Nitrogen Oxides :

electron configuration $(\sigma_1)^2(\sigma_1^*)^2(\sigma_2, \pi)^6(\pi^*)$

2. (Nitric oxide/Nitrogen monooxide; NO)

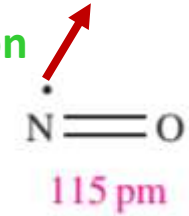
- ✓ most stable among all oxides of N

Lewis dot diagram for nitric oxide, NO

Lewis dot diagram for nitrosonium ion, NO^+

Odd-electron molecules formed by main group elements are relatively rare. Another example is ClO_2.

Odd electron



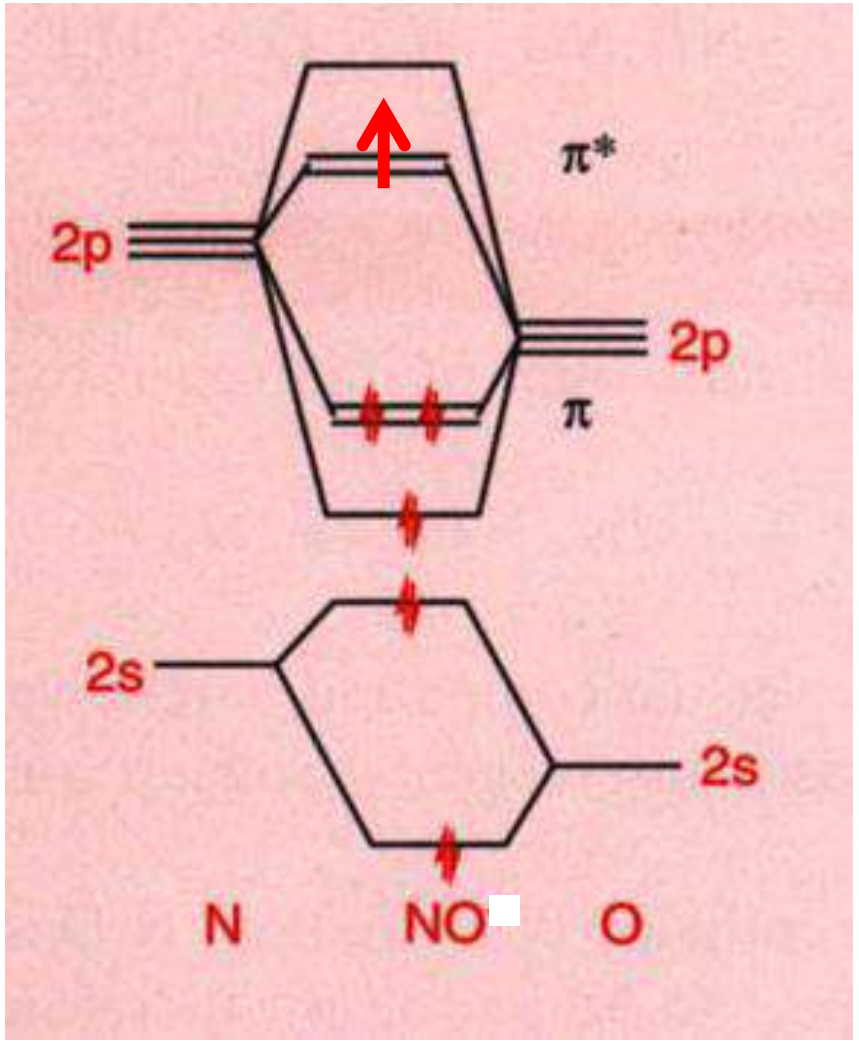
- ✓ contains only one unpaired electron
- ✓ shared over the whole molecule
- ✓ paramagnetic and chemically more reactive
- ✓ little tendency to dimerize to N_2O_2 only at RT by pairing up of this unpaired electron
- ✓ loss of odd electron gives NO^+ (nitrosonium or nitrosyl)
- ✓ odd electron molecule but different i.e. gaseous : colourless while solid/liquid : blue
- ✓ odd electron in antibonding orbital

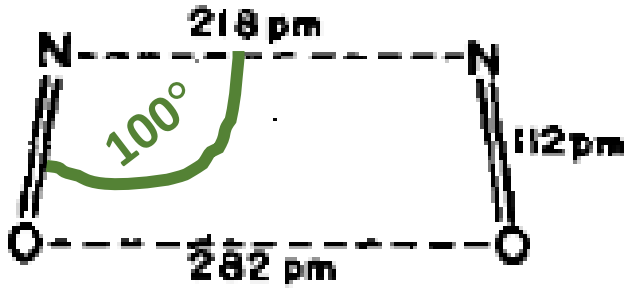
sp^2 hybridisation for N

Nitrogen Oxides :

2. Nitric oxide/Nitrogen monooxide; NO)

✓ most stable among all oxides of N





- overall 15 electrons : so odd
- shortening of bond length from NO to NO^+
- brown ring of nitrate test is due to $[Fe(H2O)_5NO]^{2+}$ complex
- The brown colour is due to the formation of $[Fe(H2O)_5NO]^{2+}$ complex an example of one of many nitrosyl complexes in which NO acts as a ligand

Nitrogen Oxides :

2. Nitric oxide/Nitrogen monooxide; NO)

✓ ❖ **Preparation**

$$4NH_3 + 5O_2 \xrightarrow{1300\ K,\ Pt\ catalyst} 4NO + 6H_2O$$

$$[NO_3]^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$2[NO_3]^- + 6Hg + 8H^+ \longrightarrow 2NO + 3[Hg_2]^{2+} + 4H_2O$$

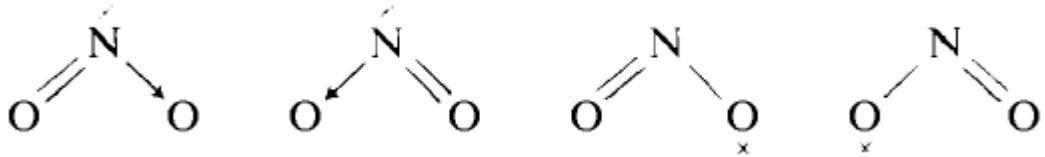
❖ **Features**

- NO is a radical. Unlike NO_2, it does not dimerize unless cooled to low temperature under high pressure. In the diamagnetic solid, a dimer with a long N-N bond (218 pm) is present
- It is produced during the during combustion of motor and aircraft fuels triggering smog formation/pollution over large cities
- Though gaseous NO shows no sign of dimerization, partial dimerization occurs in liquid NO. The dimer is diamagnetic as per the expectation due to the pairing up of the two unpaired electrons coming from the two interacting single NO monomeric molecules
- Moreover, this reluctance of dimer formation owes to the unchanged total bond order even when two NO molecules come closer i.e. 2*2.5= 5
- In gaseous state: no dimerization : colourless
- In liquid/solid state : dimerization occurs : blue coloured

Nitrogen Oxides :

3. Nitrogen dioxide; NO_2 + dinitrogen tetroxide; N_2O_4

The structure of nitrogen dioxide contains an unpaired (odd) electron and the molecule is consequently paramagnetic. The odd electron is not localised on any atom and the structure can be best represented as a resonance hybrid of the structures :



$$2NO_2 \underset{\text{Paramagnetic}}{\text{Brown}} \rightleftharpoons N_2O_4 \underset{\text{Diamagnetic}}{\text{Colorless}}$$

- **Both N-O have equal bond length**
- **unlike NO, this has more resemblance to odd electron molecule**
- **coloured (brown) and unpaired electron mainly locates on N**
- **dimerises to colourless gas N_2O_4 (dinitrogen tetroxide) ; diamagnetic**

N_2O_4 $\rightleftharpoons$	N_2O_4 $\rightleftharpoons$	$2NO_2$ $\rightleftharpoons$	$2NO + O_2$
(m.p. 262 K)	(b.p. 294 K)	(100 % at 423 K)	(100 % at 870 K)
colourless solid	pale yellow liquid	dark brown gas	colourless gases

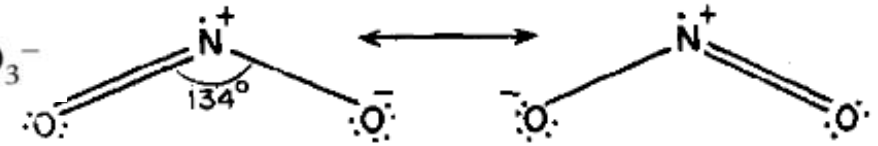
Nitrogen Oxides :

