ADVANCED CHEMISTRY BLOC

(HYDROLYSIS)

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HYDROLYSIS AND HYDRATION

In continuation to our last discussion about hydrolysis and hydration reactions, we have a bunch of many important reactions.

Carbides may be ionic or covalent or even interstitial. Ionic carbides are further classified as methanide (C^{4-}), acetylide ($\bar{C}\equiv\bar{C}$) or allylide (C_3^{4-}). These are very strong conjugate bases of their respective hydrocarbons. On treatment with water, these ionic carbides pick H^+ and become respective hydrocarbon.

Examples of methanide hydrolysis are :

$$Al_4C_3 + H_2O \longrightarrow Al(OH)_3 + CH_4$$

$$Be_2C + H_2O \longrightarrow Be(OH)_2 + CH_4$$

Hydrolysis of few acetylides are :

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$MgC_2 + H_2O \longrightarrow Mg(OH)_2 + C_2H_2$$

Besides group 2 elements, lanthanides and Li from alkali metals form acetylide.

C_3^{4-}, the allylide ion may be

$$\overset{2-}{\bar{C}}=C=\overset{2-}{\bar{C}} \quad \text{or} \quad \bar{C}\equiv C-C^{3-}$$

Accordingly on hydrolysis, it releases

$$CH_2=C=CH_2 \quad \text{or} \quad CH_3-C\equiv CH$$

The only known allylide is of Mg^{2+} *i.e.*, Mg_2C_3

$$MgC_2 \xrightarrow{\Delta} Mg_2C_3$$

What about covalent carbides?

$$SiC + H_2O \longrightarrow \text{No hydrolysis}$$

SiC has a giant covalent structure. Even conc. HNO_3 fails to disrupt the structure. Only an aq. KOH can dissolve it.

Nitrides on hydrolysis releases NH_3.

$$Mg_3N_2 + H_2O \longrightarrow Mg(OH)_2 + NH_3$$

$$Ca_3N_2 + H_2O \longrightarrow Ca(OH)_2 + NH_3$$

Ionic hydrides like NaH, CaH_2, hydrolyse to release H_2.

$$NaH + H_2O \longrightarrow NaOH + H_2$$

$$CaH_2 + H_2O \longrightarrow Ca(OH)_2 + H_2$$

BeH_2 is a polymeric acid and has characteristic intermediate between that of ionic and covalent. It can withstand water but decomposes in acid to release H_2.

In hydration reactions, compounds will just pick the water.

$$\underset{\text{(A basic anhydride)}}{CaO} + H_2O \longrightarrow Ca(OH)_2$$

Most of the metal oxides are basic anhydrides except a few like Mn_2O_7, CrO_3, etc. With high positive oxidation states, these metals have now developed considerable non-metallic character and their oxides behave as acidic oxides.

Mn_2O_7 reacts with water to form soluble MnO_4^- ions and H^+.

Though we say metal oxides are basic anhydride, practically most of them are insoluble in water. Only oxides of Group-I and few higher members of group-II dissolve in water forming hydroxides. BeO and MgO are also practically insoluble. Their basic nature becomes apparent only when they are reacted with acid. Take another simple example FeO, which is basic but completely insoluble in water, forget about reactions.

Out of non-metal oxides, CO, NO, N_2O are neutral members.

$$\underset{\text{(very little soluble)}}{CO_2} + H_2O \longrightarrow H_2CO_3$$

$$\underset{\text{(It's a mixed anhydride)}}{NO_2} + H_2O \longrightarrow HNO_2 + HNO_3$$

Quotable Quote

Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less.

Marie Curie

HNO_2 disproportionates to form HNO_3 and NO. Hence, there is nothing wrong when we write

$$NO_2 + H_2O \longrightarrow HNO_3 + NO$$
$$N_2O_5 + H_2O \longrightarrow HNO_3$$
$$N_2O_3 + H_2O \longrightarrow HNO_2$$

Similarly,

$$P_4O_6 + H_2O \text{ (cold)} \longrightarrow H_3PO_3$$
$$P_4O_6 + H_2O \text{ (hot)} \longrightarrow H_3PO_4 + PH_3$$

All the intermediate oxidation states of phosphorus has a tendency to undergo disproportionation to +5 and –3 both in acidic and in alkaline medium.

$$P_4O_{10} + H_2O \longrightarrow H_3PO_4$$

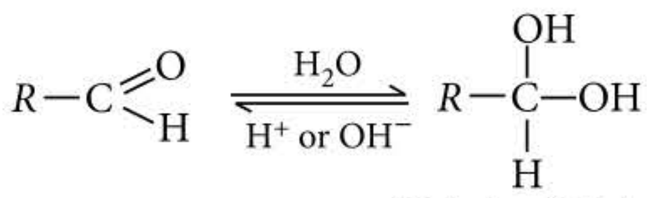
And,

$$Cl_2O_7 + H_2O \longrightarrow HClO_4$$
$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$
$$ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$$
$$Cl_2O + H_2O \longrightarrow HClO$$

Cl_2O_6 and ClO_2 are mixed anhydride.

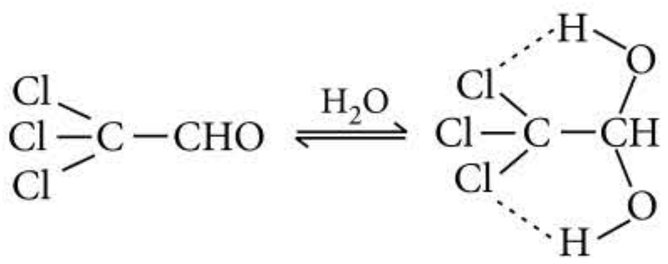
What about hydration in organic compounds?

Note that we have discussed hydrolysis in our previous episode.



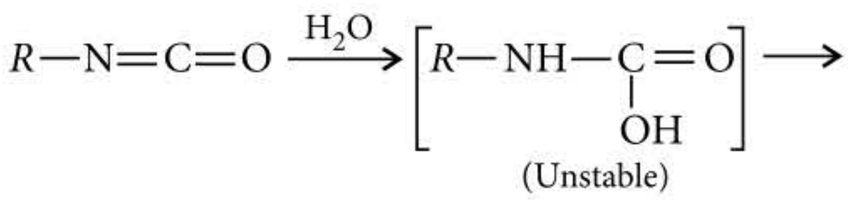
Hydrate of aldehyde

This is generally a reactant favoured equilibrium except a few like chloral, ninhydrin, etc.



Chloral hydrate

Isocyanate picks water but gets decomposed quickly.



(Unstable)

$$R{-}NH_2 + CO_2 + H_2O$$

Hydration of ketene gives carboxylic acid.