n + nR'SH \rightarrow M(SR')_n = nROH$$

During the last few years, a series of interesting and novel products have been synthesized by the reactions of monothio-β-diketones,[142] dialkyldithiophosphates[143] and alkylene dithiophosphates.[144]

Reactions of Hydogen and chlorides Acyl Halides

Reactions of hydrogen halides with metal alkoides (of say group IV elements) show the same variation[145] as the reactions of the corresponding anhydrous chlorides with alcohols.

Reactions of acetyl chloride and acetyl bromide with alkoxides (primary and secondary) of a number of metals have been shown to follow the following pattern:[146]

$$Zr(OPr^i)_4 . Pr^iOH + nCH_3COX \rightarrow Zr(OPr^i)_{4-n}X_n + n\,CH_3COOPr^i + Pr^iOH$$

The reaction of $Zr(OBu^t)_4$ with acetyl chloride was found to yield a product corresponding to $ZrCl(OBu^t)_3$ in 1 : 1 molar ratio of the reactants, but in the reactions involving more than 1 molar ratio of the acetyl chloride, the product was found to show Cl : Zr ratio of about 1.2–1.3 : 1 only even if excess of chloride was used and an attempt[147] was made to explain this on the basis of steric factors.

However, in a detailed study of the tertiary butoxides of a number of metals, the reactions have been shown[148] to follow the course represented by the equations below :

$$Zr(OBu^t)_4 + CH_3COCl \xrightarrow{\text{slow}} ZrCl(OBu^t)_3 + CH_3COOBu^t$$

$$ZrCl(OBu^t)_3 + xCH_3COCl \longrightarrow ZrCl_{1+x}(OBu^3)_{3-x} + xCH_3COOBu^t$$

$$ZrCl_{1+x}(OBu^t)_{3-x} + xCH_3COOBu^t \longrightarrow ZrCl(OOCCH_3)_x(OBu^t)_{3-x} + xBu^tCl$$

$$ZrCl_4 + 4CH_3COOBu^t \longrightarrow Zr(OOCCH_3)_4 + 4Bu^tCl$$

Asymmetric Reduction of Carbonyl Compounds

sec.—Alkoxyaluminium dichlorides, $ROAlCl_2$ prepared *in situ* by the reaction of $LiAl(OR)_4$ with anhydrous $AlCl_3$ are highly reactive reducing agents for carbonyl compounds.[4,5] The reduction going supposedly through a reversible H-transfer similar to Meerwein–Ponndorf–Verley reaction. Although derivatives of several alcohols having hydrogen at α-carbon atom, e.g., ethanol, isopropanol, phenyl carbinol, 1-phenylethanol, diphenylcarbinol, cyclopentanol, cyclohexanol, fluorenol, norborneol, borneol and isoborneol have been used for the synthesis of active alcohols from prochiral ketones, the one derived from isoborneol has been proved particularly useful for its superior reactivity, high stereselectivity and irreversibility of the reaction.[4] Its optically active form has been successfully used for enantioselective reduction of a variety of prochiral ketones. Thus the reduction of 4-*t*-butylcyclohexanone and norcamphor by isobornyloxyaluminium dichloride[149] gives very largely the less stable *cis*-4-*t*-butylcyclohexanol (90-92 per cent) and *endo*-norborneol (over 97 per cent) respectively. Synthesis of these less stable epimers is very difficult by other reducing agents *see* structure on p. 267.

Alkyl methyl ketones, *R*COMe(*R* = Et, *i*-Pr, *i*-Bu, *t*-Bu and cyclohexyl) are reduced by isobornyloxyaluminium dichloride to yield active alcohols in low optical purity ranging from 2.8 per cent for Me(Et) CHOH to 2.5 per cent for Me(Ph) CHOH. Similarly the various alkylphenyl ketones, PhCO*R*, are reduced to active alcohols in 10–84 per cent optical purity depending upon the size of the alkyl group rising steeply in the order $D < Me < Et < Pr^n < Bu^i < Pr^i >$ cyclohex $> Bu^t$. Phenyl trifluoromethyl ketone is reduced by this reagent to 2,2,2-trifluoro-1-phenylethanol in 8.4 per cent enantiometric excess. However, bornyloxy- and menthyloxy-aluminium dichloride reduce it to PhCH(OH) CF_3 in 68 and 77 per cent enantiomeric excess.

