Greenwood & Earnshaw

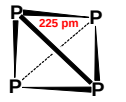
2nd Edition

Chapter 12

Phosphorus

Elemental Phosphorus

^{31}P (100% abundance), I = 1/2 , eleventh most abundant element in Earth's crust.
A = 30.973762(4) amu Most important mineral is apatite: $3Ca_3(PO_4)_2{\cdot}CaX_2$
Teeth and bones are mostly hydroxy apatite. X = OH, Cl, F
Vast deposits of fluoroapatite (Phosphate rock)

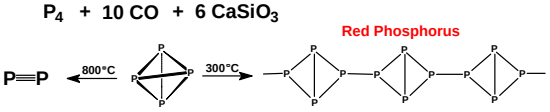


White Phosphorus

$2\ Ca_3(PO_4)_2 + SiO_2 + 10\ C \longrightarrow$

mp = 44.1°C
ρ = 1.8232 g/cm³

$P_4 + 10\ CO + 6\ CaSiO_3$



Red Phosphorus

ρ = 2.16 g/cm³

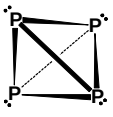
12,000+ atm.
200°C

Black Phosphorus

Three forms: orthorhombic; rhombohedral; cubic;

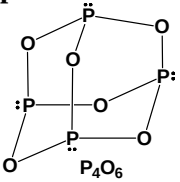
ρ = 2.69 g/cm³ ρ = 3.56 g/cm³ ρ = 3.88 g/cm³

Phosphorus Oxides



P_4

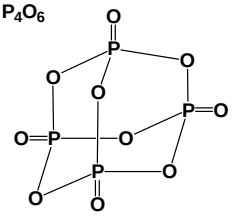
limited oxygen



P_4O_6

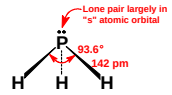
$\xrightarrow{O_2}$ P_4O_7 $\xrightarrow{O_2}$

:Ö: added each step



$P_4O_8 \xrightarrow{O_2} \xrightarrow{O_2} P_4O_{10}$

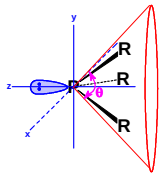
Phosphines & Organophosphines



mp -133.5°C
bp -87.7°C
$K_b = 4 \times 10^{-28}$

Insoluble in water, acidic in liquid ammonia, high barrier to inversion (6x that of ammonia). faint garlic odor, easily made by hydrolysis of calcium or aluminum phosphide, pyrolysis of phosphorous acid, reduction of PCl_3 and industrially by alkaline hydrolysis of P_4. Naturally formed by anaerobic degradation of phosphates along with some P_2H_4. PH_3 is the only stable phosphine, but P_2H_4 and P_3H_5 have been obtained pure and are pyrophoric.

Organophosphines:



σ donors:

$PBu^t_3 > P(OR)_3 > PR_3 \sim PPh_3 > PH_3 > PF_3 > P(OAr)_3$

π acceptors:

$PF_3 > P(OAr)_3 > PH_3 > P(OR)_3 > PPh_3 \sim PR_3 > PBu^t_3$

steric interference: (θ = cone angle)

$PBu^t_3 > PPh_3 > P(OAr)_3 > P(CH_3)_3 > P(OR)_3 > PF_3 > PH_3$

θ = 182°, 145°, 121°, 118°, 107°- 109°,104°, 87°.

Organophosphines are important ligands in organometallic chemistry & catalysis.