3. Nitrogen dioxide; NO_2 + dinitrogen tetroxide; N_2O_4

NO_2 with 23 electrons is again an odd electron molecule. In the gaseous state it is paramagnetic. On cooling, the gas condenses to a brown liquid and eventually to a colourless solid both of which are diamagnetic due to dimerisation. NO_2 molecule is angular with ONO angle of 134°. The O–N bond length is 120 pm, intermediate between a single and a double bond. The odd electron is on nitrogen. The dimer has been shown to have a planar structure. The N–N bond length is very large, **175 pm**, making this a very weak bond

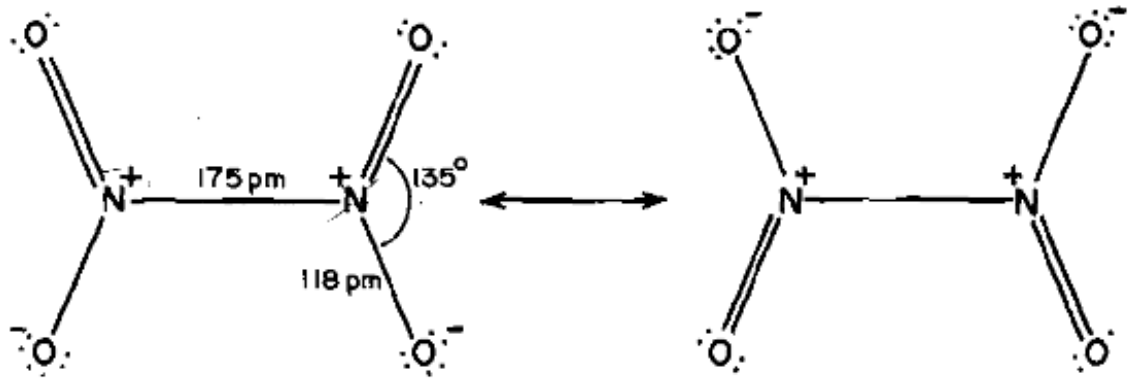
sp^2 hybridisation for N

$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$



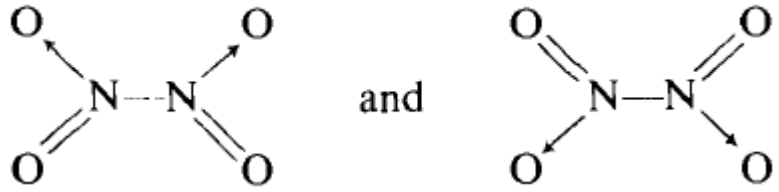
Auto-ionization to NO^+ and NO_3^- as well as two molecules of $2NO_2$+

sp^2 hybridisation for both N ; trigonal planar geometry/ sp^3 for O



Nitrogen Oxides :

3. Nitrogen dioxide; NO_2 + dinitrogen tetroxide; N_2O_4



$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ ΔH positive

- Both N-O have equal bond length
- most stable planar : O_2N-NO_2 but liq. N_2 T, may be twisted or non-planar form
- stability of former is due to maximized O-O repulsions and unusually long N-N bond

By Le Chatelier's principle, increased pressure will cause the equilibrium position to shift to the left, to favour N_2O_4, because there are two gaseous molecules on the right and one on the left. Since the reaction is endothermic, increased temperature will favour the forward reaction, producing more NO_2.

Nitrogen Oxides :

3. Nitrogen dioxide; NO_2 + dinitrogen tetroxide; N_2O_4

❖ Preparation

$$2Pb(NO_3)_2(s) \xrightarrow{\Delta} 2PbO(s) + 4NO_2(g) + O_2(g)$$

- **Unlike nitrogen monoxide, nitrogen dioxide has properties more typical of an odd electron molecule. It is a coloured (brown), reactive gas which dimerises to the diamagnetic colourless gas dinitrogen tetroxide, N_2O_4, in which the odd electron is paired**
- **The structures $NO^+NO_3^-$ and ONONO2 have also been identified. The structure shown has a very long N – N bond (~ 175 pm), but the N – N bond in N_2H_4 is only 147 pm.**
- **NO_2 is a radical with one unpaired electron. It can lose its unpaired electron to give the nitronium ion NO_2^+**
- **N_2O_4 is a planar molecule with a rather N-N** bond (1.75Å). Here N atom is likely to have sp^2 hybridisation. One hybrid orbital contains the odd electron; the other two make σ bonds with p orbitals on the two O atoms
- The unpaired electron in NO_2 seems to be more localised on N atom compared to NO, stimulating instant dimerization. The longer N-N bond attributes to delocalisation of bonding electron pair of the whole molecule

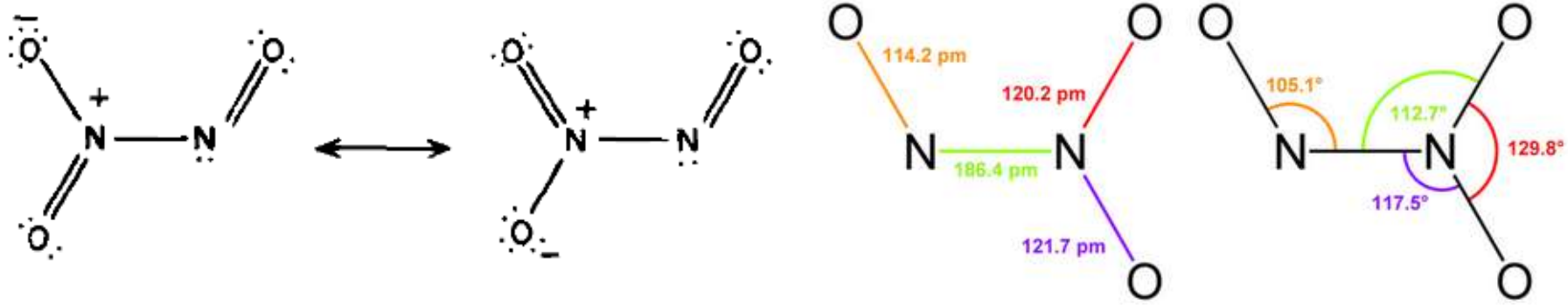
Nitrogen Oxides :

4. Dinitrogen trioxide; N_2O_3

$$N_2O_3(g) = NO^{+}(g) + NO_2^{-}(g) \qquad \Delta H = 39.7\ \text{kJ mol}^{-1}$$

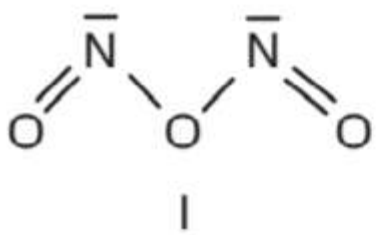
- N_2O_3 is prevalent at low T, when blue solid or liquid ; planar
- but dissociates back to NO and NO_2 at gas phase $2NO + N_2O_4 \rightleftharpoons 2N_2O_3$
- odd electrons of NO and NO_2 pair up to give product; hence this is diamagnetic and contains no odd electrons

sp^2 hybridisation for both N ; trigonal planar geometry/ sp^3 for O

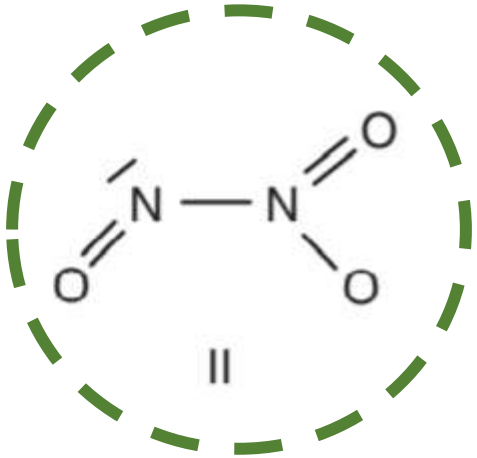


Nitrogen Oxides :

