Journal of Organometallic Chemistry, 239 (1982) 159—187
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Review

METAL PHENOXIDES *

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(Received in India November 23rd, 1981; in Amsterdam May 25th, 1982)

Contents

I. Introduction

The contributions of R.C. Mehrotra and his students to the field of metal alkoxides are seminal. They have been collected in his recent and comprehensive monograph co-authored by his close friends and colleagues, D.C. Bradley

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* Dedicated to Prof. R.C. Mehrotra on the occasion of his sixtieth birthday (February 16th, 1982).

0022-328X/82/0000—0000/$07.25

and D.P. Gaur [1]. Prior to 1950 the alkoxides of only about a dozen elements were known but since then the field has expanded rapidly, especially in the laboratories of W. Wardlaw, D.C. Bradley and R.C. Mehrotra. The chemistry of most of the metallic and metalloidal elements has been studied and more recently modern physicochemical and spectroscopic methods have increasingly been applied to elucidate the constitution of these reactive and often intractable compounds. In particular the technique of single crystal X-ray analysis is beginning to throw light on the structural principles which underlie the formation of polymeric alkoxides.

Although there are well over one thousand original references to metal alkoxides in the literature, much less attention has been directed towards the chemistry of the closely related metal derivatives of phenol. The substitution of alkyl by the phenyl group introduces new electronic and steric influences which are worthy of examination and might well modify catalytic properties which are important in many industrial applications of these compounds.

In this article a brief account of the synthesis, chemical reactions, physical properties, structures and industrial uses of metal phenoxides is presented.

A. Industrial uses

The patent literature abounds with examples of the application of metal phenoxides to improve the performance of industrial products and processes. The principal uses can be categorized for convenience as antioxidant, catalytic, surfactant or biological.

The phenoxides of alkali, alkaline earth, aluminium and zinc are used as antioxidants to stabilize mineral lubricating oils and inhibit their decomposition, especially at the high temperatures and pressures experienced in diesel and other engines. Cobalt(II) and tin(II) phenoxides are also used to inhibit oxidative deterioration of mineral lubricating oils. For example, it is claimed that the addition of 0.5—2.0% of a mixture of Mg and Zn phenoxides yields a much improved lubricating oil for internal combustion engines that ensures engine cleanliness under extreme operating conditions. For fuels of high lead content, the salts of hydroxy aromatic metallic sulphides are recommended for the stabilization of Et_4Pb in gasoline. The metal phenoxides also have the benefit of reducing the corrosive action of detergents when these are added to lubricating oils.

The antioxidant property of metal phenoxides leads to their use as inhibitors in varnishes, lacquers and paints. Thus alkaline earth phenoxides are employed as vinyl resin stabilizers and cellulose ester plastics incorporate copper(II) phenoxide to protect them against weathering arising from degradation due to UV light. Metal phenoxides are effective antioxidants in drying oils and the phenoxides of Cu, Co, Fe, Al, Pb, Ba and Zn have all been employed for this purpose.

The metal phenoxides are used as alkylation and polymerization catalysts with the most notable example being the class of phenol/aldehyde synthetic resins. For example, magnesium phenoxide is employed for cold moulding of phenolic resins.

The surfactant properties of metal phenoxides have been exploited as additives to reduce foaming of engine oils. Aluminium phenoxide has been incorporated in surface coatings and is reported to stimulate the gelation of vegetable drying oils.

Use is made of metal phenoxides as disinfectants, insecticides and fungicides. Alkylated lead phenoxide and copper phenoxide are especially effective fungicides. Sodium polychlorophenoxide is used as a germicide and as an insecticide in the treatment of wood. Sodium phenoxide is reported to rapidly penetrate tooth tissue without destroying tissue proteins and thereby prevent microbial growth.

A variety of other miscellaneous uses for metal phenoxides has been reported. They are used for generating coloured smoke signals in the aerospace industry, as corrosion inhibitors for aluminium-coated ferrous metals, as additives for primer coatings in the paint industry, as antioxidants for gas welding, and as agents for preventing the fermentation of starch. Tanning leather with phenoxides imparts good flexibility and a soft touch to the leather. The reception of dyestuffs by polyolefins is improved by blending the polymer fibre with zinc phenoxide. Metal phenoxides are used as antistatic agents. Alkali metal phenoxides are used as antifouling agents for fish nets and fibre-reinforced plastics.

Phenylorthosilicates are used as heat transfer fluids and hydraulic fluids. A non-crystalising and thermally stable heat transfer fluid is made by heating a mixture containing 80% tetraphenyl orthosilicate and 20% tetraxylyl orthosilicate at 400—500° F.

II. Synthesis

A variety of synthetic pathways has been devised for the preparation of metal phenoxides. The most direct methods involve reaction of substituted or unsubstituted phenols with either the metal or its binary compounds such as hydroxides or halides. Exchange reactions between phenols and metal alkoxides or esters have also been used widely for the synthesis of phenoxides.

A. Reaction of metal with phenol

The reaction between a metal and phenol is the simplest method for preparing metal phenoxides. The rate of the reaction increases both with the acidic character of the substituted phenol and the electropositive character of the metal. This method is confined to the more electropositive elements such as the alkali metals, beryllium, magnesium, aluminium, etc.

Alkali metals react either directly with phenols at room temperature or in the presence of an inert solvent to form phenoxides with the evolution of hydrogen. Magnesium reacts with phenol at its boiling point to form a basic phenolate [2]. Mechanically activated aluminium reacts with phenol at the boiling point of benzene to form white crystalline $Al(OPh)_3$. The reaction will not take place unless the oxide film is removed either mechanically or chemically [3]. The end-product is always impure because of the reaction,

$$Al(OPh)_3 + H_2O \rightarrow Al(OPh)_2(OH) + PhOH$$

High-molecular weight alkyl phenols react with aluminium [4] in the presence of mercury as a catalyst at 300—400° C to form $Al(OPh)_3$. Silicon does not react with phenol at ordinary temperature. However, in the presence of freshly reduced copper at 300—330° C, it reacts to form a crude product from which $Si(OPh)_4$ can be vacuum distilled [5]. Yttrium metal shavings react with phenol at its boiling point in the presence of a trace of $HgCl_2$ to form $Y(OPh)_3$. The crude product can be crystallised [6] from hot cyclohexane as $Y(OPh)_3 \cdot C_6H_{12}$.

B. Reaction of metal hydroxide with phenol

Alkali metal phenoxides may also be prepared by the reaction of a metal hydroxide with phenol.

$$MOH + PhOH \rightarrow MOPh + H_2O$$

LiOPh is obtained by treating an aqueous solution of LiOH with aq. phenol [7]. After heating to 80° C for two hours, $LiOPh \cdot 2H_2O$ crystallizes on cooling to 10—15° C. RbOPh, CsOPh and TlOPh are prepared by heating a mixture of MOH and phenol in absolute ethanol. Phenoxides of composition $MOPh \cdot 2H_2O$ are precipitated from solution by adding Et_2O and are dehydrated over P_2O_5 in a vacuum desiccator [8]. High purity KOPh can be obtained [9] by heating a solution of PhOH and KOH in ethanol for sixty minutes at 70—110° C, when crystals of KOPh separate out which may be washed with acetone and vacuum dried.

Mortimer and his coworkers [10] have suggested that phenoxides of alkali metals ionize in water but it has also been reported that they are hydrolysed [11].

$$OPh^- + H_2O \rightleftharpoons PhOH + OH^-$$

Alkali phenoxides are soluble in fused phenol and have a tendency to form ion pairs [12]. They behave as a strong base of the phenol solvo system and react with solvo acids to form acidic and neutral salts [13].

C. Reaction of metal halides with phenol

For the polyvalent metals, the above methods are inapplicable and their phenoxides may be obtained from metal halides (usually the chlorides). In general, metal halides undergo solvolysis with phenol and substituted phenols. In some cases, unlike the alcohols [14,16], there is complete replacement of the chloride while in others there is partial replacement. This is due to the stronger acidic character of phenols compared with alcohols.

In order to avoid decomposition of the product, an inert solvent such as benzene, carbon tetrachloride, xylene or carbon disulphide is generally used under reflux. The reaction is complete when evolution of hydrogen halide has ceased.

$$MX_n + mPhOH \rightarrow M(OPh)_m X_{n-m} + mHX$$

$Be(OPh)_2$ is obtained by reacting anhydrous beryllium chloride and molten phenol [17]. $Al(OPh)_3$ [3] and $Ti(OPh)_4 \cdot PhOH$ [18,19] are similarly obtained. Titanium tetrachloride reacts with excess of pentafluorophenol at 25° C to yield reddish brown $Ti(C_6F_5O)_4$ but when titanium tetrachloride is in excess, a red-brown compound of composition $Ti(OC_6F_5)_2Cl_2$ is obtained [20],

$TiCl_4 + 4C_6F_5OH \rightarrow Ti(OC_6F_5)_4 + 4HCl$

$TiCl_4 + 2C_6F_5OH \rightarrow Ti(OC_6F_5)_2Cl_2 + 2HCl$

Antimony(III) phenoxide [21] and tungsten(VI) phenoxides [22] are also obtained by this method; excess phenol is removed by leaching with CCl_4.

Funk and his coworkers [22] prepared phenoxides of niobium(V), tantalum(V), molybdenum(V) and tungsten (VI) of composition $Nb(OPh)_5$, $Ta(OPh)_5$, $W(OPh)_6$, $W(OPh)_4Cl_2$, $Mo(OPh)_3Cl_2$ [23] by heating metal chlorides with an excess of phenol in inert organic solvents. In the case of WCl_6, when benzene or xylene is used as a solvent, $W(OPh)_6$ is formed but when CCl_4 is used, $W(OPh)_4Cl_2$ is obtained [24]. Tungsten pentabromide when refluxed with the appropriate amount of phenol in benzene yields $W(OPh)_2Br_3$ but when CCl_4 or CS_2 is used as solvent, $W(OPh)_3Br_2 \cdot PhOH$ is obtained [25]. Tungsten pentaphenoxide could not be obtained by refluxing tungsten pentahalide with phenol in benzene or carbon tetrachloride.

