Phosphorus

White Phosphorus

\[ ^{31}\text{P} \text{ (100% abundance), } I = \frac{1}{2}, \text{ eleventh most abundant element in Earth's crust.} \]
\[ A = 30.973762(4) \text{ amu} \]
Most important mineral is apatite: \[ 3\text{Ca}_3(\text{PO}_4)_2\text{CaX}_2 \]
Teeth and bones are mostly hydroxy apatite. \[ X = \text{OH, Cl, F} \]

Vast deposits of fluoroapatite (Phosphate rock)

\[ 2 \text{Ca}_3(\text{PO}_4)_2 + \text{SiO}_2 + 10 \text{C} \rightarrow \text{Red Phosphorus} \]

\[ \text{Red Phosphorus} \]

\[ P_4 + 10 \text{CO} + 6 \text{CaSiO}_3 \text{ (Red Phosphorus)} \]

\[ 12,000+ \text{atm.} \]

\[ \rho = 2.16 \text{ g/cm}^3 \]

\[ \text{Black Phosphorus} \]

Three forms: orthorhombic; rhombohedral; cubic;

\[ \rho = 2.69 \text{ g/cm}^3 \]
\[ \rho = 3.56 \text{ g/cm}^3 \]
\[ \rho = 3.88 \text{ g/cm}^3 \]

Phosphorus Oxides

\[ \text{Phosphorus Oxides} \]

\[ \text{added each step} \]

\[ P_4 \rightarrow P_4\text{O}_{10} \]
Phosphines & Organophosphines

Phosphines are 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 PCl₃ and industrially by alkaline hydrolysis of P₄.

Naturally formed by anaerobic degradation of phosphates along with some P₂H₄. PH₃ is the only stable phosphine, but P₂H₄ and P₃H₅ have been obtained pure and are pyrophoric.

Organophosphines:
- ππππ ππππ acceptors:
  - PF₃ > P(OAr)₃ > PH₃ > P(OR)₃ > PPh₃ ≈ PR₃ > PBu₃
- σσσσ σσσσ donors:
  - PBu₃ > P(OAr)₃ > PPh₃ > P(CH₃)₃ > P(OR)₃ > PF₃ > PH₃

Steric interference: θ = cone angle
- PBu₃ > PPh₃ > P(OAr)₃ > P(CH₃)₃ > P(OR)₃ > PF₃ > PH₃

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

Organophosphines are important ligands in organometallic chemistry & catalysis.

Organophosphines & Phosphorus Halides

- P(CH₃)₃ – volatile liquid, bp = 37.8°C, strong garlic odor, pyrophoric, very toxic.
- PBu₃ – less volatile liquid, bp = ~240°C, faint odor, fumes in air, more air stable, toxic if ingested, flammable.
- PPh₃ – not very volatile solid, mp = 80°C, faint "nutty" odor, relatively air stable, toxic if ingested.
- PF₃ – gas, bp = -101.8°C, odorless, relatively water stable, unreactive, very toxic, ligand properties ≅ CO.
- PCl₃, PBr₃, PI₃ – Hydrolyze rapidly, react with oxygen to form O=PX₃, PX₃, X = Cl, Br act as ligands.

Phosphorus (III & V) Halides

<table>
<thead>
<tr>
<th>Halide</th>
<th>Boiling point</th>
<th>σ-donor</th>
<th>π-acceptor</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF₃</td>
<td>-101.8°C</td>
<td>96.3°</td>
<td></td>
</tr>
<tr>
<td>PCl₃</td>
<td>173.2°C</td>
<td>100°</td>
<td></td>
</tr>
<tr>
<td>PBu₃</td>
<td>176.1°C</td>
<td>101°</td>
<td></td>
</tr>
<tr>
<td>PPh₃</td>
<td>&gt;200°C</td>
<td>102°</td>
<td></td>
</tr>
<tr>
<td>PCl₅</td>
<td>76.1°C</td>
<td>107°</td>
<td></td>
</tr>
<tr>
<td>PBr₅</td>
<td>107°</td>
<td>118°</td>
<td></td>
</tr>
<tr>
<td>PI₅</td>
<td>121°</td>
<td>118°</td>
<td></td>
</tr>
</tbody>
</table>

P(V) Halides:

<table>
<thead>
<tr>
<th>Halide</th>
<th>Boiling point</th>
<th>σ-donor</th>
<th>π-acceptor</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF₅</td>
<td>44.5°C</td>
<td>96.3°</td>
<td></td>
</tr>
<tr>
<td>PCl₅</td>
<td>112°C</td>
<td>107°</td>
<td></td>
</tr>
<tr>
<td>PBu₅</td>
<td>101°C</td>
<td>118°</td>
<td></td>
</tr>
<tr>
<td>PPh₅</td>
<td>109°C</td>
<td>118°</td>
<td></td>
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<td>109°C</td>
<td>118°</td>
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PF₅ is a fluxional molecule all F's are equivalent on nmr time scale.