4. Dinitrogen trioxide; N_2O_3

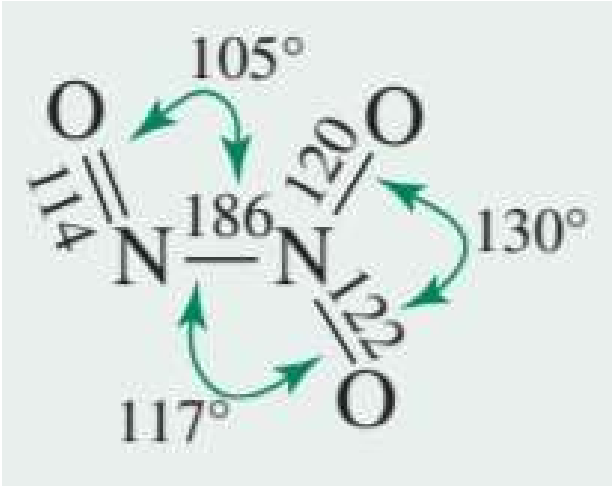


I



II

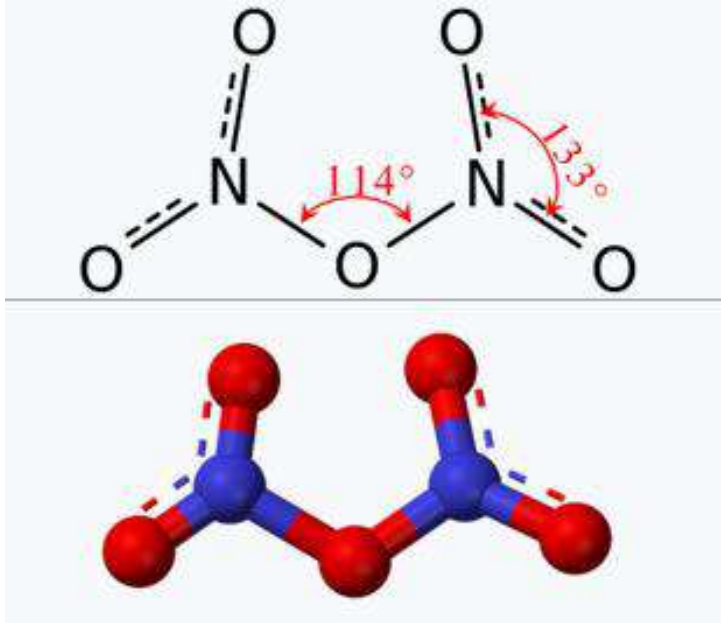
Dominant structure



N_2O_3 is formed from NO and NO_2 at low temperatures, where it is a blue solid or liquid, but it dissociates-back to NO and NO_2 in the gas phase

Nitrogen Oxides :

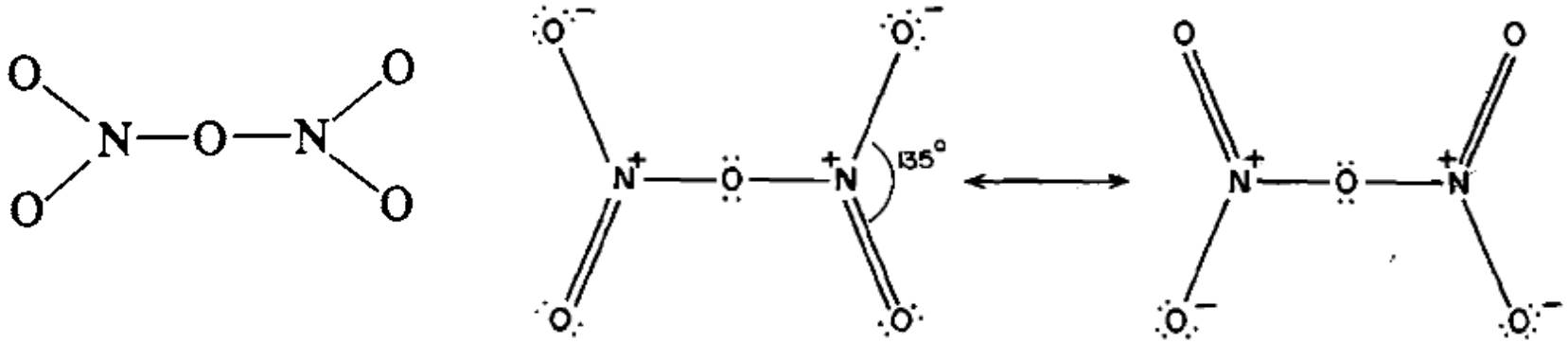
4. Dinitrogen trioxide; N_2O_3



Molecular shape	planar, C_{2v} (approx. D_{2h}) N–O–N ≈ 180°

Nitrogen Oxides :

5. Dinitrogen pentoxide; N_2O_5



• bent N-O-N group though angle can be ~180°

• generally covalent in its molecular form but crystallises as nitronium nitrate i.e. $NO_2^+NO_3^-$

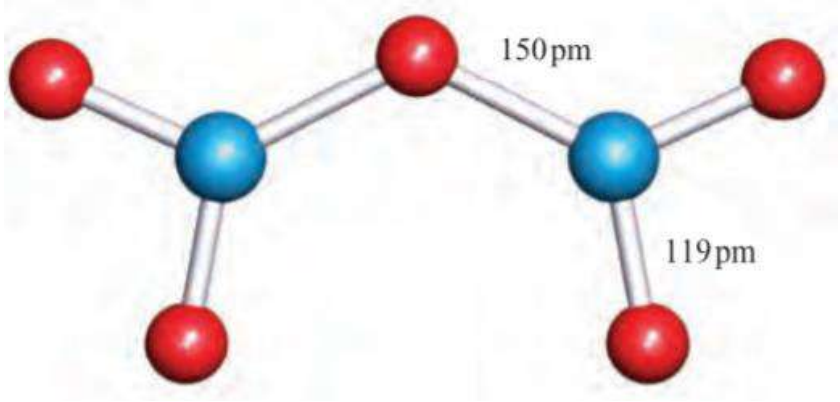
• linear NO_2^+ and planar NO_3^-

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

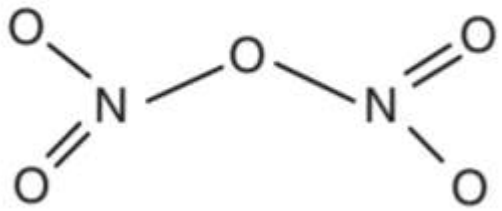
Nitrogen Oxides :

5. Dinitrogen pentoxide; N_2O_5

- **Dinitrogen pentoxide is the anhydride of nitric acid and is prepared by removing water from pure nitric acid by means of phosphorus (V) oxide. It is a crystalline solid having the ionic structure of $(NO_2)^+$ $(NO_3)^-$, nitronium nitrate**



N-O-N bond angle = 112°
O-N-O bond angle = 133°



In accord with the oxidation state of nitrogen in this oxide being 5, it is also a good oxidizing agent. There is some evidence that NO_3 exists in mixtures of N_2O_5 and ozone. Very strong oxidising agent

Phosphorous Oxides :

Phosphorus forms a number of oxides, the best established being phosphorus(III) oxide, P_4O_6, and phosphorus(V) oxide, P_4O_{10}. The +5 oxide is the more stable and the +3 oxide is easily oxidised.

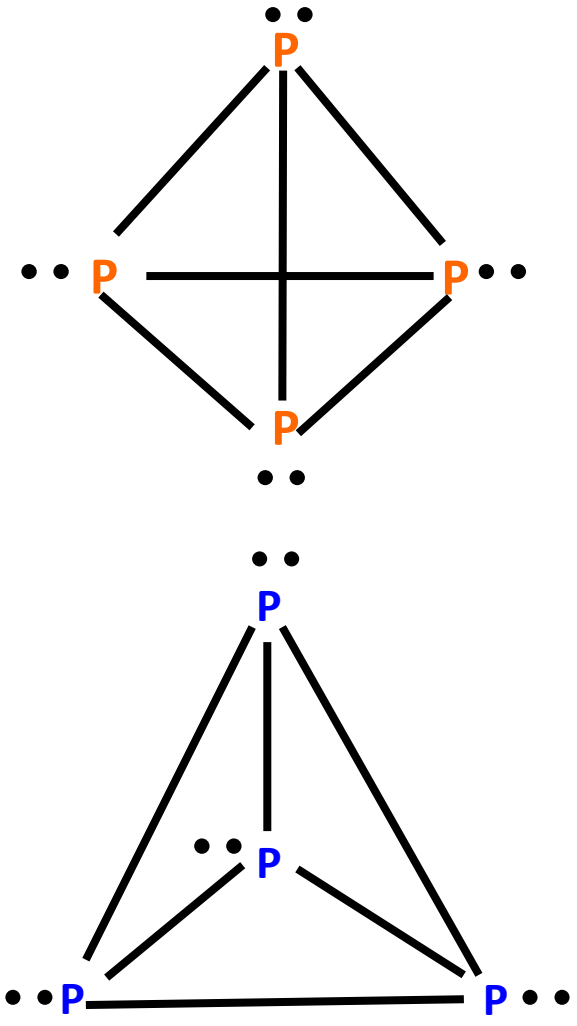
- in line with preferred +3 and +5 oxidation states

