

TDC Part I
Paper I, Group B
Inorganic Chemistry



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TOPIC:-Group 15, Oxides and Oxo Acids

Oxides and Oxo Acids of other elements

Phosphorous, arsenic and antimony form oxides in both +3 and +5 oxidation states, whereas only one oxide of bismuth, Bi_2O_3 is known. Except for Bi_2O_3 all other oxides are dimeric. They are obtained by direct combination. The structures of oxides of phosphorous are shown in fig 22.

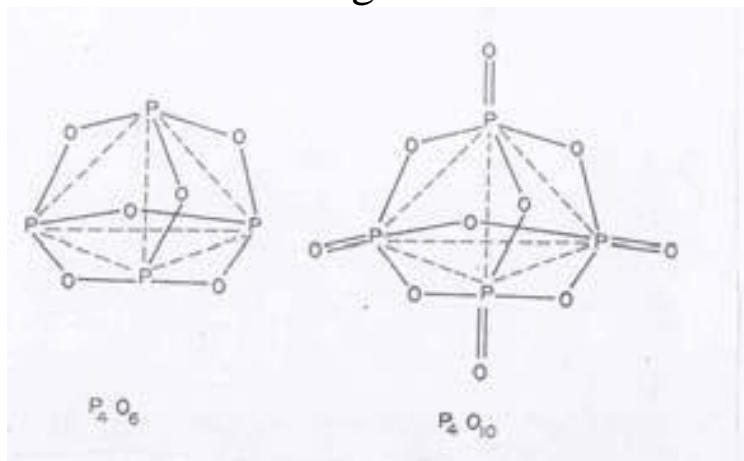


Fig. 22: Oxides of Phosphorus

The four apical bonds in P_4O_{10} have appreciable double bond character due to $p\pi-d\pi$ overlap.

The basic strength of the oxides increases on moving down the group. The oxides of P and As are acidic, those of Sb amphoteric and bismuth oxide is basic. Oxides in higher oxidation states are more acidic.

Oxoacids of Phosphorous, Arsenic & Antimony

The oxoacids of arsenic and antimony are not well – characterized but their salts are known. Phosphorous forms two series of oxo acids – phosphoric acid series containing P (V) and phosphorous acid series containing P (III)

The following generalization can be made:

- P is sp^3 hybridized.
- Acidic hydrogens are attached to oxygen
- The bond between P and non-hydroxylic oxygen has appreciable double bond character.
- The P-H bond confers reducing properties.

Some properties of the oxoacids of phosphorous are summarized in table 16.

Table 16: Oxoacids of Phosphorous

Formula	Name of Acid	Preparation	Remarks
H_3PO_2	Hypophosphorous	White P_4 + alkali	Monobasic Reducing $pK_a = 1.244$
H_3PO_3	Orthophosphorous	P_4O_6 or $PCl_3 + H_2O$	Dibasic, Reducing $pK_1 = 1.26$ $pK_2 = 6.70$
$(HPO_2)_n$	Metaphosphorous	$PH_3 + O_2$ (low pressure)	Polymerizes Structure not known
$H_4P_2O_6$	Hypophosphoric	Red P + alkali	Tetrabasic $pK_1 = 2.2$ $pK_2 = 2.8$ $pK_3 = 7.3$ $pK_4 = 10.0$
H_3PO_4	Orthophosphoric	$P_4O_{10} + H_2O$	Tribasic $pK_1 = 2.15$ $pK_2 = 7.20$ $pK_3 = 12.37$
$H_4P_2O_7$	Pyrophosphoric	Heat Phosphates or H_3PO_4	Tetrabasic $pK_1 = 1.0$ $pK_2 = 1.8$ $pK_3 = 6.6$ $pK_4 = 9.6$
$(HPO_3)_n$	Metaphosphoric	Heat H_3PO_4 to $350^\circ C$	Ring Structure

Some condensed phosphoric acids are known. The PO_4 tetrahedra are linked to form chains and structures of some of these are shown in Fig.23.