$WBr_5 + 4PhOH \rightarrow W(OPh)_3Br_2 \cdot PhOH + 3HBr$

$WOCl_4$ with phenol or nitrophenol in CS_2 yields [26] $WO(OPh)_4$. Molybdenum pentachloride reacts with phenol and chlorophenol in CCl_4 to yield phenoxides of composition $Mo(OPh)_3Cl_2$ while *p*-chlorophenol or *p*-bromophenol yield phenoxides of composition $Mo(o\text{-},p\text{-}C_6H_4X)_2Cl_3$. $M(OPh)_nBr_{5-n}$ (M = Nb, Ta) have been prepared [27] by the stepwise phenolysis of MBr_5 in CCl_4.

Both vanadium(III) chloride and vanadium(IV) chloride react with phenol in CCl_4 to form a dark-coloured oily product which could not be characterised. However, *o*-nitro- and *o*-chloro-phenols yield phenoxides of composition $V(OC_6H_4NO_2)_3$, $V(OC_6H_4NO_2)Cl_2$ and $V(OC_6H_4Cl)_2Cl_2$, respectively [28]. Funk and his coworkers [28,29] found that $VOCl_3$ reacted with phenol in CCl_4 to form $VO(OPh)_2Cl$ while $o\text{-},p\text{-}ClC_6H_4OH$ yield the fully substituted product $VO(o\text{-},p\text{-}ClC_6H_4O)_3$.

$VOCl_3 + 2PhOH \rightarrow VO(OPh)_2Cl + 2HCl$

$VOCl_3 + 3\,o\text{-},p\text{-}ClC_6H_4OH \rightarrow VO(o\text{-},p\text{-}ClC_6H_4O)_3 + 3HCl$

Substitution reactions of metal halides with phenols go to completion in the presence of strong bases such as ammonia or amines. The liberated hydrogen chloride is removed as insoluble ammonium chloride and fully substituted phenoxides are obtained.

$TiCl_4 + 4PhOH + 4NH_3 \rightarrow Ti(OPh)_4 + 4NH_4Cl$

A number of phenoxides such as $Ti(OPh)_4$, $Ti(ClC_6H_4O)_4$, $Ti(NO_2C_6H_4O)_4$ [31,33], $Ge(OPh)_4$ [34], $Si(OPh)_4$ [35], $Sc(OPh)_2(OH)$, $Sc(o\text{-},p\text{-}ClC_6H_4O)_3$ [36], $VO(OPh)_3$ [29], $Mo(p\text{-}ClC_6H_4O)_5$, $Mo(NO_2C_6H_4O)_5$, $WO(OPh)_4$ [37] and $Fe(OPh)_3$ [38] have been obtained by this technique. Funk and Andrae [39] obtained intensely coloured monomeric compounds of composition $U(OR)_4 \cdot nNH_3$ where R = Ph, $o\text{-}ClC_6H_4$, $o\text{-}NO_2C_6H_4$ and $n = 1, 2$ by a quantitative reaction of the corresponding phenol and ammonia with a suspension of uranium tetrachloride in tetrahydrofuran. Phenoxides of composition $U(OPh)_4$ are obtained when tetrahydrofuran is replaced by benzene. Phenoxides of composition $UO(OPh)_2 \cdot 4PhOH \cdot NH_3$ where Ph is either C_6H_5 or p-ClC_6H_4 are obtained when $UOCl_2$ is reacted with excess of the phenol and ammonia in benzene.

It is of interest to note that the "ammonia method" is successful for the preparation of $Sc(ClC_6H_4O)_3$ and $Sc(NO_2C_6H_4O)_3$, whereas in the case of unsubstituted phenol, a phenoxide of composition $Sc(OPh)_2(OH)$ is obtained [36].

Funk and his coworkers [25] have reported that tungsten pentaphenoxide could not be prepared either by the action of WCl_5 and phenol, either fused or in an inert solvent, chlorophenoxides being obtained. However, $W(OPh)_5$ can be prepared conveniently by the reduction of $W(OPh)_6$ with hydrogen using Raney nickel as a catalyst.

$$W(OPh)_6 + [H] \rightarrow W(OPh)_5 + C_6H_5OH$$

D. Exchange reactions of metal alkoxides

A characteristic property of metal alkoxides is their ability to exchange an alkoxide group with alcohols as well as with phenols. This property has been utilised extensively for preparing new alkoxides [40,43] and phenoxides of thallium [44], silicon [45,46], germanium [34], titanium [47], samarium [48], praseodymium and neodymium [49], and gadolinium and erbium [50].

$$M(OR)_x + nPhOH \rightleftharpoons M(OR)_{x-n}(OPh)_n + nROH$$

Alcohols so liberated have a lower boiling point than phenol; the equilibrium represented by the above equation is easily shifted towards the right by fractional distillation. When necessary, the reaction may be carried out with the predetermined stoichiometric amounts of phenol, using benzene or other solvents. In the case of benzene, the alcohol so formed can be removed by azeotropic distillation.

The importance of this method is illustrated by the preparation of Tl(OPh) [44] as thallium does not react with phenol at room or elevated temperatures. It is prepared from thallium ethoxide which in turn is best prepared by exposing chips of thallium to absolute alcohol vapour in the presence of air or oxygen.

$$2Tl + 2EtOH + [O] \rightarrow 2TlOEt + H_2O$$

Tl(OPh) is obtained as a white microcrystalline compound when equimolar amounts of the two reactants are mixed in cold dry ether.

$$TlOEt + PhOH \rightarrow TlOPh + EtOH$$

The reaction goes to immediate completion as TlOPh is insoluble in ether. Rodziewiez and his coworkers [45] and Smith [46] have used the exchange method for the preparation of a number of ethylphenyl esters of orthosilicic acid

$$Si(OEt)_4 + nPhOH \rightarrow Si(OEt)_{4-n}(OPh)_n + nEtOH$$

By using an inert medium such as benzene, it has been possible to remove ethyl alcohol azeotropically. Thus ethylphenyl esters of orthosilicic acid of composition $Si(OPh)_3(OEt)$, b.p. 360—365°C, $Si(OPh)_2(OEt)_2$, b.p. 302—304°C and $Si(OPh)(OEt)_3$, b.p. 236—238°C, have been isolated by mixing the two components in stoichiometric molar ratios.

Aluminium phenoxide [51] and titanium(IV) phenoxides [52] have been prepared by reacting phenol with t-butoxides of these metals in benzene:

$$Al(OBu^t)_3 + 3PhOH \rightarrow Al(OPh)_3 + 3Bu^tOH$$

$$Ti(OBu^t)_4 + 4PhOH \rightarrow Ti(OPh)_4 + 4Bu^tOH$$

Apart from fully substituted products, intermediate alkoxy-phenoxy derivatives of composition $Ti(OPh)_2(OBu^t)_2$, $Al(OPh)(OBu^t)_2$ and $Al(OPh)_2(OBu^t)$ have also been isolated. Mehrotra and his coworkers have prepared $Ti(OPh)_4$ [47] and $Ge(OPh)_4$ [34] by the action of phenol on their ethoxides or isopropoxides in predetermined stoichiometric ratios in benzene. Mixed isopropoxide phenoxides have been isolated in quantitative yields. It has been observed that the replacement of the last alkoxy group by the phenoxy group is quite slow, possibly because of the back reaction between titanium phenoxide and ethanol or isopropanol or because of steric hindrance [47]. Zirconium phenoxide of composition $Zr(OPh)_4 \cdot PhOH$ is similarly obtained [53]. $VO(OPh)_3$ can be obtained by the phenol interchange method [54].

$$VO(OEt)_3 + 3PhOH \rightarrow VO(OPh)_3 + 3EtOH$$

$Y(OPh)_3$, $Sm(OPh)_3$, $Sm(OPh)(OPr^i)_2$ and $Sm(OPh)_2(OPr^i)$ are synthesised using the same technique. Mehrotra and his coworkers [49,50] have used this method profitably for the preparation of alkoxy-phenoxy and phenoxy derivatives of the lanthanides,

$$Ln(OPr^i)_3 + mPhOH \rightarrow Ln(OPh)_m(OPr^i)_{3-m} + mPr^iOH$$

where $m = 1,2,3$ and Ln = Pr, Nd, Gd and Er.

In an attempt to prepare $U(OPh)_5$ by the alcohol—phenol interchange method, Bagnall et al. [55] obtained $U(OPh)_4(OEt)$ when excess phenol was refluxed with $U(OEt)_5$ for 9 hours. When refluxed for shorter periods a mixture of $U(OPh)_4(OEt)$ and $U(OPh)_3(OEt)_2$ was obtained. Addition of solid $CsUCl_6$ to a suspension of NaOPh in benzene under reflux resulted in a mixture which, on extraction with *N,N*-dimethylformamide followed by vacuum evaporation, left a brown paste of composition $U(OPh)_4Cl \cdot 2DMF$. Vacuum evaporation of the original red supernatant liquid yielded a brown pasty solid of composition $Na[U(OPh)_6]$.

Another interesting route for converting one alkoxide into phenoxide or another alkoxide is transesterification in cyclohexane employed by Mehrotra and his coworkers [56].

$$M(OR)_n + nCH_3COOPh \rightarrow M(OPh)_n + nCH_3COOR$$

The alkoxide usually employed is either the isopropoxide or tert-butoxide as the separation of isopropyl- and tert-butyl-acetate is more readily achieved by azeotropic distillation. Moreover, it is claimed that transesterification appears to be less prone to steric limitations than do alcohol interchange methods. Phenoxides of niobium [57] and tantalum [58] have been prepared by this method.

$Nb(OPr^i)_5 + 5CH_3COOPh \rightarrow Nb(OPh)_5 + 5CH_3COOPr^i$

E. Reaction of metal alkyls, aryls and carbonyls with phenol

The reaction of metal alkyls with phenol provides another convenient pathway for the preparation of phenoxides,

$R_2M + R'OH \rightarrow RMOR' + RH$

where R = Me, Et, Pr and $R'OH = C_6H_5OH, CH_3C_6H_4OH, ClC_6H_4OH, NO_2C_6H_4$-OH. Compounds resulting from the displacement of only one alkyl group are generally crystalline and soluble in organic solvents and those arising from the loss of both alkyl groups tend to be insoluble and presumably polymeric in nature. Coates and Ridley [59] have prepared alkylzinc phenoxide by reacting alkylzinc with phenol in the appropriate ratio in an inert solvent at —70° C. Formation of the disubstituted product does not take place as the equilibrium

$Zn(OPh)_2 + ZnR_2 \rightleftharpoons 2RZnOPh$

lies to the right hand side. Funk and his coworkers [60] have prepared phenoxides of beryllium of composition $RBe(XC_6H_4O)$ where X = H, Cl, Me, NO_2 by reacting dialkylberyllium with XC_6H_4OH. There is spontaneous evolution of alkanes. From the controlled conditions of the experiment it is evident that the first alkyl group is substituted below —80° C while the substitution of the second group begins at —55° C to —30° C, after which beryllium phenoxide is precipitated.

