The *p*-block Elements (Group 15 elements) - Part 2

Objectives

After going through this lesson, the learners will be able to understand the following:

- Allotropes of phosphorus
- Hydride of phosphorus
- Halides of phosphorus
- Oxoacids of phosphorus

Contents Outline

- Introduction
- Phosphorus - Allotropes and their Properties
- Hydride of Phosphorus - Phosphine
- Halides of Phosphorus
- Oxoacids of Phosphorus
- Summary

Introduction

Phosphorus is the second element in group 15 and has a valence electronic configuration of $3s^2 3p^3$ which is the configuration of stable half filled orbitals. Like nitrogen, phosphorus is a non metal. It has only one stable isotope $^{31}_{15}P$. Though valence configuration of phosphorus is similar to nitrogen, the presence of vacant 3*d* orbitals in phosphorus helps it in achieving higher covalency and hence it forms compounds beyond those known for nitrogen. Differences in the properties of nitrogen and phosphorus are in the table 2.1.

Table 2.1 : Differences in nitrogen and phosphorus

Nitrogen	**Phosphorus**
Nitrogen has a maximum covalency of four.	Phosphorus can expand its covalency beyond 4 upto six by utilizing vacant 3*d* orbitals in its valence shell.
Nitrogen can form very stable *pπ-pπ* multiple bonds with small 2*p*	Phosphorus tends to form *dπ-pπ* multiple bonds by overlapping its

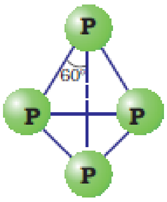
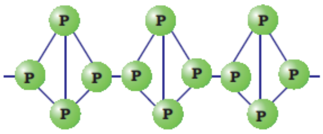
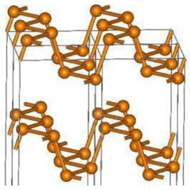
orbitals. It forms stable N≡N, N=N. N=C and N=O bonds.	vacant *d* orbitals with *p* orbitals of other atoms. It forms a stable P=O bond.
The N-N single bond is not stable because of lone pair lone pair repulsions between two nitrogen atoms.	P-P single bond with reduced lone pair lone pair repulsions is more stable than N-N single bond.

Phosphorus - Allotropes and their Properties

Phosphorus exists in many allotropic modifications that reflect the variety of ways of achieving coordination, the important ones being white, red and black. The differences in three allotropes are enlisted in table 2.2.

Table 2.2. Allotropes of phosphorus and their structure and properties

White Phosphorus	**Red Phosphorus**	**Black phosphorus**
White phosphorus is obtained when phosphate rock is heated with coke and sand in an electric furnace at 1773 K. $3Ca_3(PO_4)_2 + 6\ SiO_2 \rightarrow 6\ CaSiO_3 + P_4O_{10}$ $P_4O_{10} + 10C \rightarrow 10CO + P_4$	Red phosphorus is obtained by heating white phosphorus in an inert atmosphere at 573K for several days.	Black phosphorus (α-form) is formed when red phosphorus (β-form) is heated in a sealed tube at 803 K. Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.
It consists of a discrete tetrahedral P_4 molecule.	It is polymeric, consisting of chains of P_4 tetrahedral linked together.	Black phosphorus has layered structure in which each phosphorus atom is covalently bonded to three neighboring phosphorus atoms.
White phosphorus is less stable and therefore, the most reactive allotrope of phosphorus. P_4 has a tetrahedral structure in which	In red phosphorus, P_4 tetrahedrons link to each other to form polymeric structure. In this process some of the P-P bond angles in P_4 tetrahedrons	Here all phosphorus atoms are linked to each other to give a highly polymerised layer like structure. No angle strain is present in the

each of the vertices is occupied by phosphorus atoms. The molecule has a high angular strain as all P-P-P bond angles are only 60°.  	cleave, relieving some of the angle strain and imparting stability to the polymer. Red P is less reactive than white phosphorus.  	whole layer and the allotrope becomes thermodynamically the most stable form.  *Image source: [https://en.wikipedia.org/wiki/ Phosphorus#/](https://en.wikipedia.org/wiki/Phosphorus#/)*
White phosphorus is a translucent white waxy solid (α-form). It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence). It burns in air to produce dense white fumes of phosphorus pentoxide.	It is hard crystalline solid with iron-grey lustre. It is non-poisonous in nature. It is insoluble in water as well as organic solvent such as CS_2..	It has black metallic lustre.
White phosphorus is stored under water to protect it from the air. It burns in air to produce dense white fumes of phosphorus pentoxide.	Red phosphorus is quite stable in air.	Black phosphorus is stable in air and can be ignited only with difficulty.