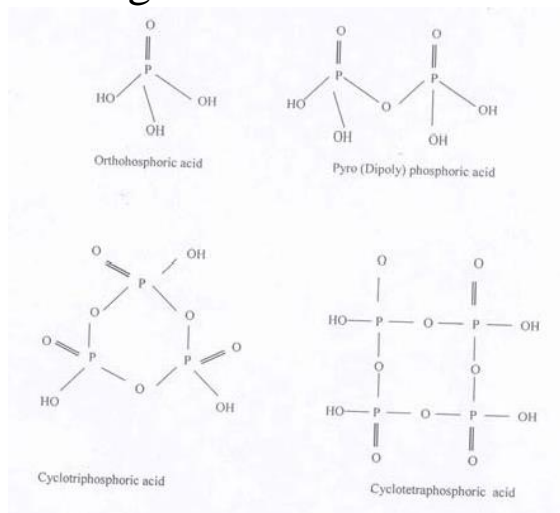


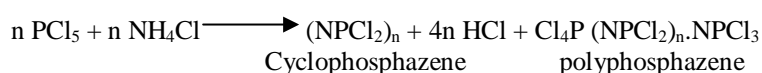
Fig. 23: Some oxoacids of Phosphorus

The $\text{P} - \text{O} - \text{P}$ linkage is very important in the biological system, as it is the prime store of energy. The energy of the bond (29 KJ mol^{-1}) is released by the hydrolysis of adenosine triphosphate.

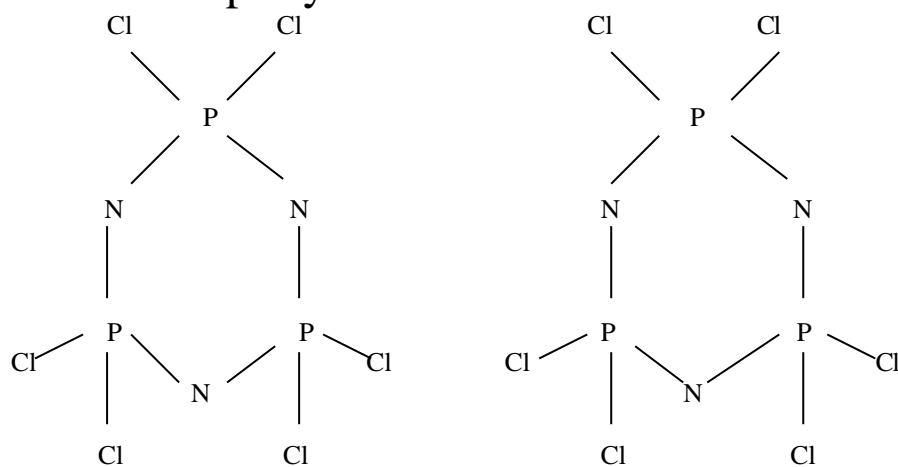
The world production of phosphates is about 50,000,000 tons. Phosphates find various uses in the food industry, in water softening, in fertilizers, toothpastes and detergents.

Phosphazenes

Nitrogen and phosphorous show little tendency to catenate by themselves. However they bond together to form cyclic and long chain polymers called phosphazenes (earlier referred to as phosphnitric polymers) containing alternate phosphorous and nitrogen atoms. In these compounds phosphorous and nitrogen are present in +5 and +3 oxidation states respectively. They may be prepared by the reaction between phosphorous pentachloride and ammonium chloride in dichloromethane at 120 to 150 C.

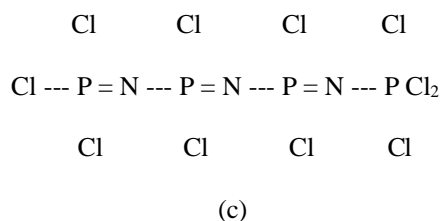


The reaction produces a mixture of ring compounds and short linear chains. Among the ring compounds the trimer and tetramer have been well characterized. The former exists as planar six membered rings with equal P—N distance (~158pm), considerably shorter than the P – N single bond (~177pm). This indicates a structure similar to benzene. The compound displays aromaticity though less than benzene. The compound can be expressed as a resonance hybrid, the N atoms are sp^2 hybridized and the P atoms are sp^3 hybridized.



The tetramer has a puckered structure.

A few chain polymers are:



Other atoms or groups can replace the Cl atoms. The amino, alkoxy, phenoxy and fluoro derivatives are stable and attracting interest as rigid plastics, plastic films, foams, fibres and elastomers. Such molecules (molar mass > 500,000) are

water repellent, flame resistant, flame resistant have good dielectric strength and are flexible at low temperatures. Due to these unique properties they have many potential uses but their cost is prohibitive. After silicones they are the most important inorganic polymers.