In order to prepare monomeric beryllium phenoxide with a coordination number of 2, Coates and Anderson [61] reacted highly hindered 2,6-di-t-butyl phenol with diethyl beryllium ether complex in ether at —78° C. It has a linear O—Be—O coordination. Puddaphatt and his coworkers [62] prepared dimethyllead diphenoxide by reacting a benzene solution of phenol with a benzene solution of dimethylbisisopropyl lead. The product $Me_2Pb(OPh)_2$ was precipitated immediately. Koton [63] obtained ethylmercury phenoxide by heating diethylmercury with phenol in a sealed tube. It is claimed by Koton and his coworkers [64] that Ph_4Sn, Ph_4Pb or Ph_3Bi when heated with various phenols, lose C_6H_6 with the corresponding phenolates being formed.

$H_2O + Ph_3Bi + p\text{-}NO_2C_6H_4OH \rightarrow BiO(OC_6H_4NO_2) + 3PhH$

Dialkyl(diaryl)tin oxide reacts with phenol to yield initially tetraalkyl(aryl) distannoxane which disproportionates to yield the final product diphenoxide.

$2R_2SnO + 2PhOH \rightarrow (PhO)R_2Sn\text{—}O\text{—}SnR_2(OPh) + H_2O \rightarrow R_2Sn(OPh)_2 + R_2SnO$

If the reaction is carried out at 80° C in benzene, the reaction stops at the intermediate stage. But if the reaction is carried out at 207° C in tetrahydronaphthalene, then dialkyl(diaryl)tin diphenoxide is the product [78].

When bistrialkyl(triaryl)tin oxide is heated with diphenyl carbonate, triphenyltin phenoxide is obtained.

$(Ph_3Sn)_2O + PhOCOOPh \rightarrow Ph_3SnOPh + Ph_3SnOCOOPh \rightarrow 2Ph_3SnOPh + CO_2$

Copper(I) phenoxide is prepared by the action of phenylcopper(I) with phenol [65].

$PhCu + PhOH \rightarrow CuOPh + PhH$

Phenylcopper(I) in turn is obtained by the action of phenyllithium and copper(I) chloride.

Phenoxides of cobalt(II) and nickel(II) have been prepared by the action of cyclopentadienylcobalt(nickel), butadiene and phenol in toluene at —40° C. When the reaction temperature was slowly raised and kept at 110° C for 8 hours, the metal phenoxides separated out [68].

$(\pi\text{-}C_5H_5)_2Co + 2PhOH \rightarrow Co(OPh)_2 + 2C_5H_6$

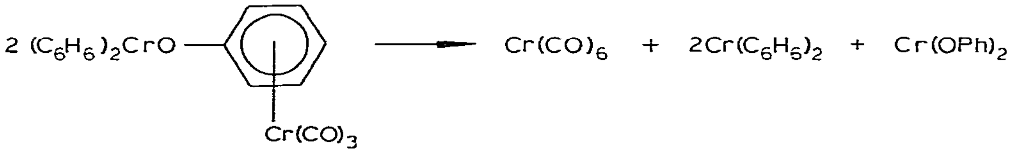
Cobalt phenoxide [69] is also prepared by the action of phenol with $MeCoL_4$ ($L = Me_3P$) obtained by the reduction of cobalt chloride by sodium amalgam in the presence of Me_3P.

Zerovalent nickel complexes such as bis(1,5-cycloctadienenickel) in the presence of tertiary phosphines, cleave C—O bonds in phenol carboxylates to form nickel carbonyl, nickel phenoxides and other gaseous and liquid products [70].

Chromium(III) phenoxide has been obtained by irradiating benzene-tricarbonylchromium solution in pentane in the presence of phenol under dry nitrogen [72].

$$3PhOH + Cr(CO)_3C_6H_6 \xrightarrow{h\nu} Cr(OPh)_3 + C_6H_6 + 3CO + 1\tfrac{1}{2}H_2$$

Chromium(II) phenoxide is obtained by thermolysis [73] of tricarbonylchromium phenoxydibenzenechromium(I).



Chromium(II) phenoxide is also obtained by the thermal decomposition of bis-arenechromium phenolate. Bis-arenechromium is oxidised by phenol at 200° C with the loss of hydrogen and the destruction of the sandwich structure [74].

F. Miscellaneous methods

A convenient and simple method for the preparation of phenoxides of some of the transition metals such as cobalt, nickel, zinc and cadmium involves distillation of their anhydrous acetates with a large excess of phenol. The carboxylic acid distills over and the precipitated phenoxide can be separated from excess phenol by the addition of anhydrous benzene. In the case of nickel and zinc, where the acetates are insoluble in phenol, propionate salts have been used. Cadmium phenoxide prepared by this method decomposes into a gummy mass on standing. Attempts to prepare phenoxides of magnesium, manganese, or thorium by the method have failed.

Vanadium pentoxide when heated with phenol yields a black solid of composition $VO(OPh)_3$. Heating is required to remove water formed during the course of the reaction [76].

$V_2O_5 + 6PhOH \rightarrow 2VO(OPh)_3 + 3H_2O$

But when gaseous phenol is passed over V_2O_5, no phenoxides are formed but oxidation of the ring takes place. Magnesium phenoxide is obtained commercially by heating magnesium oxide with phenol [2]. Lead phenoxide is commercially prepared by heating PbO and phenol in toluene, the water formed being removed by azeotropic distillation [77].

Aluminium phenoxide is used as a catalyst in various organic reactions and its efficiency is dependent upon its purity. It is claimed that aluminium phenoxide prepared by the action of aluminium metal or aluminium halide with phenol is always contaminated with decomposition products because the reactants are heated to high temperature. The phenolysis of aluminium sulphide is a simple and convenient method for the preparation of pure $Al(OPh)_3$: e.g., Al_2S_3 is mixed with freshly distilled phenol in excess of xylene and the mixture is heated to 95°C for 90 minutes. The reaction is complete when evolution of H_2S ceases [3].

$Al_2S_3 + 6PhOH \rightarrow 2Al(OPh)_3 + 3H_2S$

Phenoxides of titanium [79] and silicon [80] have also been prepared by a similar method.

$SiS_2 + 4PhOH \rightarrow Si(OPh)_4 + 2H_2S$

$TiS_2 + 4PhOH \rightarrow Ti(OPh)_4 + 2H_2S$

In case of $Si(OPh)_4$, this method is used commercially. The reaction goes to completion with excess phenol but when the amount is less than the stoichiometric ratio, phenyl silicates containing sulphur are formed.

$mSiS_2 + (m+1)Si(OPh)_4 \rightarrow (OPh)_3SiS[(OPh)_2SiS]_{2m-1}Si(OPh)_3$

Phenoxides of aluminium and silicon have been prepared by the action of aromatic ethers and metal chlorides. Piekos and his coworkers [3] have prepared $Al(OPh)_3$ by heating $AlCl_3$ and excess of freshly distilled anisol at 70—80°C for 50 hours when crystalline $Al(OPh)_3$ separated out. The product contained some $AlCl_3$ as impurity.

$AlCl_3 + 3PhOMe \rightarrow Al(OPh)_3 + 3MeCl$

Schwarz and his coworkers [82] studied the reaction of ether cleavage in $SiCl_4$ in more detail. Aromatic ethers are not attacked by $SiCl_4$ even at 300°C. Alkyl aryl ethers when heated with $SiCl_4$ at 250°C yield RCl and $Si(OPh)_4$,

$SiCl_4 + 4PhOR \rightarrow Si(OPh)_4 + 4RCl$

where $R = CH_3, C_2H_5$.

When higher alkyl aryl ethers are used, the alkyl group migrates into the ring. A similar reaction with aliphatic ethers gives $ROSiCl_3$ and RCl. The aliphatic isoethers under similar conditions are dehydrated with the formation of unsaturated hydrocarbons and RCl. Ikuko and his coworkers [83] have utilised the formation of metal chloroalkoxides, formed by the reaction of $TiCl_4$ and $ZrCl_4$ and cyclic ethers such as ethylene oxide, propylene oxide, etc., for the preparation of metal phenoxides, since phenols readily react with these intermediates to form phenoxides such as $Ti(OPh)_4$ or $Zr(OPh)_4$.

Phenolysis of silylamido adducts of manganese(II) with 2,6-di-t-butylphenol [81] yields the phenoxide,

$$Mn[N(SiMe_3)_2]L_n + DTBP \rightarrow Mn(DTBP)_2 + 2HN(SiMe_3)_2 + nL$$

where L = THF, pyridine, etc. and $n = 0, 1$ and 2.

Copper(II) phenoxides with unsubstituted phenoxide groups have not been prepared to date as they would be unstable towards reductive elimination, forming the phenoxy radical which might polymerise to yield phenylene ethers, etc. However Calderazzo and his coworkers [66] have been able to isolate coordinated diphenoxo derivatives of copper(II) by the following reactions.

$$CuCl_2(bipy) + 2NaOPh \xrightarrow{THF} Cu(OPh)_2(bipy) + 2NaCl$$

$$CuCl_2(en) + 2NaOPh\cdot PhOH \xrightarrow{THF} Cu(OPh)_2(en)\cdot PhOH + 2NaCl + PhOH$$

A series of bis(aryloxo)iron(II) complexes with 2,2-bipyridyl of composition $Fe(OC_6H_4X)_2(bipy)_n$ have been prepared [67] by the reaction of diethylbis-(2,2′-bipyridyl)iron(II) with the corresponding *p*-substituted phenols in tetrahydrofuran,

$$Fe(Et)_2(bipy)_2 + 2XC_6H_4OH \rightarrow Fe(OC_6H_4X)_2(bipy)_n + 2C_2H_6$$

where $n = 1$ when X = H, CH_3, Cl, CN and $n = 2$ when X = NO_2, CN.