Hydride of Phosphorus - Phosphine (PH_3)

Preparation

Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.

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

$Ca_3P_2 \ + \ 6HCl \rightarrow 3CaCl_2 \ + \ 2PH_3$

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

$P_4\,(s) \ + \ 3NaOH\,(aq) \ + 3H_2O(l) \rightarrow 3NaH_2PO_2\,(aq) \quad + \quad PH_3(g)$

Sodium hypophosphite Phosphine

When pure, it is non flammable but becomes inflammable owing to the presence of P_2H_4 or P_4 vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treatment with KOH gives off phosphine.

$PH_3\,(g) + HI\,(g) \ \rightarrow \ PH_4^{+}I^{-}\,(s)$

$PH_4^{+}I^{-}\,(s) + KOH\,(aq) \rightarrow KI\,(aq) + H_2O\,(l) + PH_3(g)$

Properties

It is a colorless gas with rotten fish smell and is highly poisonous. It explodes in contact with traces of oxidizing agents like HNO_3, Cl_2 and Br_2 vapours. It is only slightly soluble in water and is not associated like NH_3 because of decreased bond polarity. The solubility of phosphine in organic solvents is high. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2. When absorbed in copper sulfate or mercuric chloride solution, the corresponding phosphides (containing phosphorus in rare - 3 oxidation state) are obtained.

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

Copper phosphide

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

Mercuric phosphide

Phosphene is very weakly basic though it gives phosphonium compounds with acids e.g.,

$PH_3\,(g) \ + HBr\,(g) \rightarrow PH_4 + Br^{-}\,(s)$

The pure gas oxidizes in air at 150 °C but when contaminated with diphosphine P_2H_4, it is spontaneously flammable.

$PH_3 + 2O_2 \rightarrow H_3PO_4$

Phosphene is a strong reducing agent and reduces many metal salts to metals.

Structure

Phosphene (Fig.2.1) has pyramidal geometry with three P-H bond pairs and one lone pair on phosphorus atoms. The H-P-H bond angle is 93.7^0.

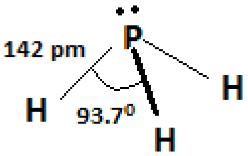


Fig.2.1. Structure of Phosphene

Uses

The spontaneous combustion of phosphine is technically used in *Holme's signals*. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gasses evolve to burn and serve as a signal. It is also used in *smoke screens*.

Halides of Phosphorus

Phosphorus reacts with halogens to form halides of two different compositions PX_3 and $PX_{5.}$ The most important halides are chlorides.

Phosphorus Trichloride

Preparation

It is obtained by passing dry chlorine to overheated white phosphorus.

$P_4(s) + 6Cl_2(g) \rightarrow 4\,PCl_3(l)$

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

$$\underset{\text{Thionyl chloride}}{P_4(s) + 8SOCl_2(l)} \rightarrow 4\,PCl_3(l) + 4SO_2(g) + 2S_2Cl_2(g)$$

Properties

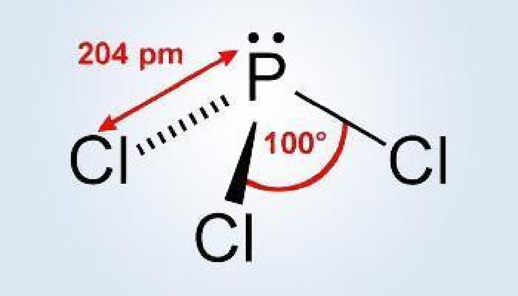


Fig. 2.2. Structure of phosphorus trichloride

(Image source: https://en.wikipedia.org/wiki/Phosphorus_trichloride#/)

Phosphorus trichloride has a pyramidal shape (Fig.2.2) with sp^3 hybridisation of phosphorus atoms. There are three bond pairs (P-Cl bond) and one non bonding electron pair on phosphorus atom.The Cl-P-Cl bond angle is 100°.

It is a colorless oily low boiling liquid (b.pt. 349 K) which undergoes a violent hydrolysis with water to give phosphorus acid.