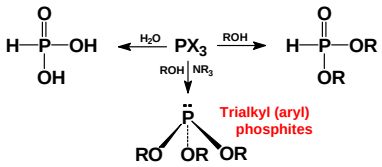
Organophosphines & Phosphorus Halides

- **$P(CH_3)_3$ – volatile liquid, bp = 37.8°C, strong garlic odor, pyrophoric, very toxic.**
- **PBu_3 – less volatile liquid, bp = ~240°C, faint odor, fumes in air, more air stable, toxic if injested, flammable.**
- **PPh_3 – not very volatile solid, mp = 80°C, faint "nutty"odor, relatively air stable, toxic if injested.**
- **PF_3 – gas, bp = -101.8°C, odorless, relatively water stable, unreactive, *very toxic*, ligand properties ≅ CO.**
- **PCl_3 PBr_3 PI_3 – Hydrolyze rapidly, react with oxygen to form $O{=}PX_3$, PX_3, X = Cl, Br act as ligands .**

Phosphorus (III & V) Halides

P(III) Halides:

	Boiling point	∠XPX
PF_3	-101.8°C	96.3°
PCl_3	76.1°C	100°
PBr_3	173.2°C	101°
PI_3	>200°C	102°



P(V) Halides:

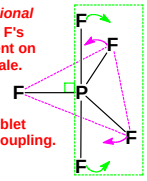
PF_5 gas, bp = -84.5°C, trigonal bipyramidal molecule, fluoride ion acceptor.

PCl_5 solid is: $PCl_4^+ PCl_6^-$ T_{subl} = 162°C gas is trigonal bipyramidal molecule.

PBr_5 solid is: $PBr_4^+ Br^-$ T_{dec} = 106°C

PI_5 solid is: $PI_4^+ I^-$

PF_5 is a *fluxional* molecule all F's are equivalent on nmr time scale.

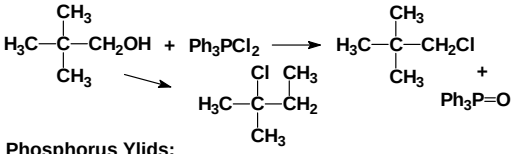


^{19}F nmr is a doublet due to ^{31}P-^{19}F coupling.

Phosphoranes & Phosphorus Ylids

$R_3PX_2 \longleftarrow R_3P + X_2$ X = F, Cl species are molecular. X = Br, I species are ionic.

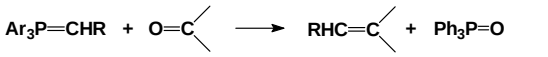
Useful in organic chemistry to convert alcohols to alkyl halides without forming a carbocation intermediate.



Phosphorus Ylids: ("ill-eds")

Wittig Reagent 1979 Nobel Prize

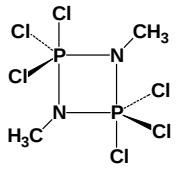
$Ar_3P + RCH_2X \longrightarrow [Ar_3PCH_2R]^+ X^- \xrightarrow[-R'H\ -LiX]{R'Li} Ar_3P{=}CHR$



Phosphorus-Nitrogen - Phosphazanes

P(V) Most common. Have formally P-N single bonds.

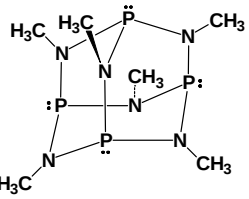
$2\ PCl_5 + 2\ MeNH_3^+\ Cl^- \longrightarrow$



The phosphorus atom is trigonal bipyramidal, the axial P-N bond is longer than the equatorial bond.

P(III)

$4\ PCl_3 + 6\ MeNH_3^+\ Cl^- \longrightarrow$



Isoelectronic with P_4O_6 adamantane structure.

Phosphorus-Nitrogen - Phosphazenes

P(V) Most common. Have formally P-N double bonds.

$Ph_3P + PhN_3 \longrightarrow N_2 + Ph_3P{=}NPh$ Simplest Ph—N: "nitrene"

$Ph_3PCl_2 + PhNH_2 \longrightarrow 2\ HCl + Ph_3P{=}NPh$

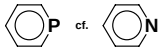
$2\ Ph_3PCl_2 + NH_4^+Cl^- \longrightarrow [Ph_3P{=}N{=}PPh_3]^+\ Cl^- + 4\ HCl$

The "bistriphenylphosphine immonium" ion is an excellent counter-ion for stabilizing transition metal carbonyl anions, many salts become "air stable".