Electrochemical synthesis of organic metal compounds has been used to prepare $Ni(OEt)_2$ and $Ni(OPh)_2$ [71]. The metal undergoes an electrochemical reaction with H-acidic alcohol or phenol. Nickel is used as the electrode and the electrolyte consists of a 4 per cent mixture of $LiClO_4$/LiCl and pure phenol which is electrolysed at 500 mA and 10 volt for 22 hours.

III. Structure

Relatively few single crystal X-ray structure determinations have been reported for alkoxides and phenoxides of the metallic elements. Generally, compounds of this type are sensitive to moisture and hydrolyse readily yielding insoluble oxo- and hydroxo-bridged polymers. In spite of this difficulty, several structure determinations have revealed the principal structural features of this class of compound.

A. Metal alkoxides

Thallium methoxide [84], the tert-butoxides of potassium, rubidium and caesium [85], and methylzinc methoxide [86] are all tetrameric and possess a cubane M_4O_4 core distorted to varying degrees. Each oxygen atom is approximately tetrahedral and bonded to three metal atoms. X-ray crystal structures of lithium [87] and sodium [88] methoxides reveal two-dimensional polymers involving layer-type structures. Potassium methoxide adopts a double layer structure [89] of a kind quite different to that of the lithium and sodium analogues. In LiOMe, the bridging methoxide ion coordinates four Li atoms via three electron pairs, suggesting a delocalized electron-deficient structure. The axial methyl group completes a tetragonal pyramid about the central oxygen atom. In contrast, each oxygen atom in KOMe is hexacoordinated to potassium which is again suggestive of an electron deficient structure.

The few crystal structure determinations available for alkoxides of the transition metals confirm the marked tendency towards oligomerization via alkoxy bridges thereby increasing the coordination number of the central metal atom. The structure of $VO(OMe)_3$ confirms its dimeric nature with distorted six-coordination of vanadium(V) being achieved through methoxy bridges [90]. The dimers form a linear polymeric structure in the crystal by further sharing of octahedral edges. Interestingly, the longest methoxy bridges are *trans* to the vanadyl V=O oxygen atoms. The structures of various titanium(IV) alkoxides have been determined and in each case tetramers involving octahedral coordination about the central metal atom have been found. The compounds $Ti(OMe)_4$ [91], $Ti(OEt)_4$ [92] and $Ti(OMe)_3(OEt)$ [93] all possess the structure illustrated in Fig. 1 with the four metal atoms lying at the corners of a planar rhomb. The Ti_4O_{16} framework involves terminal non-bridging alkoxy groups and two types of bridging alkoxide, triply bridging or doubly bridging of the metal atoms to give Ti_3OR or Ti_2OR entities in the structure [162].

The hydrolysis of titanium(IV) ethoxide yields a crystalline product which has been shown to be heptametric by a crystallographic study [94]. The ques-

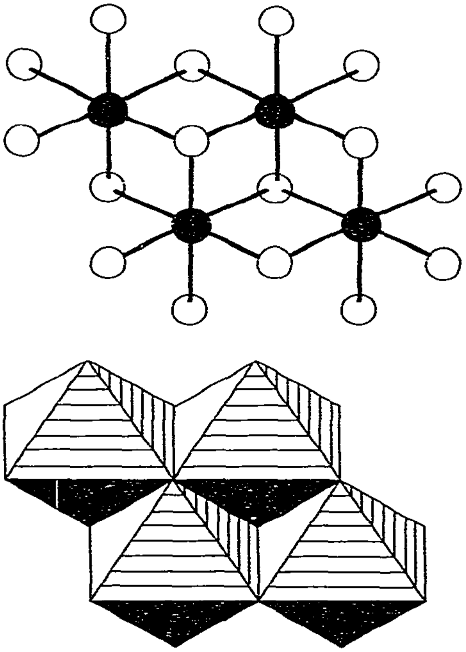


Fig. 1. Structure of $Ti_4(OR)_{16}$.

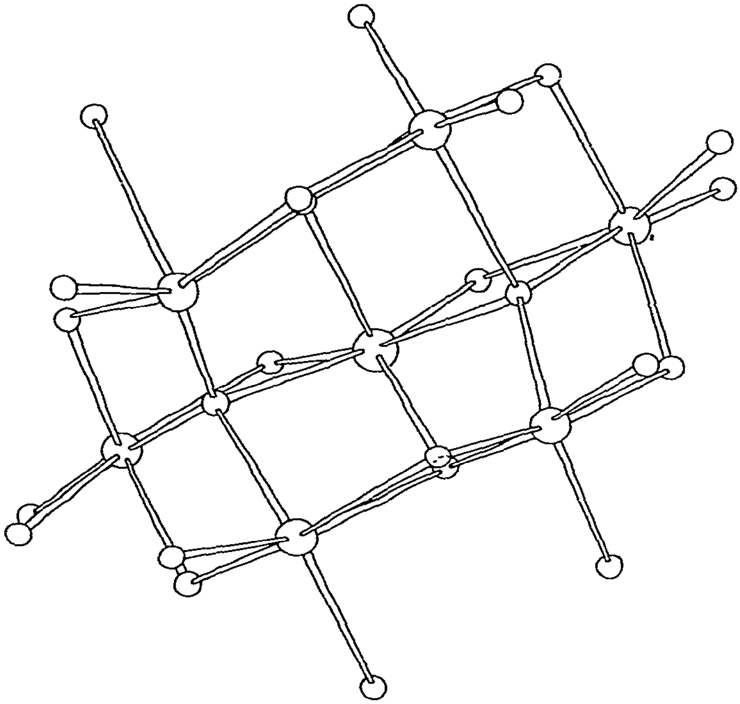


Fig. 2. Structure of "$Ti_7O_5(OEt)_{19}$".

tionable composition $Ti_7O_5(OEt)_{19}$ was suggested although the location of the ethyl groups was not determined. The alternative formulation $Ti_7O_4(OEt)_{20}$ suggested by Bradley [95] gives the correct oxidation state for a titanium(IV) compound as would the composition $Ti_7O_4(OH)(OEt)_{19}$. The close relationship of the structure to that of $Ti_4(OEt)_{16}$ is revealed in Fig. 2.

The crystal structure of $Nb(OMe)_5$ reveals two crystallographically different centrosymmetrical dimers distinguished by different conformations of the methoxide groups [96]. The Nb (or Ta) atoms are coordinated octahedrally by both terminal and bridging methoxy groups. A crystalline product of composition $Nb_8O_{10}(OEt)_{20}$ has been characterized and shown to consist of two independent Nb_3O_{13} skeletons (comprising three edge-sharing octahedra as in Fig. 1) linked by two NbO_6 octahedra which share four corners with each. Three of the four corners shared are marked in Fig. 3.

B. Metal phenoxides

Only three crystal structures appear to have been reported for phenoxides of transition metals and in each case, dimerization occurs via bridging phenoxide groups. The red compound $Ti(OPh)_2Cl_2$ involves pairs of titanium atoms joined by oxygen bridges with each titanium being pentacoordinated in the form of a trigonal bipyramid [97]. The two chlorine atoms and a bridging oxygen atom form the equatorial plane; one bridging oxygen and one terminal phenoxy group lie in the axial positions as shown in Fig. 4. There are several noteworthy fea-

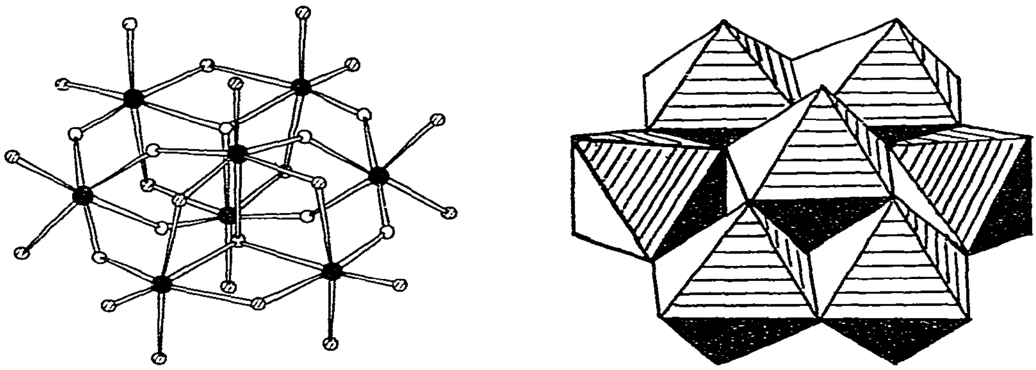


Fig. 3. Structure of $Nb_8O_{10}(OEt)_{20}$.

tures about the dimer. The two titanium atoms and the two bridging oxygen atoms together with their attached carbon atoms from the phenyl rings form a $Ti_2O_2C_2$ coplanar array. Likewise the two titanium atoms, the two bridging oxygen atoms, and the other two non-bridging oxygen atoms also form a plane. The Ti—O distances vary considerably (1.744, 1.910 and 2.122 Å) compared with that observed in rutile of 1.944 Å. The dihedral angle between the plane formed by the Ti—O bridges and the phenyl ring of the bridging oxygen is 77.2°.

The crystal structure of $Ti(OPh)_4 \cdot PhOH$ has also been determined and the compound shown to be a dimer based on phenoxy bridges but in this case each titanium atom is octahedrally coordinated (see Fig. 5). The Ti—O distances again show substantial variations and the dihedral angle associated with the

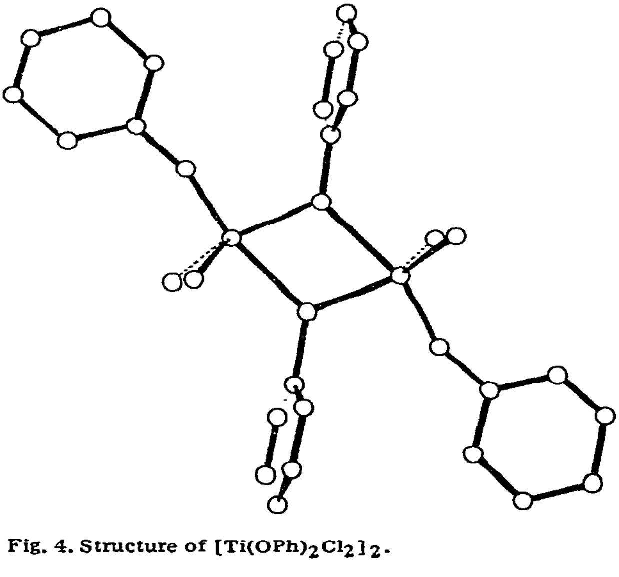


Fig. 4. Structure of $[Ti(OPh)_2Cl_2]_2$.

