TDC Part I
Paper I, Group B
Inorganic Chemistry

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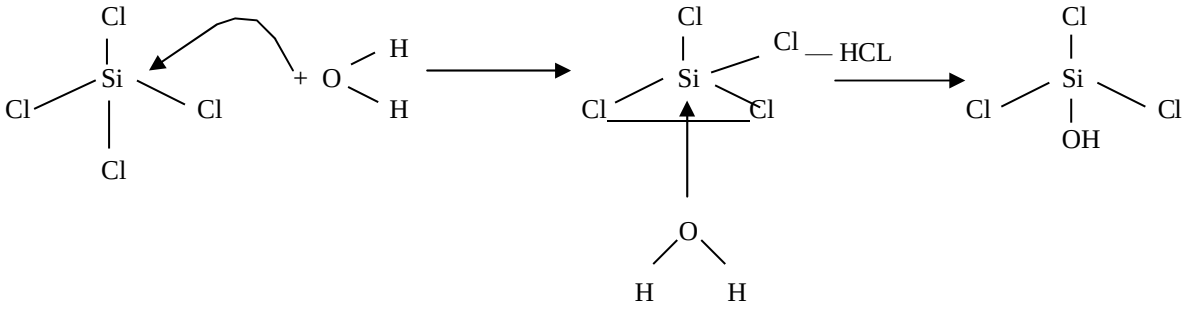
TOPIC:-Group-14,Halides

Halides

Tetra-halides (MX_4) of all elements are known; but Pb (IV) readily oxidizes iodide and hence the compound PbI_4 is not known. The stability of the tetra-halides decreases down the group. The fluorides, by virtue of high electronegativity of fluorine, are the most ionic. SnF_4 and PbF_4 are high melting solids; the others are covalent, tetrahedral and volatile. The halides of carbon are inert towards water, however the halides of silicon readily hydrolyze.

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4$$

The hydrolysis proceeds via an intermediate where silicon has a coordination number of five.



This process continues till Si-OH bonds replace all the Si-Cl bonds. Since carbon does not have d orbitals it cannot form such an intermediate and therefore tetra-halides of carbon do not hydrolyze.

Germanium, tin and lead form both tetra-halides and di-halides. The tetra-halides have a tendency to hydrolyze, but the hydrolysis can be suppressed by adding the appropriate halogen acid

$$SnCl_4 \underset{HCl}{\overset{H_2O}{\rightleftharpoons}} Sn(OH)_4$$

The halides of Si, Ge, Sn and Pb can increase the coordination number to 6 by forming complexes like $[SiF_6]^{2-}$, $[SnCl_6]^{2-}$ etc where the vacant d orbitals are used.

There is an increase in stability of dihalides on moving down the group

$SiX_2 << GeX_2 < SnX_2 < PbX_2$

SiF_2 can be made at high temperature by the reaction

$$SiF_4 + Si \rightleftharpoons 2SiF_2$$

Divalent germanium halides are stable. GeF_2 is polymeric having fluorine bridges. Tin (II) halides are well – characterized and the most important one is $SnCl_2$. it undergoes partial hydrolysis and is soluble in organic solvents. It is a mild reducing agent as shown by the following reactions:

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCL_4$$

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

Lead (II) halides are the most stable di-halides of this group. In fact, lead is the only element of this group with well- defined cation, Pb^{2+}. All lead halides are insoluble in water. In qualitative analysis Pb (II) is precipitated in group I of qualitative analysis as $PbCl_2$ and is confirmed as the yellow PbI_2 (s).

Fluorocarbons

Fluorocarbons are the equivalents of hydrocarbons where some or all hydrogen atoms are replaced by fluorine eg. CF_4, C_2F_4 etc. Replacement of hydrogen by fluorine increases the thermal stability and chemical inertness as the C-F bond is much stronger than the C-H bond (bond energies 489 and 414 KJ mol^{-1}). The fluorocarbons are prepared by treating the corresponding hydrocarbons with fluorine.

$$C_8H_{18} + 9F_2 \longrightarrow C_8F_{18} + 18HF$$

Fluorinating agents like CoF_3, AgF_2 and MnF_3 may also be used. Fluorocarbons of chain length of several hundred-carbon atoms are known. They are resistant to attack by acids, alkalis, oxidizing and reducing agents. They are attacked by molten sodium. On burning they split at the C-C bond and not at C-F bond.
The best-known fluorocarbon is polytetrafluoroethylene (Teflon).

$$_nC_2F_4 \xrightarrow[\text{\& Pressure}]{\text{High temp}} (-CF_2-CF_2-)_n$$

Teflon has a low coefficient of friction. It is thermally and chemically inert and a good insulator. It is used as a coating material in non-stick utensils, razors and bearings.

Mixed chlorofluorocarbons eg. $CFCl_3$, CF_2Cl_2 and CF_3Cl are called Freons. They are inert and non-toxic and widely used as refrigerants and propellants in aerosol. Their use in aerosols has been banned as they cause considerable environment damage. They persist unchanged on the atmosphere for a considerable period of time and are known to damage the ozone layer. Freons are also responsible for the ‘greenhouse effect’ alongwith carbon dioxide.