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

It reacts with organic compounds containing –OH group and –COOH group to give chlorinated derivatives.

$$3RCO(OH) + PCl_3 \rightarrow 3RCOCl + H_3PO_3$$

$$3R(OH) + PCl_3 \rightarrow 3RCl + H_3PO_3$$

Phosphorus Pentachloride (PCl_5)

Preparation

Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess dry chlorine.

$$P_4(s) + 10Cl_2(g) \rightarrow 4PCl_5(s)$$

It can also be prepared by the action of SO_2Cl_2 (sulphuryl chloride) on white phosphorus.

$$P_4(s) + 10SO_2Cl_2 \rightarrow 4PCl_5(s) + 10SO_2(g)$$

Properties

PCl_5 is moisture sensitive yellowish white powder. In moist air, it hydrolyses to phosphoryl chloride, $POCl_3$ which finally gets completely hydrolysed to phosphoric acid.

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

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

or

$$PCl_5 + \underset{\text{(excess)}}{H_2O} \rightarrow H_3PO_4 + 5HCl$$

When heated, it sublimes but decomposes on strong heating into PCl_3 and Cl_2

$$PCl_5 \overset{\Delta}{\rightarrow} PCl_3 + Cl_2$$

Like PCl_3 it also reacts with organic compounds containing –OH and –COOH groups converting them to their chloro derivatives.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + PCl_5 \rightarrow \underset{\text{Chloroethane}}{CH_3CH_2Cl} + POCl_3 + HCl$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

It oxidizes and chlorinates finely divided metals also on heating to give corresponding chlorides.

$$Ag(s) + PCl_5 \overset{\Delta}{\rightarrow} AgCl + PCl_3$$

$$2Sn(s) + PCl_5 \overset{\Delta}{\rightarrow} SnCl_4 + 2PCl_3$$

Structure

PCl_5 has a trigonal bipyramidal geometry (Fig.2.3) with sp^3d hybridisation on phosphorus atoms. Equatorial P-Cl bonds are shorter than the axial P-Cl bonds. Two different Cl-P-Cl bond angles observed in the molecule are 90° (involving one axial and one equatorial Cl atom) and 120° (involving both equatorial Cl atoms).

PCl_5 is molecular in the gaseous phase, ionic in the crystalline phase, $[PCl_4]^+[PCl_6]^-$ and either molecular or ionically dissociated in solution depending on the nature of the solvent. In $[PCl_4]^+[PCl_6]^-$, the cation $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$ is octahedral.

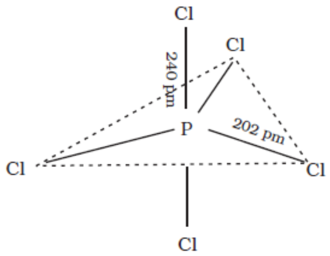


Fig.2.3. Phosphorus pentachloride

Oxoacids of Phosphorus

All the oxoacids of phosphorus contain at least one P=O bond and at least one P-OH bond. Some oxoacids of phosphorus also contain P-P bond or P-H bond but not both in the same acid. They are generally present in oxoacids which contain P in oxidation state less than +5. The oxoacids in +3 oxidation state undergo disproportionation reaction on heating

$$4H_3PO_3 \overset{\Delta}{\rightarrow} PH_3 + 3H_3PO_4$$

Phosphorus acid Phosphine orthophosphoric acid

The acids containing P–H bonds have strong reducing properties. Thus, hypophosphorous acid, H_3PO_2 , is a good reducing agent as it contains two P–H bonds and reduces $AgNO_3$ to metallic silver.

$$4\,AgNO_3\,(aq) + 2H_2O\,(l) + H_3PO_2\,(aq) \rightarrow 4Ag\,(s) + 4HNO_3\,(aq) + H_3PO_4\,(aq)$$

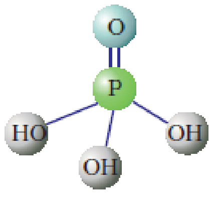
H_3PO_3 also acts as a reducing agent though weaker than H_3PO_2 because it contains only one P-H bond as compared to two in H_3PO_2.

The P-H bonds do not contain acidic hydrogen and hence do not release hydrogen as H^+ ion. Reducing property is observed for these acids by loss of hydrogen as [H] atom. Only those H atoms which are attached with oxygen in the P–OH group are ionisable and make the compound acidic. Thus, H_3PO_3 and H_3PO_4 are dibasic and tribasic, respectively as the structure of H_3PO_3 has two P–OH bonds and H_3PO_4 three P-OH bonds. Structure of oxoacid is shown in Fig.2.4. and their oxidation states are given in table 2.3.