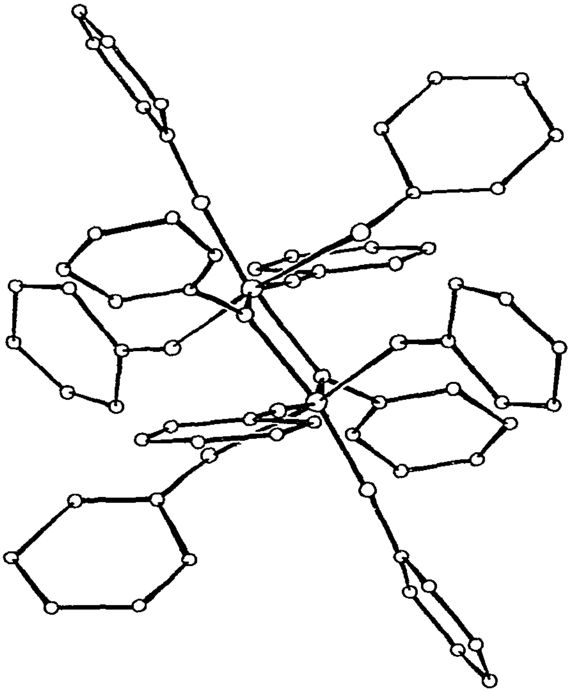


Fig. 5. Structure of $[Ti(OPh)_4 \cdot PhOH]_2$.

bridging phenyl ring is 66.3°. It has been inferred that since these rings are tilted quite far from the Ti_2O_2 bridging plane that little π-bonding is introduced into the bridging ring system through delocalization of the electrons within the phenyl ring [98,99].

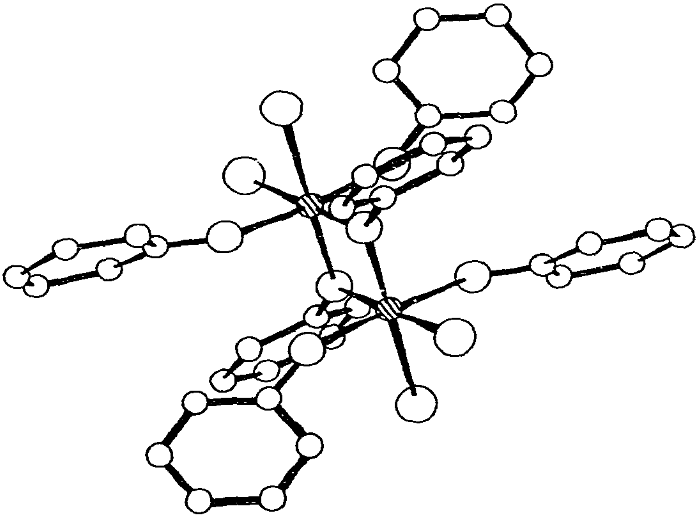


Fig. 6. Structure of $[Mo(OPh)_3Cl_2]_2$.

The deep red mixed chloro-phenoxide of molybdenum, $Mo(OPh)_3Cl_2$, has also been shown to be dimeric with two phenoxo bridges [100]. Both molybdenum atoms are bonded to two chlorine atoms and four phenoxy-oxygen atoms, two of which are terminal and two bridging. The coordination polyhedra about molybdenum are slightly distorted octahedra sharing a common edge of oxygen atoms (see Fig. 6). It is noteworthy that the Mo—Mo distance of 2.801 Å is significantly longer than the value which has been considered to correspond to a single Mo—Mo bond of 2.6 Å. It is likely then that the observed low magnetic moment of this complex arises from a superexchange interaction via the two phenoxy bridges leading to spin pairing of the $4d^1$—$4d^1$ electron configuration of the two molybdenum atoms.

The bis(phenoxo) derivative of copper, $Cu(OPh)_2(en)_2 \cdot 2PhOH$, has been shown by X-ray diffraction to be a centrosymmetric phenoxo-bridged dimer with terminal phenoxo and ethylenediamine groups and hydrogen-bonded phenol molecules. The copper atoms are five coordinated and the stereochemistry is that of a distorted square pyramid. The Cu—Cu distance is 3.215 Å and the dimer has a nearly normal magnetic moment at room temperature [66].

IV. Physical properties

Metal phenoxides, like alkoxides, have at least one M—O—C grouping which is strongly polar because of the large electronegativity of oxygen. The polarity of the M—O bond is further enhanced by the inductive effect of the phenyl group. The physical and chemical properties of metal phenoxides are determined by the polarity of this bond, the well-developed tendency of the coordinatively unsaturated metal atom to expand its coordination number by intermolecular bonding with oxygen, and the steric effects of the unsubstituted and substituted phenyl ring which inhibits oligomerization. Indeed, in some circumstances, steric hindrance can preclude intermolecular bonding so that a volatile monomeric phenoxide results of low coordination number.

A. Solubility and oligomerization

Most of the metal phenoxides are oligomers and like alkoxides are soluble in organic polar solvents. A comparative study of the solubility of metal phenoxides and alkoxides in organic solvents would be worthwhile but no such systematic study has been undertaken. Mehrotra and his coworkers [49,50] observed, in the preparation of mixed alkoxide-phenoxides of lanthanides, that while the alkoxides were soluble in benzene, the alkoxide-phenoxides were only sparingly soluble and the phenoxides were insoluble in benzene. The gadolinium and erbium triphenoxides are insoluble in cyclohexane and a similar observation has been made by Kapoor and his coworkers [48] for the triphenoxide of samarium from $Sm(OPr^i)_3$.

Determination of molecular weight in organic solvents has been helpful in establishing the polymeric nature of some of the metal phenoxides. Cryoscopy and ebulliometry in solvents like benzene, n-hexane and cyclopentane have been widely used and the results are summarized in Table 1. In general, higher degrees of molecular association are observed at lower temperatures and higher concentrations. Substitution of the phenyl ring inhibits molecular association.

TABLE 1

MOLECULAR COMPLEXITY OF METAL PHENOXIDES

Compound	Solvent	Method [a]	Molecular complexity	Ref.
$Tl(OPh)$	benzene	a	dimer (low conc.); 3.8 (higher conc.)	101
$Be(DTBP)_2$ [b]	benzene	a	monomer	61
$HMg(OPh)$	THF	b	dimer	109
$Mn(DTBP)_2$ [b]	benzene	a	monomer	81
$MeZn(OPh)$	benzene	b	tetramer	59
$EtZn(OPh)$	benzene	b	tetramer	59, 102
$EtZn(OC_6Cl_5)$	benzene	b	dimer	102
$EtZn(OC_6F_5)$	benzene	b	dimer	102
$MeZn(OPh) \cdot py$	benzene	b	dimer	102
$Me_2Al(OPh)$	cyclopentane	b	dimer $\rightleftharpoons$ trimer; dimer (crystalline)	103, 104
$Me_2Al(OPh)$	benzene	a	trimer	104
$MeAl(OPh)Cl$	benzene	a	trimer	104
$Al(OPh)_3$	benzene	a	dimer $\rightleftharpoons$ trimer	3, 51
$Al(OC_6H_4CH_3)_2(OPr^i)$	benzene	a	dimer	51
$B(OPh)_3$	benzene	a	monomer	105
$Ti(OPh)_4 \cdot PhOH$	benzene	a	dimer	106
$Ti(OPh)_2Cl_2$	benzene	a	dimer	107
$Ti(OPh)_2Cl_2$	benzene	b	monomer	108
$Ge(OPh)_4$	n-hexane	b	monomer	34
$Ge(OPh)_{4-n}(OR)_n$	n-hexane	b	monomer	34
$Sb(OPh)_3$	benzene	a	monomer	21
$W(OPh)_6$	benzene	a	monomer	10, 22
$Sb(OPh)Cl_4$	nitrobenzene	a	dimer	110
$Nb(OPh)_5$	nitrobenzene	a	dimer	111
$Ta(OPh)_5$	nitrobenzene	a	dimer	111

[a] a, cryoscopy; b, ebullioscopy. [b] DTBP = 2,6-ditertiarybutylphenol.

Jasunki and his coworkers [45] have determined the boiling points, densities, refractive indices and the molecular weights of phenoxide and alkoxy-phenoxides of silicon and have found a general trend that with the increase in the molecular weight (Table 2), there is a gradual increase in the boiling point and density of the phenoxides. All of these compounds are monomers in benzene.

B. Thermochemistry

Very little information is available about the thermochemistry of metal phenoxides, though a number of references, especially to Group III elements,

TABLE 2

PHYSICAL PROPERTIES OF SILICON ETHOXIDE PHENOXIDES

Compound	Molecular weight	Boiling point (°C)	Density	Refractive index
$Si(OEt)_4$	208	165.5	0.933	1.3834
$Si(OPh)(OEt)_3$	256	236—238	1.027	1.4528
$Si(OPh)_2(OEt)_2$	304	302—304	1.089	1.4982
$Si(OPh)_3(OEt)$	352	360—365	1.141	1.5435
$Si(OPh)_4$	400	417—420	—	—

are available in the case of alkoxides [112,113]. Fenwick et al. [114] measured the vapour pressure of boron triphenoxide and substituted triphenoxides and determined the enthalpies of hydrolysis against standard NaOH. The standard heat of formation of gaseous boron triphenoxide was calculated to be $\Delta H_f^\circ \mathrm{B(OPh)_3(g)} = 591.0 \pm 1.9$ kJ/mol. The calculated bond dissociation energy $D(\mathrm{B{-}OPh}) = 437.0 \pm 14.0$ kJ/mol is markedly less than the values observed for the B—O bond dissociation energy in boron alkoxides. This is consistent with the higher acceptor character of boron triphenoxide compared with alkoxides, which probably permits more O → B p_π—p_π bonding than the phenoxides.

