Metal Alkoxide

Lecture - 1

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Metal Alkoxide

Metal alkoxide is the compound which is formed by metal ion with o atom of alkoxide ion. Its general formula is M(-O-R)n it involves alkoxides is to consider them as derivatives of metal hydroxides $M(OH)_X$. Metal alkoxides involve M^+ O-C bonds which are polarized in the direction shown due to the highly electronegativity character of oxygen. The degree of polarization in an alkoxide molecule depends on the electronegativity of the central atom.

$B(OC_2H_3)_{3,}$ $Si(OC_2H_5)_{4,}$ $P(OCH_3)_3$

where M =metal ion

RO-= alkoxide ion

Here alkoxide ion is organic functional group which is formed when one H atom is removed from hydroxyl gr. of alcohal. n= valency of metal M.

R-O-H = RO^- + H^+

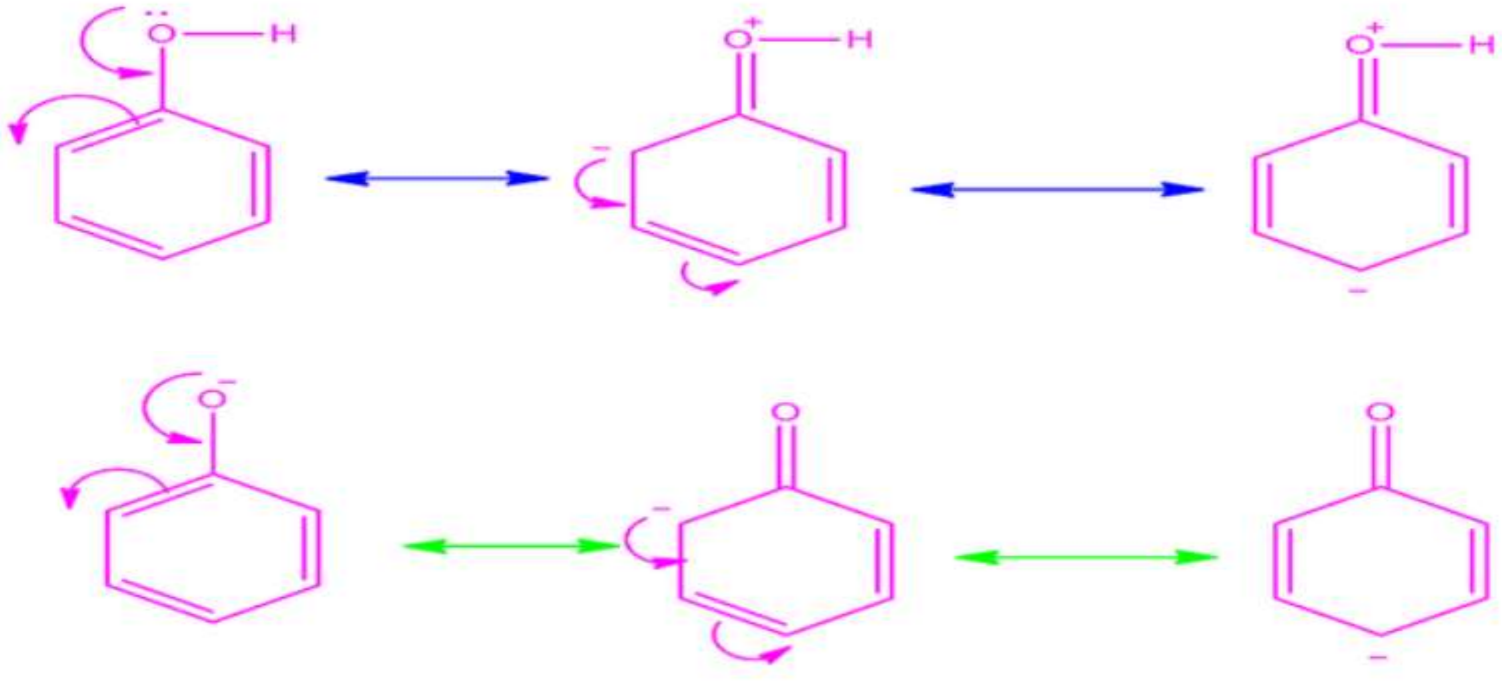
Alcohol Alkoxide ion

- having lone pair electron on O atom
- conjugate base of alcohol
- strong base due to polarisation of -ve charge
- acts as good ligand
- acts as nucleophile
- unstable in protic solvent
- used as catalyst

Stability of alkoxide ion depends upon nature of R (alkyl or aryl gr.) R has tendency to electron repelling density towards O atoms to increase electron density on O atom & hence alkoxide ion acts as strong base (ligand).

When R is no bulky then alkoxide ion acts as good ligand but when aryl gr. Is present then phenoxide ion is less basic aryl gr.

Phenoxide ion is more stable than phenol, although both phenol and phenoxide have same number of resonating structure . In phenoxide ion the negative charge on oxygen atom takes part in resonance with the pi electron of benzene ring , through which phenoxide ion got stability . But in phenol , the lone on oxygen atom participate in resonance with the pi electron of benzene ring .



Comparison with H_2O

H_2O has no charge i.e. it does not bound with compound but OH^- has negative charge & hence readily attract towards +ve charge of metal & hence OH^- is better nucleophile than H_2O. At the same time alkoxide ion is better nucleophile then OH^- & phenoxide ion.