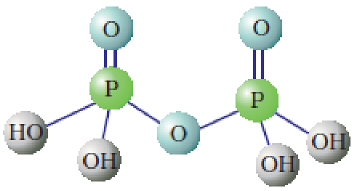
Phosphorus as phosphate esters play an important role in life processes. These phosphate containing biomolecules are DNA, RNA, and cyclic AMP. The energy giving reactions in bioprocesses involve a transfer of phosphate groups between ADP and ATP.

Table 2.3: Oxoacids of phosphorus with their oxidation state

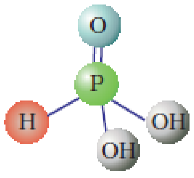
Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous (Phosphinic)	H_3PO_2	+1	One P – OH Two P – H One P = O	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Two P – OH Two P – H Two P = O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+4	Four P – OH Two P = O One P – P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three P – OH One P = O	$P_4O_{10}+H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four P – OH Two P = O One P – O – P	heat phosphoric acid
Metaphosphoric*	$(HPO_3)_n$	+5	Three P – OH Three P = O Three P – O – P	phosphorus acid + Br_2, heat in a sealed tube



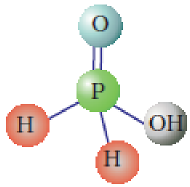
H_3PO_4
Orthophosphoric acid



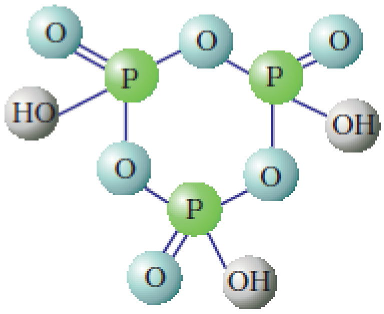
$H_4P_2O_7$
Pyrophosphoric acid



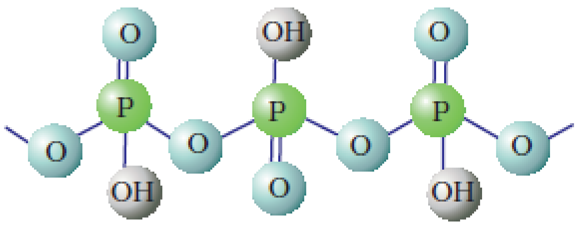
H_3PO_3
Orthophosphorous acid



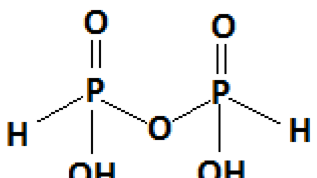
H_3PO_2
Hypophosphorous acid



Cyclotrimetaphosphoric acid, $(HPO_3)_3$



Polymetaphosphoric acid, $(HPO_3)_n$



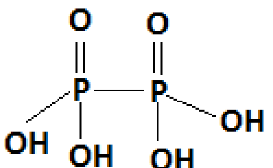


Fig 2.4. Solution state structures of oxoacids of phosphorus

Pure aqueous orthophosphoric acid and its salts -phosphates, find applications in food, detergent and toothpaste industries. When highly diluted, the aqueous acid does not have any specific odour and is non toxic. It is extensively used to impart sour or tart taste to carbonated soft drinks.

Summary

Phosphorus plays a crucial role in the biochemistry of all living beings. It is a constituent element of the bones and energy giving molecules in the body. As phosphate fertilizers it has its importance in plant life as well. Phosphorus exists in many allotropic modifications, the common ones being white phosphorus, red phosphorus and black phosphorus. White phosphorus is the most reactive allotrope and gives rise to faint greenish glow on oxidation in air. Phosphorus forms stable binary compounds with metals, hydrogen, oxygen and halogens.These are phosphides, phosphine, halides and oxoacids. The compounds formed contain phosphorus in -3, +3 and +5 oxidation states. It forms trihalides and pentahalides out of which mainly chlorides are important. Phosphorus forms a large number of oxoacids in which oxidation states of phosphorus range +1 to +5, with variable types of bonds like P=O, P-OH, P-H and P-P bonds. The number of these bonds differ from one type of oxoacid to the other. The oxoacids containing P-H bonds are reducing in nature. The presence of ionisable O-H groups makes these compounds acidic in nature.