Applications of Metal Alkoxides in other Organic and Organometallic Synthesis

(*i*) *As Substrates for the Syntheses of Compounds having M–C Bonds*—Although Herman and Nelson in 1952, prepared $PhTi(OPr^i)_3$, the first compound having transition-metal-carbon σ-bond by the reaction of $Ti(OPr^i)_4$ and LiPh as given below :

$$Ti(OPr^i)_4\ LiPh \xrightarrow{\text{ether}} PhTi(OPr^i)_3 \cdot LiOPr^i \cdot LiBr \cdot Et_2O$$

$$\downarrow\ \tfrac{1}{4}TiCl_4$$

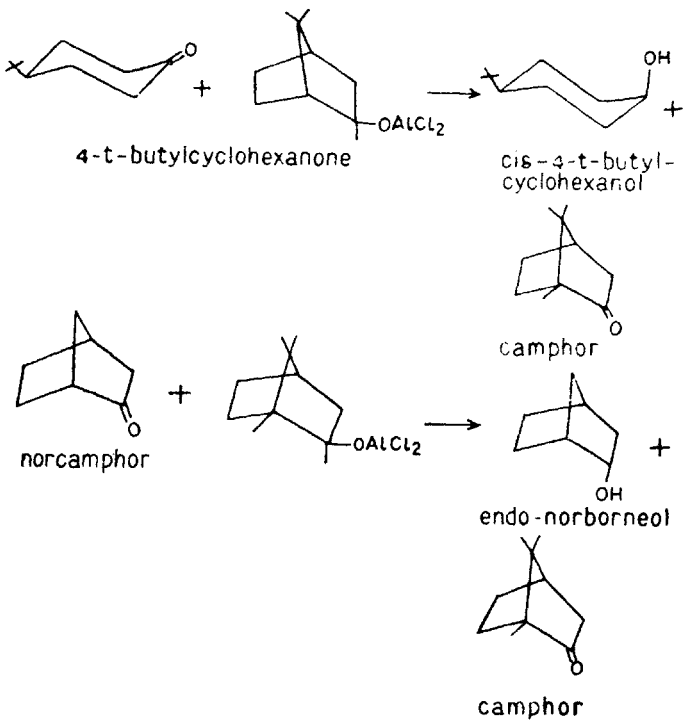
$$PhTi(OPr^i)_3 + \tfrac{1}{4}Ti(OPr^i)_4 + LiCl + LiBr + Et_2O$$

This reaction has not been fully exploited for the synthesis of compounds having metal-carbon bonds. However, in few cases the metal alkoxides have been found to be better substrates than the corresponding metal halides. For examples, the reaction of $LiBu^t$ with $CrlC_3 \cdot 3THF$ gives $CrBu^t_4$ only in 10 per cent yield whereas the reaction with $Cr(OBu^t)_4$ yields $CrBu^t_4$ in 60% yield:[150]

$$Cr(OBu^t)_4 + 4LiBu^t \xrightarrow[n\text{-pentane}]{-78^\circ} CrBu^t_4 + 4LiOBU^t$$

Similarly, the alkylation of $(MoCl^3)_n$ with $LiCH_2SiMe_3$ leads to the dinuclear compound $Mo_2(CH_2SiMe_3)_6$ in not more than 25 per cent yield, alkylation of $Mo_2(OPr^i)_6$ gives the above in 75 per cent yield :[151]

$$Mo_2(OPr^i)_6 + 6LiCH_2SiMe_3 \longrightarrow Mo_2(CH_2SiMe_3)_6 + 6LiOPr^i$$



Recently, the reactions of $(PhO)_4\ M(dmpe)_2$ with LiMe have been carried out to synthesise $Me_4\ M(dmpe)_2$:[152]

$$(PhO)_4 M(dmpe)_2 + 4LiMe \xrightarrow{\text{Toluene}} Me_4M(dmpe)_2 + 4LiOPh$$

(M = Th and U)

In contrast to chromium, molybdenum and thorium, the alkylation of alkoxides of niobium and tantalum generally leads to the trialkylated derivatives except for the reaction of $Ta(OMe)_5$

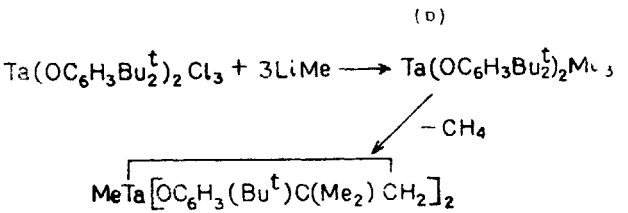
$$M(OR)_5 + 3LiR' \longrightarrow M(OR)_2 R'_3 + 3LiOR$$

(where M = Nb and Ta, R = Me, OPr^i, $OC_6H_3Me_2$-2,6, $OC_6H_3Bu^t_2$-2, 6; R' = Me, CH_2SiMe_3 and CH_2CMe_3) with $LiCH_2SiMe_3$ which resulted in the formation of tetrasubstituted product:

$$Ta(OMe)_5 + 4LiCH_2SiMe_3 \longrightarrow Ta(OMe)(CH_2SiMe_3)_4 + LiOMe$$

Cyclometallation of 2,6-Di-Tert-Butyloxide

Although numerous examples of cyclometallation reactions involving low valent group of later transition metals (d^5-d^8) with N and P containing ligands are known Rothwell *et al.*[151] have recently reported the cyclotantalation of 2,6-di-tert-butylphenoxide :



