The p-Block Elements

Phosphorus

The allotropic forms of phosphorus:

Phosphorus exists mainly in three allotropic forms – white (yellow) phosphorus, red phosphorus and black phosphorus

1. **White phosphorus:** It is a translucent white waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3 (phosphine).

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2 \text{ (sodium hypophosphite)}$$

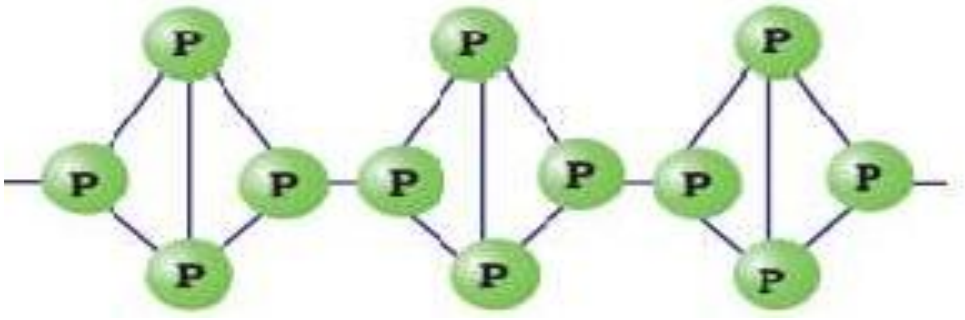
White phosphorus is less stable and therefore, more reactive. This is because in white phosphorus, th P-P-P bond angles are only 60°. So it has greater angular strain and highly unstable.

It readily catches fire in air to give dense white fumes of P_4O_{10}.

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

It consists of discrete tetrahedral P_4 molecule

2. **Red phosphorus:** It is obtained by heating white phosphorus at 573K in an inert atmosphere for several days. Red phosphorus has iron grey luster. It is odourless, non-poisonous and insoluble in water as well as in carbon disulphide. Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark. It contains polymeric chains of P_4 tetrahedral.



3. **Black phosphorus**: It has two forms- α-black phosphorus and β-black phosphorus. α-black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K. It does not oxidise in air. β-Black phosphorus is prepared by heating white phosphorus at 473K under high pressure. It does not burn in air up to 673K.

Phosphine (PH_3)

Preparation: It is prepared by the reaction of calcium phosphide with water or dilute HCl.

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3 \quad Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$$

In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$

(sodium hypophosphite)

Properties: It is a colourless gas with rotten fishy smell and is highly poisonous. It is slightly soluble in water. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2. When absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$$

$$3HgCl_2 + 2PH_3 \rightarrow\rightarrow Hg_3P_2 + 6HCl$$

Like NH_3, Phosphine is weakly basic and gives phosphonium compounds with acids.

$$PH_3 + HBr \rightarrow PH_4Br$$

Uses: Phosphine is technically used to produce Holme's signal. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea. The gases evolved burn and serve as a signal.

It is also used in smoke screens.

Phosphorus Halides

Phosphorus forms two types of halides- PX_3 and PX_5

Phosphorus trichloride (PCl_3)

Preparation: It is obtained by passing dry chlorine over heated white phosphorus.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

It is also obtained by the action of thionyl chloride with white phosphorus.

$$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

It is a colourless oily liquid and hydrolyses in the presence of moisture.

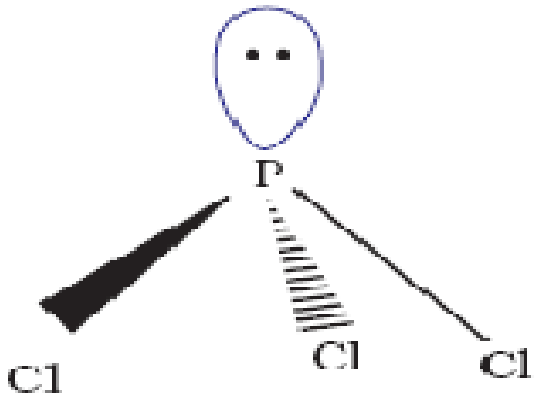
$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

It reacts with organic compounds containing –OH group such as CH_3COOH, C_2H_5OH.

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

$$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

Structure: It has a pyramidal shape as shown, in which phosphorus is sp^3 hybridized.



Phosphorus Pentachloride (PCl_5)

Preparation: Phosphorus Pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

It can also be prepared by the action of SO_2Cl_2 on phosphorus.

$$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$$

Properties

PCl_5 is a yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally gets converted to Phosphoric acid.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

When heated, it sublimes but decomposes on strong heating.

$$PCl_5 \rightarrow PCl_3 + Cl_2$$

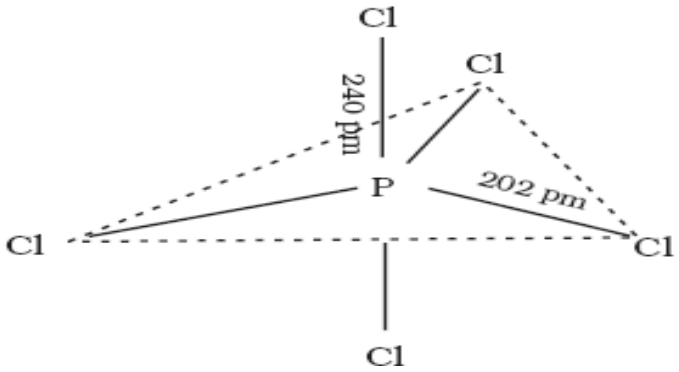
It reacts with organic compounds containing –OH group to give chloro derivative.

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

Structure:

In gaseous and liquid phases, it has a trigonal bipyramidal structure. The three equatorial P–Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.



In the solid state it exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$ is octahedral.

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