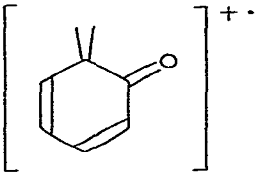
Federov and his coworkers [161] calculated the $D(\mathrm{Ge{-}O})$ in germanium alkoxides and phenoxides. They determined the heat of combustion, heats of evaporation and heats of formation of $\mathrm{Ge(OMe)_4}$, $\mathrm{Ge(OEt)_4}$ and $\mathrm{Ge(OPh)_4}$. The heats of combustion ΔH° of liquid $\mathrm{Ge(OMe)_4}$, $\mathrm{Ge(OEt)_4}$ and $\mathrm{Ge(OPh)_4}$ were found to be -713.2, -1323.2 and -2959.3 kcal mol^{-1} and the heats of evaporation ΔH° under vacuum at 20—400°C were 9.60, 10.30 and 8.95 kcal mol^{-1}, respectively. The heats of formation ΔH_f° are -205.2, -244.6 and -113.4 kcal mol^{-1} for the liquid compounds and -195.60, -234.30 and -104.45 kcal mol^{-1} for the gaseous compounds, respectively. The average $D(\mathrm{Ge{-}O})$ was calculated from the equation

$$D(\mathrm{Ge{-}O}) = \tfrac{1}{4}\,[\Delta H_f^\circ \mathrm{Ge} + 4\Delta H_f^\circ(\mathrm{OR}) - \Delta H_f^\circ\,\mathrm{Ge(OR)_4}]$$

where $\Delta H_f^\circ \mathrm{Ge}$ is the heat of the formation of gaseous germanium which is 91.56 kcal/g atom and $\Delta H_f^\circ(\mathrm{OR})$ is the heat of the formation of tetramethoxy, tetraethoxy and tetraphenoxy radicals. The bond dissociation energy has been found to be 72, 73 and 76 kcal/mol^{-1} for $\mathrm{Ge(OMe)_4}$, $\mathrm{Ge(OEt)_4}$ and $\mathrm{Ge(OPh)_4}$, respectively. This value is less than $D(\mathrm{B{-}O})$ in $\mathrm{B(OPh)_3}$ [115] which is 110 ± 5 kcal mol^{-1} and indicates that the B—O bond is stronger than the Ge—O bond, i.e. there is a more significant contribution of p_π—p_π overlap in the B—O bond compared with that in the Ge—O bond. In the case of germanium phenoxides and germanium alkoxides, the p_π—p_π overlap is more significant in the former than in the latter compounds, whereas a reverse trend is observed in boron triphenoxide and boron alkoxides.

C. *Mass spectrometry*

Comparatively little information is available on mass spectral studies of metal phenoxides. Only the mass spectrum of thallous phenoxide has been reported. Lee [116] observed that the mass spectrum of thallous phenoxide contains both dimeric and monomeric species as well as the ions $[\mathrm{Tl_2O}]^+$ and $[\mathrm{Tl_2OH}]^+$. It is supposed that the intermediate form of the phenol molecular ion has the contribution from the structure



which loses CO. No rearrangement of the resulting ions of the type $[C_5H_5Tl]^+$ has been observed though TlC_5H_5 is known to be a stable compound.

D. Magnetism

Magnetic properties of pure metal phenoxides have not been investigated, although some first-row transition metal alkoxides have been studied in some detail [117,118]. Magnetic susceptibility measurements are confined to only a few mixed phenoxides. Williams et al. [119] observed that the compound $Mo(OPh)_3Cl_2$ has a low magnetic moment of 0.42 B.M when compared with the spin-only value for a d^1 system. This value is very much lower than that observed [120] for $MoCl_5$ and has been attributed to intermolecular anti-ferromagnetism. The strong metal—metal interaction is enhanced by the very short Mo—Mo distance of 2.80 Å in the dimer $[Mo(OPh)_3Cl_2]_2$ compared with the longer Mo—Mo distance in $MoCl_5$ of 3.84 Å. The magnetic moment of the dimer $[Cu_2(OPh)_4(en)_2]$ 2PhOH has been found to be 1.75 B.M at room temperature [121] which is unusually high for oxygen-bridged complexes of divalent copper [122].

E. NMR spectroscopy

NMR spectroscopy has been used successfully for the elucidation of the structure of metal alkoxides. No attempt seems to have been made to apply this technique to the metal phenoxides. However PMR studies of some mixed phenoxides have been made.

Wilkinson and his coworkers [107] have studied the ^1H NMR spectrum of the compound $Ti(OPh)_2Cl_2$ to establish its dimeric character in solution. At —60°C in CD_2Cl_2, the spectrum consists of three broad resonances at δ 7.55, 7.25 and 6.45 ppm of approximate relative intensities 3 : 5 : 2. The high field resonance is due to the *ortho* protons of the bridging phenoxo moieties as they would be more shielded than the others on account of interaction with the two metal centres. On warming, the three resonances broaden further and coalesce and at room temperature a single resonance is observed at δ 7.1 ppm. This is due to the rapid exchange between the terminal and bridge phenoxo groups at higher temperature.

Coates et al. [59] studied the PMR spectrum of methylzinc phenoxide in fully deuterated toluene solution and found that the spectrum consisted of a sharp singlet due to Zn—Me at τ 10.289 and a triplet due to phenyl groups at τ 2.981, 2.945 and 2.905. ^{19}F NMR spectra of aryloxy derivatives of thionyl tetrafluoride have been examined by Sharp and his coworkers [123]. Bis(aryloxy)thionyl difluorides show only one ^{19}F signal which is at the same position as the signal for the axial fluorine of the trifluorides. In the case of tris(aryloxy)thionyl fluorides, only one ^{19}F signal is observed but the chemical shift appears to indicate that they are equatorial fluorines. It is possible that the entire geometry of the molecule has been altered in these tris(aryloxy)-thionyl fluorides. This is most unexpected as only a few examples are known where the steric effects of bridging groups leave an equatorial fluorine in preference to an axial fluorine in substituted derivatives of trigonal bipyramidal fluorides.

TABLE 3

CHARACTERISTIC INFRARED BANDS OF METAL PHENOXIDES

Compound	Vibrations	Frequency (cm^{-1})	Ref.
$[HMg(OPh)]_2$	ν(C—O)	1065—1100	109
	ν(Mg—O)	695—720	
$[Al(OPh)_3]_{2,3}$	ν(C—O)	1175	3
	ν(Al—O)	662	
	ν(Al—O—Al)	570	
$Me_2Al(OPh)$	ν(C—O)	1160	104
$MeAl(OPh)Cl$	ν(C—O)	1160	
$Al(OPh)Cl_2$	ν(C—O)	1140	
$Tl(OPh)(Me_2SO_2)$	ν(C—O)	1120	125
	ν(Tl—O)	430	
$Ln(OPh)_3$	ν(C—O)	995, 1162, 1270, 1450	50
	ν(Ln—O)	560—685	
	ν(Ln—O—Ln)	430	
$[Sb(OPh)Cl_4]_2$	ν(Sb—O)	580—600	110
	ν(Sb—O—Sb)	520—530	
$[Zr(OPh)_4]_n$	ν(C—O)	1152	126
	ν(Zr—O—Zr)	480	
$[Nb(OPh)_5]_2$	ν(C—O)	1196	111
	ν(Nb—O)	580	
	ν(Nb—O—Nb)	530	
$[Ta(OPh)_5]_2$	ν(C—O)	1186	111
	ν(Ta—O)	596	
	ν(Ta—O—Ta)	542	
$Fe(OPh)_2(bipy)_2$	ν(C—O)	1290	67

F. IR spectroscopy

Infrared spectroscopy has been utilised to characterise metal phenoxides by locating the bands characteristic of the bound phenoxy group, especially the M—O and C—O stretching vibrations. Discrimination of the terminal and the bridging phenoxy groups is also obtained as the M—O vibrations due to the bridging phenoxy group are expected to lie at lower frequencies compared with the terminal phenoxy group vibrations. Due to the low molecular symmetry of metal phenoxides, assignment of the vibrational spectra has proved difficult and the technique has not been definitive in structure determination. Table 3 summarizes ν(C—O) and ν(M—O) for various metal phenoxides.

V. Chemical properties

Metal phenoxides are very reactive due to the presence of electronegative phenoxy groups making the metal atom prone to nucleophilic attack. Metal phenoxides, like metal alkoxides, are extremely susceptible to hydrolysis and require strictly anhydrous conditions for their handling.

Metal phenoxides undergo a variety of reactions but these are mainly confined to reactions with hydrogen chloride, acetyl chloride and compounds containing reactive hydrogen. Unlike metal alkoxides, no systematic study of the chemical properties of metal phenoxides has been carried out.

A. Hydrolysis

Metal phenoxides, like alkoxides, are readily susceptible to hydrolytic attack. Although a systematic study of hydrolytic reactions of metal alkoxides has been made by Bradley and his coworkers [127], a similar study for metal phenoxides is lacking. Most of the metal and non-metal phenoxides undergo rapid hydrolysis to form basic phenoxides. In the presence of excess water, basic oxides are formed. Phenoxides of alkali and alkaline earth metals yield phenoxide ions in water [10], but this claim by Mortimer and his coworkers has been contested [11] with the counterclaim that the phenoxides of alkali metals undergo hydrolysis in water. Flora and his coworkers [52] studied the hydrolytic decomposition of mixed alkoxy-aryloxy phenoxides of aluminium and titanium and observed that the introduction of phenoxide in place of butoxide in $Al(OBu)_3$ increased the susceptibility to the hydrolytic attack. The order of the hydrolytic stability in the series $Al(OPh)_3$, $Al(OPh)_2(OBu)$, $Al(OPh)(OBu)_2$, $Al(OBu)_3$ is $Al(OBu)_3 > Al(OPh)(OBu)_2 > Al(OPh)_2(OBu) > Al(OPh)_3$.