Nomenclature of Metal alkoxide

Common name of metal alkoxide have been retained but in case of higher alkoxide nomenclature is derived from IUPAC convention

$B(OC_2H_3)_{3,}$ - Triethoxy borane

$Si(OC_2H_5)_4$ - Tetra ethoxy silane

$P(OCH_3)_3$ – Trimethoxy phosphane

SYNTHESIS OF METAL ALKOXIDES

Metal alkoxide have been prepared by several methods most important methods are given below

1. Direct Reaction of Metal & alcohol:-

This method involves the direct reaction of a metal with alcohol:

$M + nROH \bullet M(OR)_n + 1/2H_2$

(Where R= alkyl or aryl group, M - metal)

In view of the acid character of alcohol, its reactivity would be limited by strongly electropositive elements, such as alkali metals and alkaline earth and in case of the less electropositive elements such as magnesium, beryllium and aluminum, a catalyst is needed. Recently, this method has been extended to lanthanons including yttrium and scandium.

2. THE EXCHANGE ROUTE FOR METALALKOXIDES:

Generally reactions of alkoxides with alcohols are collectively termed alcoholysis or alcohol interchange reactions and they can be represented by the following simple equation:

$$M(OR)n + xROH \quad \bullet \; M(OR)_{nx} \, (OR)_{X} + xROH$$

(Where M = metal and R=alkyl or aryl group)

The alcoholysis reactions are widely used to preparation of mixed metal alkoxides.

3. REACTIONS OF METAL DIALKYLAMIDES WITH ALCOHOLS

This method has been reviewed for the preparation of uranium tetra alkoxides of the type:-

$$M(NR_2)_X + ROH \qquad \bullet\ M(OR)_X + R_2NH$$

(Where R = alkyl or aryl group)

4. REACTIONS OF METAL HYDROXIDES AND OXIDES WITH ALCOHOLS:-

The reactions of hydroxides and oxides of nonmetals with alcohols to form esters and water have been reviewed in sufficient depth:

$$M(OH)_n + nROH = M(OR)_n + nH_2O$$

$$MOn + 2nROH \qquad \bullet\ M(0R)_{2n} + nH2O$$

(Where M = metal R = alkyl group, n = 1,2,...etc)

Continuous removal of water is necessary to obtain good yields of the final alkoxide products.

This technique is now well established and is thus widely used to synthesize metal alkoxides of various elements.

1. Reactions with alkyl halides

The alkoxide ion can react with a primary alkyl halide in an SN_2 reaction to form a methyl ether.

Hydrolysis and transesterification

2. Metal alkoxides hydrolyse with water according to the following equation

$2\ L_nMOR\ +\ H_2O \rightarrow [L_nM]_2O\ +\ 2\ ROH$where R is an organic substituent and L is an unspecified ligand (often an alkoxide) A well-studied case is the irreversible hydrolysis of titanium ethoxide:

$1/n\ [Ti(OCH_2CH_3)_4]_n\ +\ 2\ H_2O \rightarrow TiO_2\ +\ 4\ HOCH_2CH_3$

3. Formation of oxo-alkoxides

Many metal alkoxide compounds also feature oxo-ligands. Oxo-ligands typically arise via the hydrolysis, often accidentally, and via ether elimination:

$2\ L_nMOR \rightarrow [L_nM]_2O\ +\ R_2O$

Additionally, low valent metal alkoxides are susceptible to oxidation by air

4. Formation of polynuclear and heterometallic derivatives Characteristically, transition metal alkoxides are polynuclear, that is they contain more than one metal. Alkoxides are sterically undemanding and highly basic ligands that tend to bridge metals. $Re_4O_{6-y}(OCH_3)_{12+y}$ allowed one to obtain complexes $Re_{4-x}Mo_xO_{6-y}(OCH_3)_{12+y}$

5. Thermal stability:

Many metal alkoxides thermally decompose in the range ~100–300 °C. Depending on process conditions, this thermolysis can afford nanosized powders of oxide or metallic phases. This approach is a basis of processes of fabrication of functional materials intended for aircraft, space, electronic fields, and chemical industry: individual oxides, their solid solutions, complex oxides, powders of metals and alloys active towards sintering. Decomposition of mixtures of mono- and heterometallic alkoxide derivatives has also been examined. This method represents a prospective approach possessing an advantage of capability of obtaining functional materials with increased phase and chemical homogeneity and controllable grain size (including the preparation of nanosized materials) at relatively low temperature (less than 500−900 °C) as compared with the conventional techniques.

HYDROLYSIS AND CONDENSATION REACTIONS OF METAL ALKOXIDES

Metal alkoxides are recognized to be very reactive substances due to their electronegative alkoxy groups making the metal atoms susceptible to nucleophilic attack. Therefore metal alkoxides are apt to hydrolysis by atomspheric moisture and require careful handling.The alkoxides react with the protons of a large number of organic hydroxy-compounds such as alcohols Organosilicon alkoxides are indefinitely insoluble in water.

Therefore are stable to water they readily hydrolyzed when converted to solution by adding an alcohol. The hydrolysis is slow in neutral solution and took months to produce a precipitate, but strongly catalyzed by acid or alkalis. In alkaline solution nucleophilic attack by hydroxide ion take place as in:-

$HO'' + R_3SiOR \; = \; R_3SiOH + OR''$

$OR' + H_2O \; = \; R\text{-}OH + \text{-}OH$

In acid solution, protonation of the oxygen atom precedes nucleophilic attack by water on silicon as can be seen from below:-

$R_3SiOR \; = \; R_3Si0^{+}HR^{x} + H_2O$

$R_3Si0^{+}HR'' + H_20 = R_3Si0^{+}H_2 + ROH$

$R_3SiO^{+}H_2 + H_2O \; = R_3SiOH + H_3O^{+}$

The mechanisms depicted above involve cleavage of Si-0 bond and not the O-R bond. The ease of hydrolysis of compounds of the type $R_xSi(OR)_{4\cdot x}$. substantially increases in the order

$R_3SiOR'' < R_2Si(OR'')_2 < RSi(OR'')_3 < Si(OR'')4$

and decreases with increasing size of R.