- differences between N and P oxides/oxoacids are essentially due to following:

Nitrogen	Phosphorus
(a) Very strong $p\pi$–$p\pi$ bonds	No known $p\pi$–$p\pi$ bonds
(b) $p\pi$–$d\pi$ bonding is rare	Weak to moderate but important $d\pi$–$p\pi$ bonding
(c) No valence expansion	Valency expansion

Phosphorous Oxides :

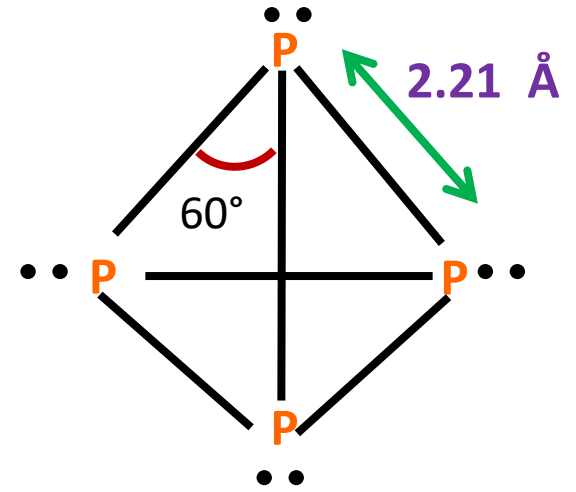
White phosphorous or yellow phosphorous : P_4

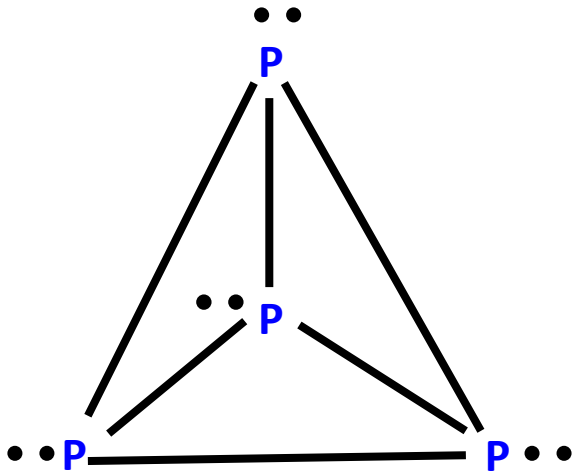


- Tetrahedral type
- three P are in triangular face
- basically fourth P lying separately actually inside the plane
- 6 P-P single bonds
- each P with one LP and three σ BP
- definitely sp^3 hybridisation
- Td geometry with distorted trigonal pyramidal molecular shape
- 6 P-P bonds present

Phosphorous Oxides :

White phosphorous or yellow phosphorous : P_4





- P-P-P bond angle ~60° which is really smaller than expected angle of ~109°
- always angle lower than expected means extensive twist/distortion exists in the compounds
- essentially due to increased neighbouring BP-BP repulsions
- high angular twist and distortion in the molecule
- ring strain and unstable
- requires less energy to break the bonds
- highly reactive and reacts with air further
- total 4 LP of electrons

Phosphorous Oxides :

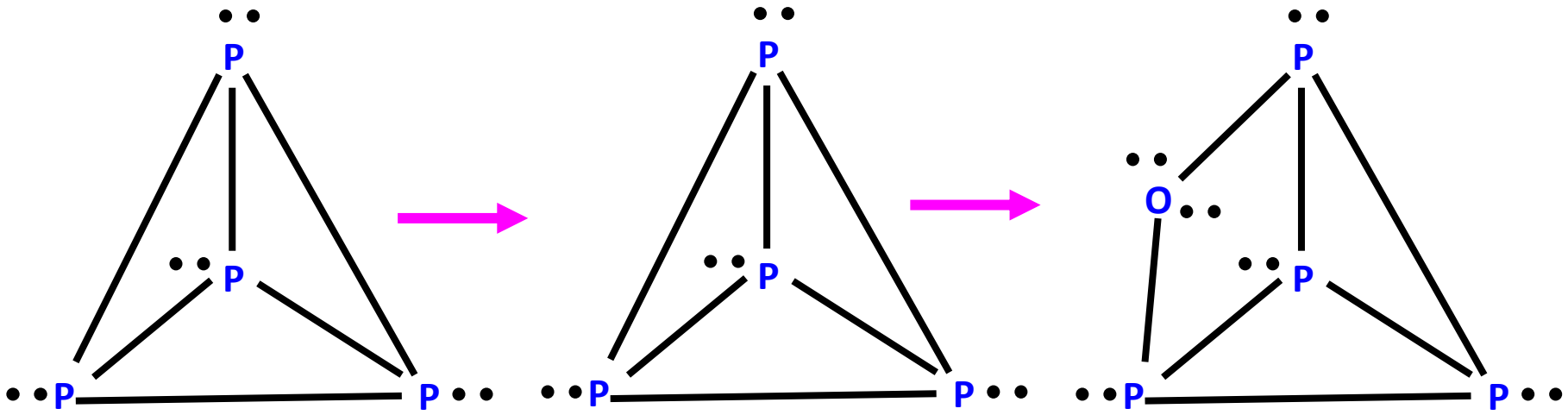
- **Oxides can be of different types considering the basic P_4 moiety :**

  - P_4O
  - P_4O_2
  - P_4O_3
  - P_4O_4
  - P_4O_5
  - P_4O_6
  - P_4O_7
  - P_4O_8
  - P_4O_9
  - P_4O_{10}

Phosphorous Oxides :

- Generating the oxide structures:
- substitute P-P bonds with P-O-P bonds gradually with increased number of O atoms. Insert O between the two P atoms

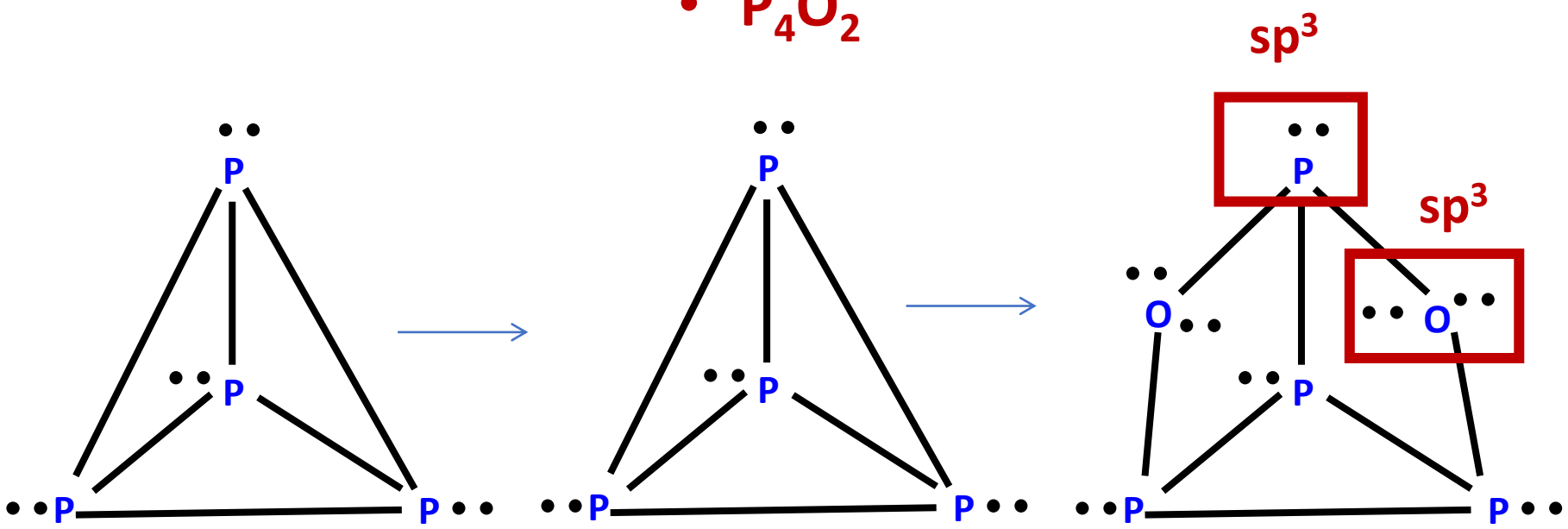
- P_4O



Phosphorous Oxides :