The relative stability of the phenoxides and phenyl-substituted phenoxides of silicon has also been investigated using a number of hydrolysing media [128]. It was found that, regardless of the hydrolysing medium, the hydrolytic stability of the following silanes is of the order of $Si(OPh)_4 < PhSi(OPh)_3 < Ph_2Si(OPh)_2 < Ph_3Si(OPh)$. The hydrolytic stability depends upon the nature of the ArO group, i.e., *ortho*- and *para*-substituted phenoxides are more stable than the phenoxides, the order of the hydrolytic stability being $OPh < o\text{-}OC_6H_4X < p\text{-}OC_6H_4X$. This explains why phenoxides of composition $Sc(o,p\text{-}OC_6H_4NO_2)_3$, $Sc(o,p\text{-}OC_6H_4Cl)_3$ could be obtained whereas in the case of phenol, a hydrolysed product of composition $Sc(OPh)_2(OH)$ was obtained [36]. In the case of the hydrolysis of mixed alkoxide-phenoxides of silicon, it was observed [15] that the phenoxide group was hydrolysed first followed by the alkoxide. The process of hydrolysis was independent of the number of substituents.

$$2Si(OPh)(OEt)_3 + HOH \rightarrow (EtO)_3Si{-}O{-}Si(OEt)_3 + 2PhOH$$

$$2Si(OPh)_3(OEt) + HOH \rightarrow (OEt)(OPh)_2Si{-}O{-}Si(OPh)_2(OEt) + 2PhOH$$

Tungsten hexaphenoxide does not undergo hydrolysis even in alkaline conditions [10]. However, it undergoes hydrolysis under acidic conditions the proposed mechanism being

$$W(OPh)_6 + H^+ \rightarrow (PhO)_5W(OH^+Ph) \rightarrow [W(OPh)_5]^+ + PhOH$$

$$[W(OPh)_5]^+ + OH^- \rightarrow W(OPh)_5OH$$

$WO(Ph)_4$, on the contrary, is readily hydrolysed. $W(OPh)_6$ owes its stability either to the absence of an unoccupied coordination position or to steric hindrance of the approaching nucleophile. Carbon tetraphenoxide does not undergo alkaline hydrolysis but surprisingly it decomposes in moist air and is more susceptible to acid hydrolysis than tungsten hexaphenoxide.

B. Action of heat

No systematic study of the thermal effects on metal phenoxides has been made although scattered references are available in literature. Alkali metal phenoxides decompose at 400—500°C to yield gaseous products such as methane and hydrogen [129]. Sodium phenoxide when heated in a current of carbon dioxide, yielded an unidentified liquid product, carbon monoxide and hydrogen. Decomposition in a stream of carbon monoxide gave methane, phenol and benzene. Alkaline earth metal phenoxides on heating yielded liquid products, hydrogen, methane, carbon monoxide and carbon dioxide. Silver phenoxide is only stable at —78°C and explodes on gentle heating [130]. Methylzinc phenoxide, when heated at 120°C, disproportionates to zinc phenoxide and dimethyl zinc

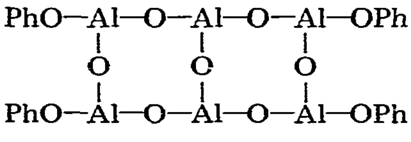
$$2\mathrm{MeZnOPh} \rightarrow \mathrm{Zn(OPh)_2} + \mathrm{Me_2Zn}$$

Methylzinc alkoxides sublime unchanged under similar conditions [59].

Aluminium phenoxide decomposes below red heat yielding unidentified liquid products, benzene, diphenyl ether, methyldiphenylene oxide, *p*-cresol, hydrogen and methane [129]. More detailed observations [52] indicate that the decomposition process of the phenoxides and phenoxide-alkoxides of aluminium and titanium is analogous to that of the alkoxides and is catalysed by oxygen. Decomposition of phenoxides such as $\mathrm{Al(OPh)_3}$, $\mathrm{Al(OPh)_2(OBu^t)}$ and $\mathrm{Al(OPh)(OBu^t)_2}$ is assumed to proceed through the formation of the intermediate $\mathrm{Ph[OAl(OH)]_4OPh}$. It is claimed [130] that under autogenous pressure, $\mathrm{Al(OPh)_3}$ does not give reproducible results while $\mathrm{Al(OPh)_2(OBu^t)}$ decomposes at 280—293°C via this intermediate. The mixed phenoxide-alkoxide of titanium also decomposes similarly.

$$\mathrm{Ti(OPh)_2(OBu^t)_2} \xrightarrow{150\text{—}300^\circ\mathrm{C}} \mathrm{Ph[OTi(OPh)(OBu^t)]_4OPh} \xrightarrow{300\text{—}400^\circ\mathrm{C}} \mathrm{Ph[OTi(OBu^t)(OH)]_4OPh}$$

Strauss and his coworkers [3] have observed that $\mathrm{Al(OPh)_3}$ starts decomposing at about 100°C. From the DTA studies, the first decomposition product of $\mathrm{Al(OPh)_3}$ is proposed as,



The second exothermic stage involves hydrolysis of $\mathrm{Al_6O_7(OPh)_4}$ which absorbs moisture from air, followed at higher temperatures by dehydration to $\mathrm{Al_2O_3}$.

$$\mathrm{Al_6O_7(OPh)_4} + 4\mathrm{H_2O} \rightarrow \mathrm{Al_6O_7(OH)_4} + 4\mathrm{PhOH} \rightarrow 3\mathrm{Al_2O_3} + 2\mathrm{H_2O}$$

A detailed study of thermal decomposition of ester chlorides of silicic acid has been made by Volnov [131] who observed that their thermal stability increased with increasing molecular weight and that aromatic esters of silicic acid are more stable than aliphatic esters. When $\mathrm{Si(OPh)Cl_3}$ is heated for 5 hours, most of it remains unchanged with only a trace of $\mathrm{SiCl_4}$ and $\mathrm{Si(OPh)_2Cl_2}$ being formed. However, when $Si(OPh)_3Cl$ is heated for 6 hours, it is mostly changed to $SiCl_4$, $Si(OPh)_2Cl_2$ and $Si(OPh)_4$.

Mehrotra et al. [34] observed that whereas mixed ethylaryl orthogermanates are not very thermally stable, the compounds decomposing when distilled under reduced pressure, the germanium alkoxides or phenoxide distil without decomposition.

C. Reaction with halides

Metal chlorides are the most convenient starting materials for the synthesis of metal phenoxides and not surprisingly they can be regenerated easily by reacting metal phenoxides with excess hydrogen chloride or acetyl chloride. The ratio of chloride to phenoxide may be controlled conveniently by varying the proportions of the reactants. Mehrotra and his coworkers studied the reaction of hydrogen chloride with phenyl orthotitanate [47] and phenyl orthogermanate [34] in detail. In the case of phenyl orthogermanate, germanium tetrachloride was the final product,

$$Ge(OPh)_4 + 4HCl \rightarrow GeCl_4 + 4PhOH$$

but in the case of phenyl orthotitanate, only one of the phenoxy groups was replaced by chlorine, e.g.

$$Ti(OPh)_4 + HCl \rightarrow Ti(OPh)_3Cl \cdot PhOH$$

The corresponding reaction of hydrogen chloride with alkyl orthotitanates yielded dichlorodialkoxides [132]. An S_N2 type mechanism for the reaction of metal phenoxide and hydrogen chloride has been proposed.

It has been observed by Muetterties [133] that hydrogen fluoride reacts with a series of compounds containing B—O bonds to give the corresponding fluoro derivatives. Boron triphenoxide reacts with hydrogen fluoride to form $BF_3 \cdot PhOH$

$$B(OPh)_3 + 3HF \rightarrow BF_3 \cdot PhOH + 2PhOH$$

The corresponding reaction with hydrogen chloride does not yield BCl_3.

Very little is known about the reaction of metal phenoxides with acetyl chloride, although the corresponding reactions in the case of metal alkoxides are well characterised [134,135]. Titanium tetraphenoxide when refluxed with excess of acetyl chloride yields a yellow $TiCl_4$ adduct of phenyl acetate,

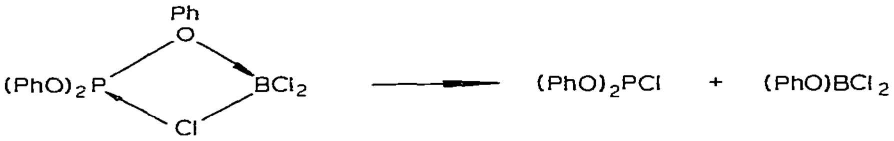
$$Ti(OC_6H_5)_4 + 4CH_3COCl \rightarrow TiCl_4 \cdot 2CH_3COOC_6H_5 + 2CH_3COOC_6H_5$$

A similar reaction in the case of niobium pentaphenoxide yields an adduct of $NbCl_5$

$$Nb(OPh)_5 + 5CH_3COCl \rightarrow NbCl_5 \cdot CH_3COOC_6H_5 + 4CH_3COOC_6H_5$$

The reaction of metal phenoxides and metal halides has not been studied in detail. Depending upon the electronegativity of the second metal and the free energy of formation of the various products formed, exchange reactions take place sometimes yielding mixed halophenoxides. In the aryloxysilane-phosphorus halide and aryloxysilane-boron trichloride systems, it has been observed that a mixture of chloresters of the two non-metals are formed. In the case of boron trichloride-phosphorous triphenoxide, boron triphenoxide is the final product

[136]. Intermediate compounds of composition $B(OPh)Cl_2$, $B(OPh)_2Cl$ which further react to yield BCl_3 and $B(OPh)_3$ are also formed. The driving force of the reaction is the nucleophilic oxygen atom. In the case of boron triphenoxide, the electron density on oxygen is low because of p_π—p_π back-bonding and the mesomeric effect of the phenyl ring. A four-centre intermediate has been postulated [137] to explain the initial reaction,



The reaction between phosphorus triodide and silicon tetraphenoxide leads to the formation of phosphorus triphenoxide [138],

$$3Si(OPh)_4 + PI_3 \rightarrow 3Si(OPh)_3I + P(OPh)_3$$

Silicon tetraethoxide does not give similar products. Aluminium trichloride does not react with boron triphenoxide but does react with boron tributoxide to form butyl chloride [139]. No reaction takes place between the tetrabispentafluorophenoxide of titanium and titanium tetrachloride [20].

D. Reaction with alcohols or phenol

Metal alkoxides react with a variety of primary, secondary and tertiary alcohols as well as with phenols to establish the equilibrium:

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

The forward reaction can be completed either by fractionating out the displaced alcohol or removing it as an azeotrope by adding a suitable solvent [140,141]. Information on the reaction of alcohols with metal phenoxides is much more limited. Mehrotra and Verma [47] have observed that by passing ammonia through titanium tetraphenoxide and isoproponol in benzene, it was possible to replace only one phenoxy group by an isopropoxy group to give the compound $Ti(OPh)_3(OPr^i)$.