19F nmr is a doublet due to 1P-1F coupling.
Phosphoranes & Phosphorus Ylids

\[ R_3PX_2 \rightarrow R_3P + X_2 \]

\( X = F, Cl \) species are molecular.
\( X = Br, I \) species are ionic.

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

\[ \text{Phosphorus Ylids: } \]

\[ \text{Wittig Reagent } \]

1979 Nobel Prize

Phosphorus-Nitrogen - Phosphazenes

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

\[ 2 \text{PCl}_3 + 2 \text{MeNH}_3^+ \text{Cl}^- \]

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

P(III)

\[ 4 \text{PCl}_3 + 6 \text{MeNH}_3^+ \text{Cl}^- \]

Isoelectronic with \( \text{P}_4\text{O}_6 \) adamantane structure.

Phosphorus-Nitrogen - Phosphazanes

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

\[ \text{P} + \text{Ph}_3\text{N} \rightarrow \text{Ph}_3\text{P} = \text{NPh} \]

Simplest "nitrene"

\[ \text{Ph}_3\text{PCl}_2 + \text{PhNH}_2 \rightarrow 2 \text{HCl} + \text{Ph}_3\text{P} = \text{NPh} \]

2 \( \text{Ph}_3\text{PCl}_2 + \text{NH}_4^+ \text{Cl}^- \rightarrow [\text{Ph}_3\text{P} = \text{NPh}]^+ \text{Cl}^- + 4 \text{HCl} \]

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

The d\text{π}-p\text{π} double bond, unlike in allene need not be 180°. For example:

\[ [\text{Ph}_3\text{P} = \text{C} = \text{Ph}]_2 \]

Two molecules in unit cell, each different. \( \angle \text{COP} = 130^\circ/144^\circ \)

Other Species: \( \text{P} = \text{C} \quad \text{P} = \text{C} \quad \text{P} = \text{P} \)

Unstable wrt polymerization, as a ligand will displace ethylene.

\[ \text{R} = \text{H}, \text{Bu}^+, \text{F}, \text{CF}_3 \]

\[ \text{cyclo(CF}_3\text{P)}_2 \]

\[ \text{Ph} = \text{CH}_2 \quad \text{H} = \text{CH}_2 \]

\[ \text{cyclo(CF}_3\text{P)}_2 + \text{P(\text{CH}_2)}_3 \xrightarrow{\Delta \text{C}} (\text{CH}_2)_3\text{P} = \text{PCF}_3 \]
Phosphorus-Nitrogen - Phosphazenes

\[
\text{PCl}_5 \xrightarrow{\text{MgCl}_2, \text{NH}_4\text{Cl}} \text{[Cl}_3\text{P=N-P-Cl]}^+ \text{PCl}_6^-
\]

\[
\text{PCl}_3^+ \text{PCl}_6^- - \text{NPN}[\text{Cl}_3\text{P}]
\]

\[
\text{NH}_4\text{Cl PhCl}
\]

\[
\text{[R}_3\text{P=N-P-R]}_n \xrightarrow{\text{MgCl}_2, \text{NH}_4\text{Cl}} \text{[Cl}_3\text{P=N-P-Cl]}^+ \text{PCl}_6^-
\]

"Phosphonitrilic Rubber"

\[\text{MgCl}_2, \text{NH}_4\text{Cl} 150 - 300^\circ C\]

Trimers are planar. Tetramers are mostly non-planar. Planarity is not necessary for \(d\pi-d\pi\) conjugation. \([\text{NPF}_2]_4\) is planar!

Trimers may use an "exocyclic" conjugation.

Symmetry is broken!

Symmetry is unbroken!

Phosphazenes - Bonding

For a 6-membered ring symmetry is broken!

For an 8-membered ring symmetry is unbroken!

Oxoacids of Phosphorus(V)

Orthophosphoric Acid
Diphosphoric Acid
Pyrophosphoric Acid
Triphosphoric Acid

Cyclotriphosphoric Acid
Trimetaphosphoric 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 Acid
- Isohypophosphoric Acid
- Diphosphoric Acid
- Phosphonic Acid
- Phosphorous Acid
- Diphosphonic Acid
- Pyrophosphorous Acid
- Phosphinic Acid
- Hypophosphorous Acid