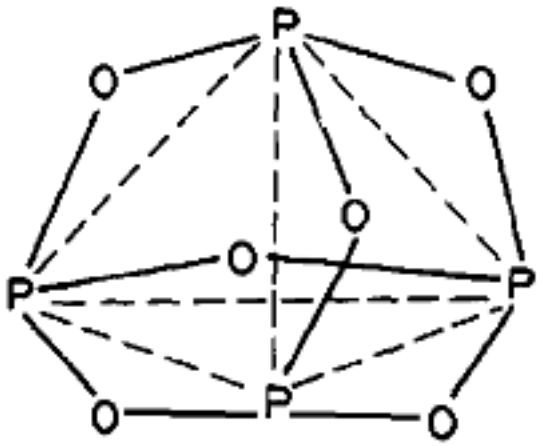
- Generating the oxide structures:
- substitute P-P bonds with P-O-P bonds gradually with increased number of O atoms. Insert O between the two P atoms

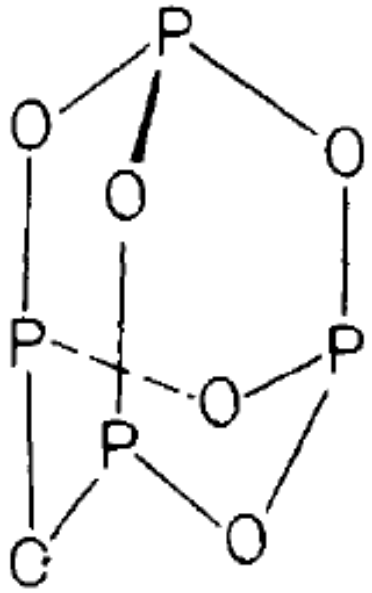
- P_4O_2



Phosphorous Oxides :

1. Phosphorous (III) oxide (P_4O_6) :

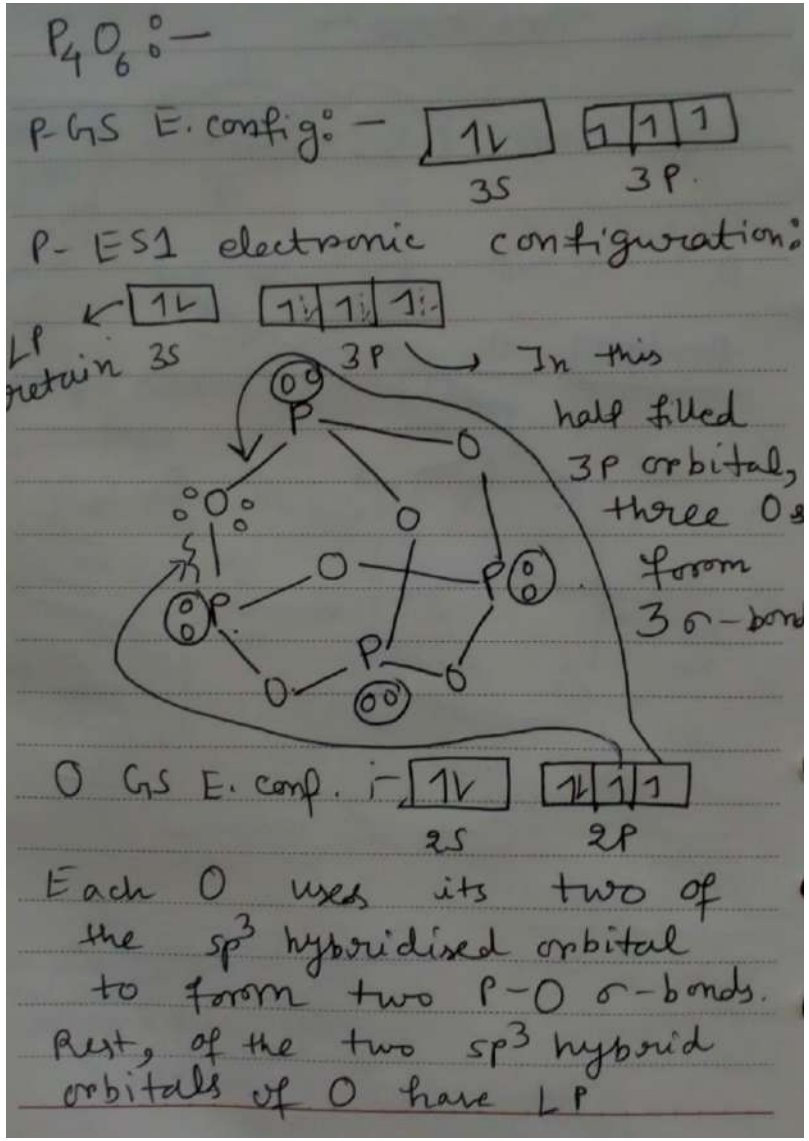




- All P have sp^3 hybriidisation
- All O have sp^3 hybridisation
- overall we have 6 P-O-P bonds
- causes broadening of P-O-P bond angle to ~129°
- P-O distance≈ 1.67 Å
- led to reduced BP-BP repulsions
- Each P with one LP
- Each O with two LP
- So total, (12+4) = 16 LP present

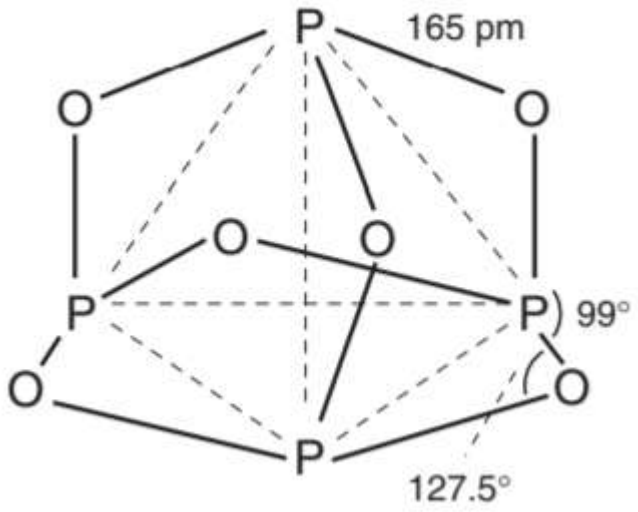
Phosphorous Oxides :

1. Phosphorous (III) oxide (P_4O_6) :



Phosphorous Oxides :

1. Phosphorous (III) oxide (P_4O_6) :



- A tetrahedral arrangement of phosphorus atoms is retained in the P_4O_6 molecule, giving a structure like that shown. Although dotted lines show the arrangement of phosphorus atoms, they do not represent bonds between the atoms.