The $d\pi$-$p\pi$ double bond, unlike in allene need not be 180°. For example: $[Ph_3P{=}C{=}PPh_3]$ Two molecules in unit cell, each different. $\angle_{PCP}$ = 130°&144°

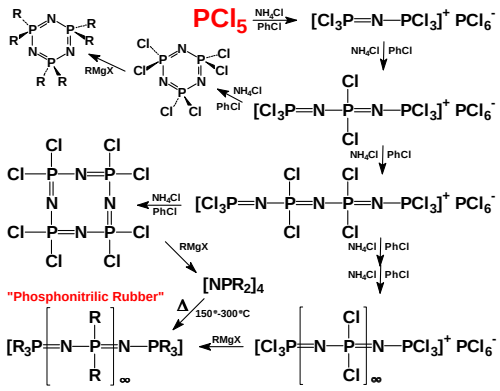
Other Species: P═C P≡C P═P

R—C≡P: R = H, Bu^t, F, CF_3 Unstable wrt polymerization, as a ligand will displace ethylene.

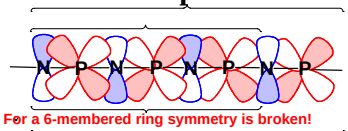
 cf. HP═CH_2 cf. HN═CH_2

cyclo$(CF_3P)_4 + P(CH_3)_3 \underset{r.\ t.}{\overset{dec\ T}{\rightleftharpoons}} (CH_3)_3P{=}PCF_3$

Phosphorus-Nitrogen - Phosphazenes



Phosphazenes - Bonding



Trimers are planar.

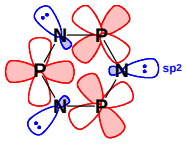
Tetramers are mostly non-planar. Planarity is not necessary for $d\pi$-$p\pi$ conjugation.

$[NPF_2]_4$ is planar!

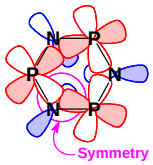
For a 6-membered ring symmetry is broken!

For an 8-membered ring symmetry is unbroken!

Trimers may use an "exocyclic" conjugation.

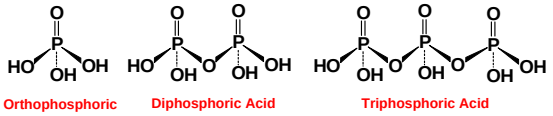


Symmetry is unbroken!



Symmetry is broken!

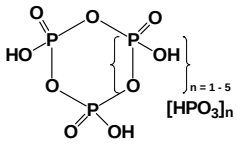
Oxoacids of Phosphorus(V)



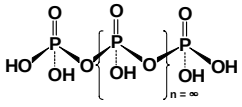
Orthophosphoric Acid

Diphosphoric Acid
Pyrophosphoric Acid

Triphosphoric Acid



Cyclotriphosphoric Acid
Trimetaphosphoric Acid

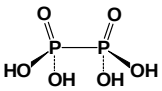


H_3PO_3

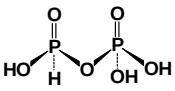
Polyphosphoric Acid
Metaphosphoric Acid

Polyphosphoric acids do not hydrolyze rapidly in water. Sometimes very slowly.
Poly phosphoric acids strongly influence the properties of water.

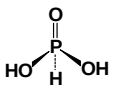
Oxoacids of Phosphorus(IV)-(III)



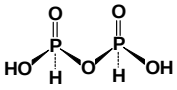
Hypophosphoric Acid
Diphosphoric(IV) Acid



Isohypophosphoric Acid
Diphosphoric(III-V) Acid



Phosphonic Acid
Phosphorous Acid



Diphosphonic Acid
Pyrophosphorous Acid

Phosphinic Acid
Hypophosphorous Acid