A compound of similar composition was obtained when $Ti(OPh)_4$ was refluxed in benzene with ethanol or isopropanol in the molar ratio 1:4. Mortimer and his coworkers [10] found that $W(OPh)_6$ remains unchanged when refluxed with butanol for 8 hours. A parallel study of the reaction of tungsten hexaphenoxide with *m*- or *p*-nitrophenol provides a route for the synthesis of *m*- or *p*-nitrophenoxides. This reaction is similar to the alcohol interchange method for preparing a variety of alkoxides. It has been observed that the yield of *o*-nitrophenoxide is low, suggesting that at the *ortho* position space is too limited for the bulky groups to be accommodated. However, nitration of tungsten hexaphenoxide takes place readily.

E. Insertion reactions

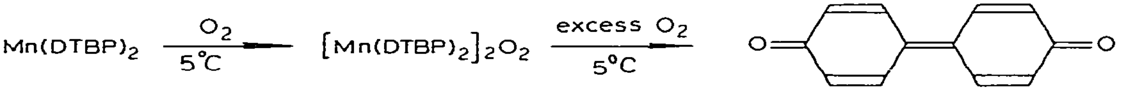
Insertion of sulphur dioxide into metal—carbon bonds may yield a sulphone containing the M—S—C grouping, an *O*-sulphinate containing the grouping M—O—S(O)—C or an *S*-sulphinate containing the M—S(O)—O—C grouping [142].

Sulphur dioxide is known to insert in metal—carbon bonds of aluminium trialkyls [143] and gallium trialkyls [144]. Insertion reactions of sulphur dioxide with metal alkoxides are also well known [145,146], but in the case of metal phenoxides only one reaction has been reported [125].

Sulphur dioxide reacts with dimethylthallium ethoxide to yield $Me_2Tl(EtSO_3)$. Thallium(I) phenoxide reacts with liquid SO_2 to form Tl[OS(O)OPh]. The IR spectrum of the compound exhibits strong absorption bands at 1230 and 1160, $[\nu_{asym}(SO_3)]$ and 907 $[\nu_{sym}(SO_3)]$, and 440 cm^{-1} $[\nu(Tl—O)]$. Carbon disulphide reacts quantitatively with TlOPh to yield Tl[SC(S)OPh]. The mass spectrum of the compound obtained on heating at 150°C shows strong peaks due to Tl^+, $TlOCS_2{}^+$ and $TlOPh^+$. Peaks containing no thallium atoms were due to CS_2OPh^+ and $CSOPh^+$.

The thallium—oxygen bond in thallium(I) phenoxide is more covalent than the thallium—oxygen bond in thallium hydroxide and CS_2 does not react with thallium hydroxide. Reaction of thallium(I) phenoxide with phenyl isocyanate is more complex. Trimerisation of the isocyanate occurs to give triphenyl isocyanurate and the resulting thallium product is unstable and decomposes readily to yield metal thallium.

An interesting "insertion" reaction of the manganese(II) derivative of ditertiary butyl phenoxide (DTBP) has been reported [81]. Oxygen forms a green compound of composition $[Mn(DTBP)_2]_2O_2$ with the yellow $Mn(DTBP)_2$. The former is stable at room temperature under argon and the reflectance spectrum shows no change in oxidation state of manganese. Further addition of oxygen, at room temperature yields 2,5,7,10-tetra-t-butyl-*p*-diphenoquinone and manganese-containing products



F. Reaction with coordinating ligands

Metal phenoxides, like metal alkoxides, have poor acceptor properties, which is in contrast to the pronounced acceptor properties of the metal halides. This stems from the polymeric nature of many metal phenoxides in which the metal atom has achieved coordination saturation via phenoxy bridging. Nevertheless, under suitable conditions, the intermolecular bridge can be ruptured and addition of another ligand can take place. Examples of such adducts are given in Table 4.

The Lewis acid character of metal phenoxides, i.e., the tendency to form adducts with bases, tends to be enhanced if some of the phenoxy groups are replaced by more electronegative substituents. For example, $Nb(OPh)_5$ does not form addition compounds with ketones whereas $Nb(OPh)Cl_4$ forms the adduct $Nb(OPh)Cl_4 \cdot$ketone [147]. Many other examples are listed in Table 4.

The inductive effect of the phenyl ring appears to favour adduct formation. Thus MeZn(OR) can be recovered unchanged from pyridine whereas MeZn(OPh) forms a 1:1 adduct [57].

An interesting alternative to simple adduct formation has been observed recently by Malhotra et al. [158]. They have shown that treatment of Nb-

TABLE 4

ADDUCTS OF METAL PHENOXIDES

Phenoxide	Adduct	Ref.
$\mathrm{MeZn(OPh)}$	$\mathrm{MeZn(OPh)\cdot py}$	59
$\mathrm{EtZn(OPh)}$	$\mathrm{EtZn(OPh)\cdot py}$	102
	$\mathrm{[EtZn(OPh)]_2\cdot TMED}$	102
	$\mathrm{EtZn(OC_6Cl_5)\cdot TMED}$	102
	$\mathrm{EtZn(OC_6Cl_5)\cdot 2py}$	102
	$\mathrm{EtZn(OC_6F_5)\cdot py}$	102
	$\mathrm{EtZn(OC_6F_5)\cdot TMED}$	102
$\mathrm{MeBe(OPh)}$	$\mathrm{MeBe(OPh)\cdot Et_2O}$	151
$\mathrm{Cu(OPh)_2}$	$\mathrm{Cu(OPh)_2(en)\cdot PhOH}$	66
	$\mathrm{Cu(OPh)_2\cdot bipy}$	66
$\mathrm{Fe(OC_6H_4X)_2}$	$\mathrm{Fe(OC_6H_4X)_2(bipy)}_n$ $n = 1, 2$	67
$\mathrm{B(OPh)_3}$	$\mathrm{B(OPh)_3\cdot Et_3N}$	149, 150
	$\mathrm{B(OPh)_3\cdot Et_2NH}$	149, 150
	$\mathrm{B(OPh)_3\cdot EtNH_2}$	149
	$\mathrm{B(OPh)_3\cdot py}$	149, 150
$\mathrm{Me_2Si(OPh)_2}$	$\mathrm{Me_2Si(OPh)_2\cdot PhOH}$	152
$\mathrm{Me_3Si(OPh)}$	$\mathrm{Me_3Si(OPh)\cdot PhOH}$	152
$\mathrm{Zr(OPh)_4}$	$\mathrm{Zr(OPh)_4\cdot PhOH}$	57
	$\mathrm{Zr(OPh)_4\cdot 2py}$	126
	$\mathrm{Zr(OPh)_4\cdot bipy}$	126
	$\mathrm{Zr(OPh)_4\cdot phen}$	126
	$\mathrm{Zr(OPh)_4\cdot 2(pyridine\ oxide)}$	126
	$\mathrm{Zr(OPh)_4\cdot (bipyridine\ oxide)}$	126
$\mathrm{Ti(OPh)_4}$	$\mathrm{Ti(OPh)_4\cdot PhOH}$	153
	$\mathrm{Ti(OPh)_4\cdot NH_3}$	153
	$\mathrm{Ti(OPh)_4\cdot C_{10}H_7NH_2}$	154
	$\mathrm{Ti(OPh)_4\cdot PhCOMe}$	155
	$\mathrm{Ti(OPh)_4\cdot BuOCOMe}$	155
	$\mathrm{Ti(OPh)_4\cdot PhOCOMe}$	155
$\mathrm{Ti(OC_6H_4Cl)_4}$	$\mathrm{Ti(OC_6H_4Cl)_4\cdot C_6H_4ClOH}$	156
$\mathrm{Nb(OPh)_2Cl_3}$	$\mathrm{Nb(OPh)_2Cl_3\cdot CH_3CN}$	148
$\mathrm{Nb(OPh)Cl_4}$	$\mathrm{Nb(OPh)Cl_4\cdot CH_3CN}$	148
	$\mathrm{Nb(OPh)Cl_4\cdot ketone}$	147
	$\mathrm{Nb(OPh)Cl_4\cdot amide}$	157
$\mathrm{Nb(OPh)_5}$	$\mathrm{Nb(OPh)_5\cdot Ph_3AsO}$	111
	$\mathrm{Nb(OPh)_5\cdot py}$	111
	$\mathrm{Nb(OPh)_5\cdot pyridine\ oxide}$	111
$\mathrm{Ta(OPh)Br_4}$	$\mathrm{Ta(OPh)Br_4\cdot CH_3CN}$	27
$\mathrm{Ta(OPh)Cl_4}$	$\mathrm{Ta(OPh)Cl_4\cdot CH_3CN}$	148
$\mathrm{Ta(OPh)_5}$	$\mathrm{Ta(OPh)_5\cdot CH_3CN}$	148
$\mathrm{U(OPh)_4}$	$\mathrm{U(OPh)_4\cdot}n\mathrm{NH_3}$ $n = 1, 2$	39
	$\mathrm{U(OPh)_4\cdot 2PhOH\cdot NH_3}$	39
	$\mathrm{U(OPh)_4\cdot 2PhOH\cdot NEt_3}$	39
$\mathrm{UO(OPh)_2}$	$\mathrm{UO(OPh)_2\cdot 4PhOH\cdot NH_3}$	39
$\mathrm{UO_2(OPh)_2}$	$\mathrm{UO_2(OPh)_2\cdot 4PhOH\cdot NEt_3}$	39
	$\mathrm{UO_2(OPh)_2\cdot py}$	39
$\mathrm{U(OPh)_4Cl}$	$\mathrm{U(OPh)_4Cl\cdot 2DMF}$	55

$\mathrm{(OPh)_4Cl}$ or $\mathrm{Ta(OPh)_4Cl}$ with $\mathrm{SbCl_5}$ (or $\mathrm{AlCl_3}$) results in chlorine abstraction and the formation of the phenoxy cations $\mathrm{[Nb(OPh)_4]^+}$ and $\mathrm{[Ta(OPh)_4]^+}$ either as $\mathrm{[SbCl_6]^-}$ or $\mathrm{[AlCl_4]^-}$ salts.

Compounds containing reactive hydrogen such as α-hydroxy ketones and aldehydes readily form chelates with metal phenoxides and one or more phenoxide groups is eliminated as phenol. Benzoin and acetonylacetone react with niobium phenoxides [159] to form chelates,

$$M(OPh)_2Cl_3 + acacH \rightarrow M(OPh)Cl_3(acac) + PhOH$$

Similarly salicylaldehyde forms chelates with the elimination of phenol [150].

Metal phenoxides readily undergo substitution reactions of the aromatic ring but these reactions are beyond the scope of the present review.

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