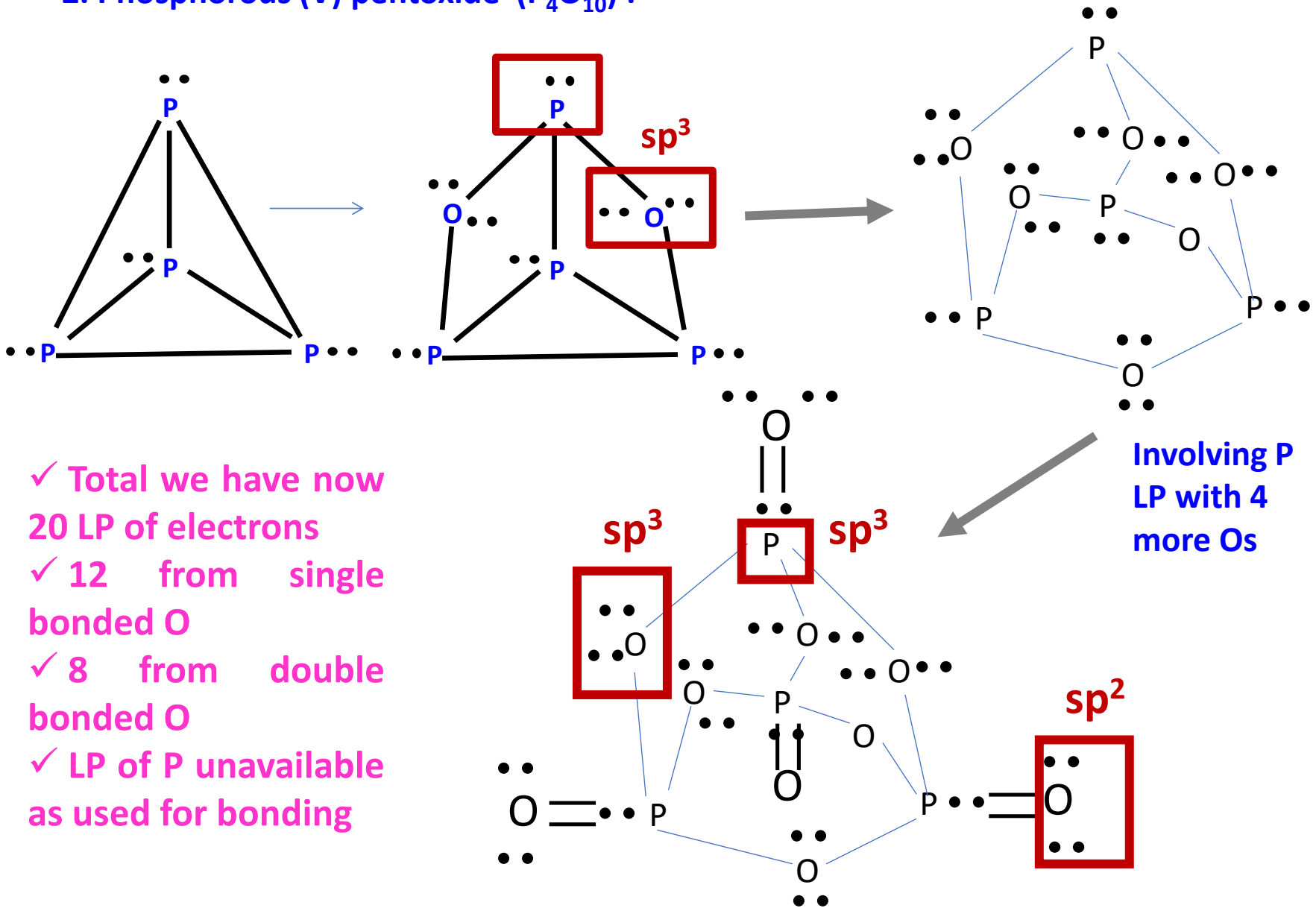
$$P_4 + 3\ O_2 \rightarrow P_4O_6$$

- P atoms at the corners of tetrahedron, with six O atoms along the edges, each O being bonded to two P atoms
- As P-O-P angle is 127°, the O atoms are strictly above the edges
- Phosphorous trioxides are dimeric and therefore represented as P_4O_6 and not P_2O_3

$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$

Phosphorous Oxides :

2. Phosphorous (V) pentoxide (P_4O_{10}) :



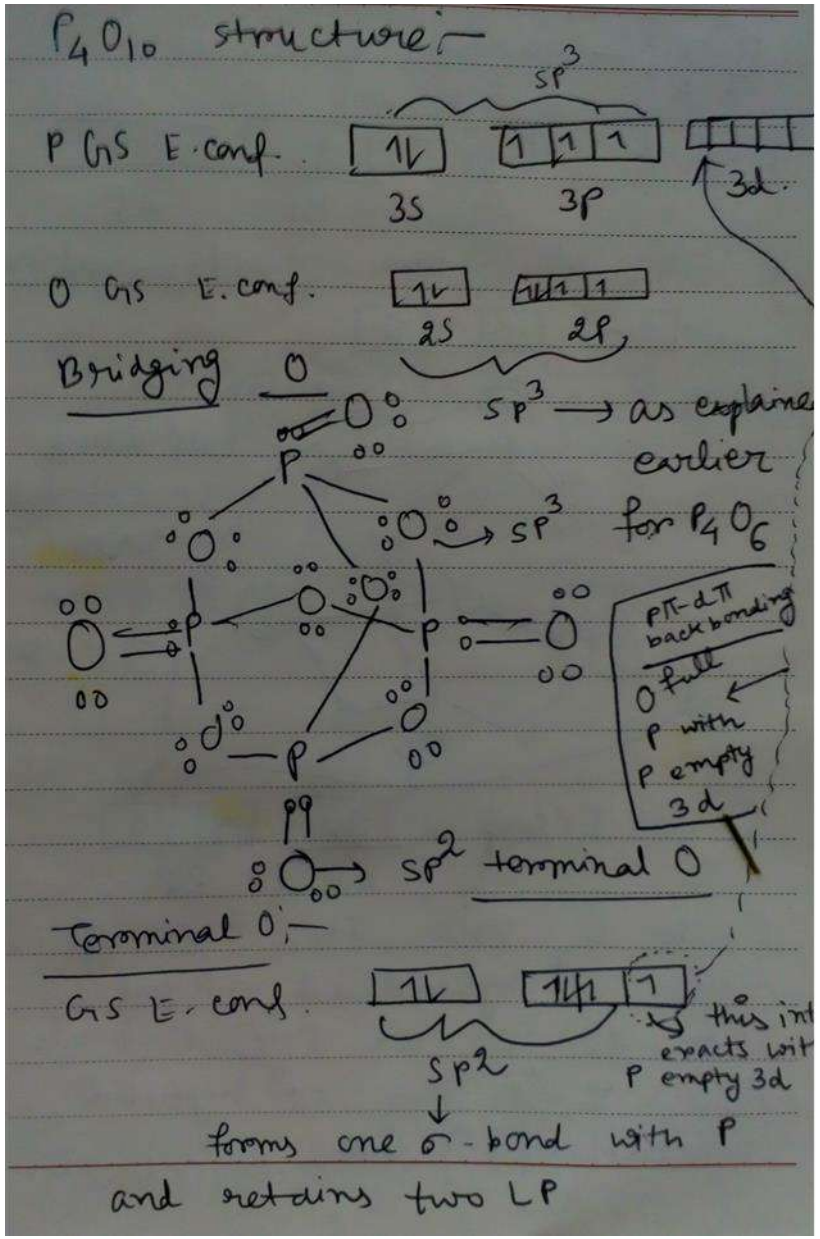
✓ Total we have now 20 LP of electrons

✓ 12 from single bonded O

✓ 8 from double bonded O

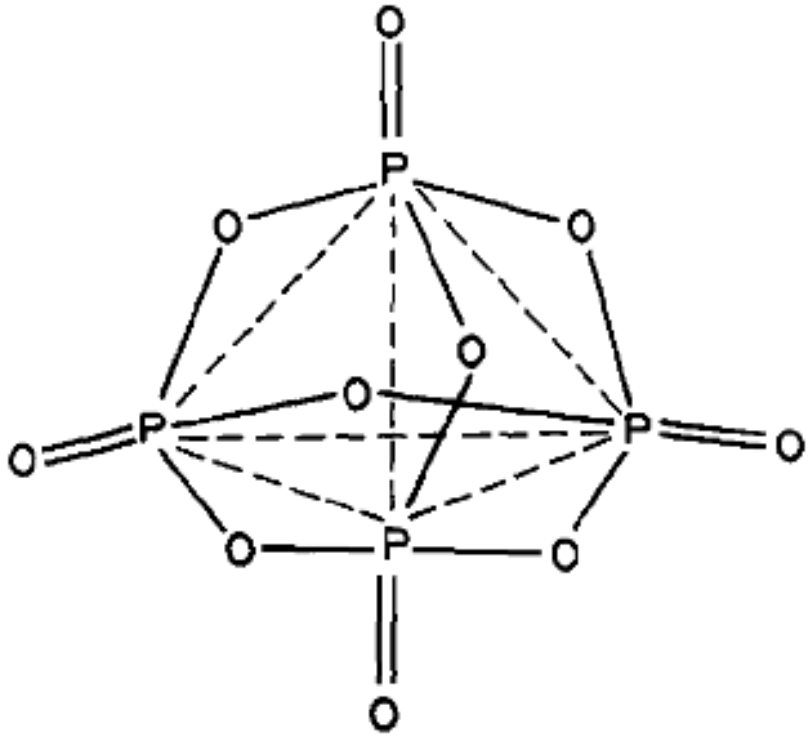
✓ LP of P unavailable as used for bonding