Carbonylation of Organic Halides

Benzylic bromides react with CO and borate esters under mild conditions (75° and 1 atm.) in the presence of 1,5-hexadienerhodium(I) chloride catalyst to afford esters in excellent yield :

$$3ArCH_2Br + B(OR')_3\ 3CO \longrightarrow 3ArCH_2COOR' + BBr_3$$

The reactions proceed smoothly for various benzylic bromides and is applicable to different borates including tert-butyl borate, thereby providing an entry to *tert.* as well as primary and secondary esters. However, for carbonylation of less reactive non-benzylic, aromatic, alkyl and vinyl bromides with borate esters, a bimetallic catalyst system of 1,5-hexadienerhodium(I) chloride dimer and tetrakis-(triphenylphosphine) palladium (O) is required and esters are formed in good yields. Aluminium ethoxide, isopropoxide and sec-butoxide (but not tert-butoxide) also react similarly with carbon monoxide and benzylic and non-benzylic bromides in the presence of mono-metallic and bimetallic catalyst systems respectively yielding esters in high yields. However, in contrast to the borate esters, aluminium alkoxides do

not react with CO and alkylbromides even in the presence of bimetallic catalyst systems.[153] Titanium and zirconium alkoxides[7] react with CO and benzylic bromides under mild conditions in the presence of [(1,5-hexadiene) $RhCl]_2$ to form esters in good yields:

$$ArCH_2Br + 4CO + M(OR)_5 \longrightarrow 4ArCH_2COOR + MX_4$$

Alkoxide Chemistry of Platinum Group Metals

As discussed in a recent review article[154] from our laboratories, the alkoxychemistry of platinum group metals has received only scant attention so far but a vigorous interest is now developing in view of their potential in catalytic process. (COD) $Ir(OMe)_2$ has been used[155] as a catalyst for the carbonylation of methanol to acetic acid ($CH_3OH + CO \longrightarrow CH_3COOH$).[(COD) $Rh(OMe)]_2$ in the presence of some Schiff bases catalyzes[156] the hydrogen transfer from isopropanol to cyclohexane or acetophenone.

Reactions of alkoxy derivatives of platinum group metals are beginning to receive greater attention. For example, [(COD) $Rh(OMe)]_2$ has been shown to undergo facile replacement with other alcohols, β-diketones[157] and O,O-dialkyl/alkylene dithiophoric acids[158] to yield products of the types, (COD) $Rh(OR)_2$; (COD) Rh(β-dik) and [(COD) $Rh(S_2P(OR)_2)$]. Similarly, [(COD-OMe)]$_2$ $Pt(OMe)_2$ has been shown[159] to undergo alcoholysis reactions with alcohols and enolic form on β-diketones.

An interesting study[160] of the synthesis and reactivity of (dppe)$Pt(OMe)_2$ {dppe = 1,2-*bis*-(diphenylphosphino) ethane} has shown that whereas the above methoxy derivative is unstable, it undergoes a facile insertion reaction with CO to give a stable carboxylate product :

$$(dppe)Pt(OCH_3)_2 + 2CO \longrightarrow (dppe)Pt(OOCCH_3)_2$$

Such reactions are opening up new dimensions in the alkoxy chemistry of platinum group metals, which are being pursued actively in our laboratories.

Hydrolysis Reactions

Alkoxy (simple as well as bimetallic) derivatives of elements are extremely susceptible to hydrolysis and hence, stringent precautions have to be taken to exclude moisture from any source including atmosphere in the synthesis and handling of alkoxy derivatives of metals.

Systematic studies[1] on hydrolysis of various metals was undertaken by Bradley and coworkers[161] and these studies were later extended to silyloxides also. The formation of a number of intermediate products with interesting structural models has postulated to account for changes in the observed molecular weights of metal alkoxides when treated in suitable solvents with controlled quantities of water.

Hydrolysis of a number of metal alkoxides has been used for the preparation of oxides (i.e., TiO_2) with controlled grain size etc. for the purpose of making paints

and for other uses. In view of the easy purification of metal alkoxides and many bimetallic alkoxides, these are now being extensively employed for the preparation of pure oxides or mixed oxides in a desired molar ratio. Controlled hydrolysis of bi-metallic alkoxides could lead to a certain degree of ordered structure which has the potential of their wide applicability as high technology oxides for electronic industry and ceramics etc. Although considerable work is being carried out in a number of laboratories around the world, results are not revealed yet in view of wide-reaching technological applications.

Finally, an interesting, unique and unexpected feature of some alkoxy derivatives of platinum group metals has been observed that not only these are resitant to hydrolysis, but some of these can be synthesised in alkaline aqueous/alcoholic media. The reasons for this special behaviour of platinum metals-alkoxy linkage deserve more penetrating physico-chemical studies.

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