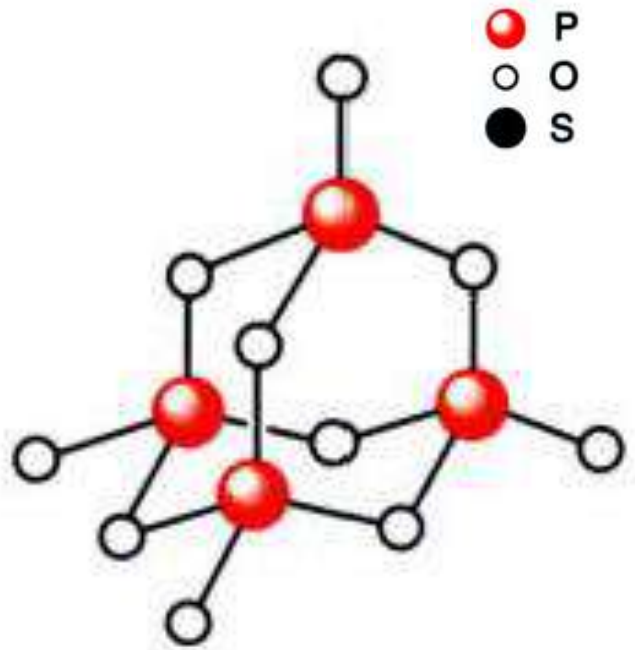
Phosphorous Oxides : 2. Phosphorous (V) pentoxide (P_4O_{10}) :



Phosphorous Oxides :

2. Phosphorous (V) pentoxide (P_4O_{10}) :





P_4O_{10}
(P_4S_{10} has the same shape)

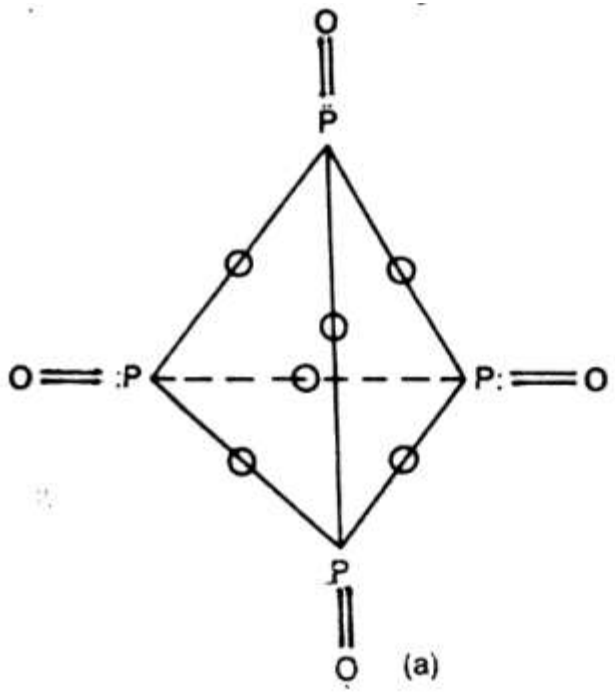
Phosphorous Oxides :

2. Phosphorous (V) pentoxide (P_4O_{10}) :

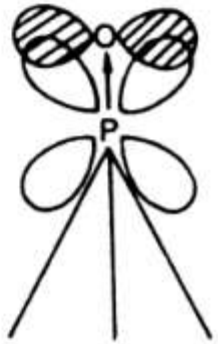
- ✓ **Each P forms three bonds to O atoms**
- ✓ **There are five electrons in valence shell of P**
- ✓ **Three electrons have already used for bonding with O leaving one LP behind**
- ✓ **This LP is located on the outside of tetrahedral unit**
- ✓ **This LP actually constitute coordinate bond to terminal O atom in this structure**
- ✓ **The P atoms reside at the corners of a tetrahedron with six O atoms lying along the edges and the remaining four occupying position along the extended three fold axes of the tetrahedron**
- ✓ **Bridging P-O** bond lengths are 1.60 Å while the coordinate bonds at the corners are 1.43 **Å**
- ✓ The former bonds are P-O single bonds while the latter ones are double bonds with appreciable pπ-dπ interaction
- ✓ Full 2p orbital on O atom overlaps sideways with the empty 3d orbital of P
- ✓ It is not conventional double bond as p orbital overlaps with d orbital rather than p
- ✓ Both electrons come from one O atoms and hence the bond is dative bond through back donation (pπ-dπ back bonding)

Phosphorous Oxides :

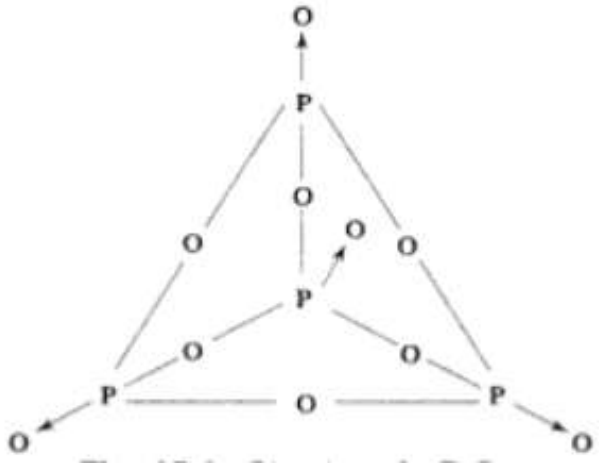
2. Phosphorous (V) pentoxide (P_4O_{10}) :



(a)

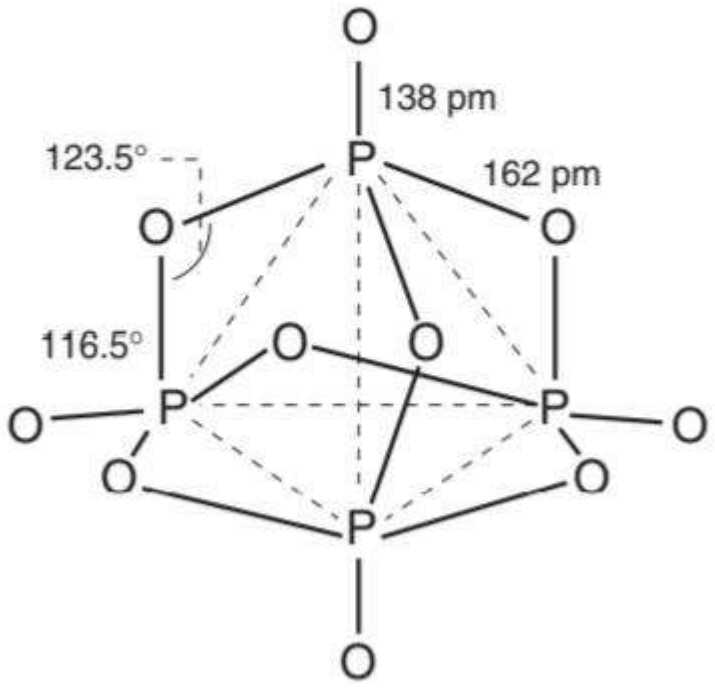


(b)



Phosphorous Oxides :

2. Phosphorous (V) pentoxide (P_4O_{10}) :



$$P_4 + 5\ O_2 \rightarrow P_4O_{10} \qquad \Delta H = -2980\ \text{kJ mol}^{-1}$$

Phosphorus(V) oxide or tetraphosphorus decoxide, P_4O_{10}, is the anhydride of the series of phosphoric acids. It is produced in the first step of the manufacture of H_3PO_4 by burning phosphorus,

Phosphorus(V) oxide is an extremely effective desiccating agent, Phosphorus(V) oxide has a great affinity for water and hygroscopic.

It is used as strong drying and dehydrating agent. It is used to manufacture optical and heat insulating glass. It is also used in manufacturing of pesticides and pharmaceuticals.

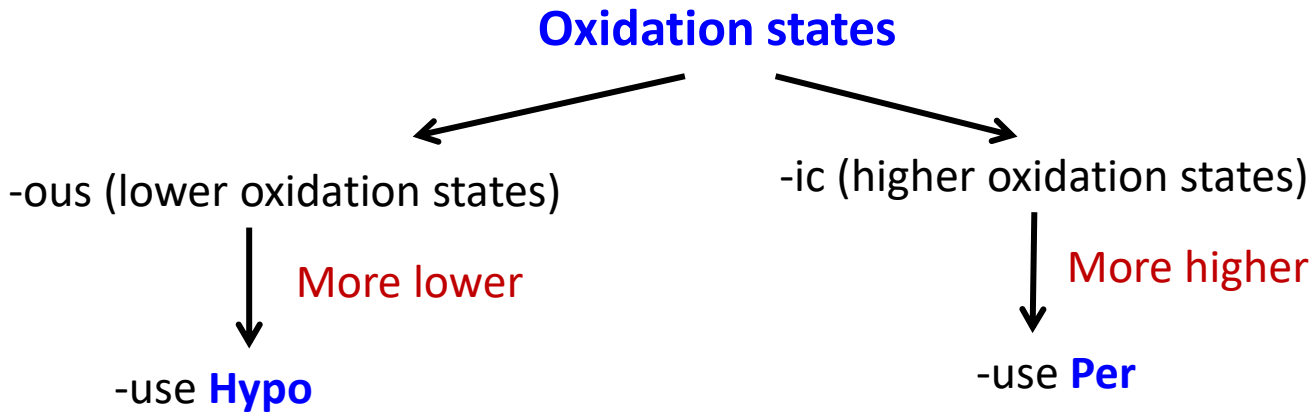
$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

Phosphorous Oxoacids:

Characteristics :

- acids that contain O
- P is sp^3 hybridised giving tetrahedral geometry around it
- all possess atleast one P=O and one P-OH bond
- H attached to O have acidic character
- bond between P and non-hydroxylic O has predominant double bond character
- oxoacids where P oxidation state is less than +5 additionally contain P-P and P-H bonds as well
- P-H bonds induce reducing properties in these oxo-acids
- H in P-OH only ionizable but H in P-H is non-ionizable

Phosphorous Oxoacids:



Acids with 'ortho' prefix : basic unit $[E(OH)_n]$
i.e. $[B(OH)_3]$: orthoboric acid and $[P(OH)_3]$: **ortho**phosphorous acid

Acids with 'ortho' prefix : **if** basic unit $[E(OH)_n]$ does not exist even after removal of water from that, resultant product can be assigned the 'ortho' prefix
i.e. $[P(OH)_5]$: H_5PO_5 does not exist ; but

$$H_5PO_5 \xrightarrow[-H_2O]{} H_3PO_4$$ (**ortho**phosphoric acid)

Acids with 'meta' prefix : removal of H_2O from any orthoacids

i.e.

(orthophosphoric acid) $H_3PO_4 \xrightarrow[-H_2O]{} HPO_3$ (**meta**phosphoric acid)

(orthophosphorous acid) $H_3PO_3 \xrightarrow[-H_2O]{} HPO_2$ (**meta**phosphorous acid)

Acids with 'pyro' prefix : removal of H_2O from two molecules of same orthoacid

Two molecules of ortho acid – H_2O = pyro acid

$2*H_3PO_4 \xrightarrow[-H_2O]{} H_4P_2O_7$ (**pyro**phosphoric acid)

$2*H_3PO_3 \xrightarrow[-H_2O]{} H_4P_2O_5$ (**pyro**phosphorous acid)

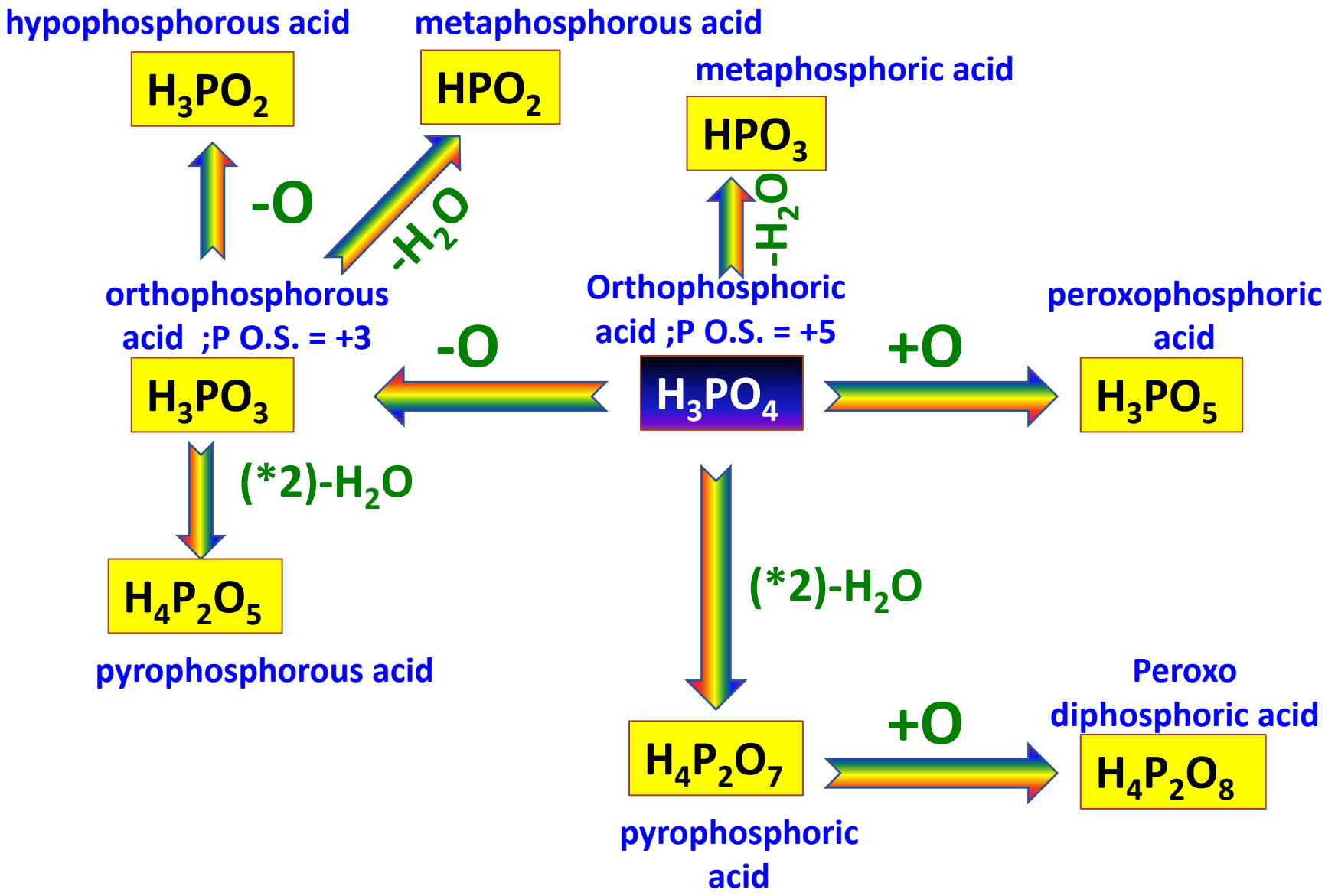
Sometimes, 'di' is also used instead of pyro

Acids with 'peroxo' prefix : obtained by replacement of –O- by -O-O i.e.

(orthophosphoric acid) H_3PO_4 → (Replace O with O-O) H_3PO_5 (**peroxo**phosphoric acid)

Acid	Nature	Preparation	Anion	Remarks
H_3PO_2 or $H_2P(OH)O$ Hypophosphorous	crystalline white solid	white P_4 + alkali	$H_2PO_2^-$ hypophosphite	strongly reducing, monobasic $pK \sim 2$
H_3PO_3 or $HPO(OH)_2$ Orthophosphorous	deliquescent colourless solid	P_4O_6 or $PCl_3 + H_2O$	$H_2PO_3^-$, HPO_3^{2-} phosphite	reducing, but slow, dibasic $pK_1 \sim 2$ $pK_2 \sim 6$
$H_4P_2O_3$ Pyrophosphorous	white solid	$PCl_3 + H_3PO_3$	$H_2P_2O_5^{2-}$ pyrophosphite	reducing, dibasic
$H_4P_2O_6$ Hypophosphoric	white solid	red P + alkali	$P_2O_6^{4-}$ hypophosphate	not reducing or oxidising, tetrabasic $pK_1 \sim 2$
H_3PO_4 Orthophosphoric	white solid	$P_4O_{10} + H_2O$	$H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, phosphate	not oxidising, tribasic
$H_4P_2O_7$ Pyrophosphoric	colourless solid	heat phosphates or phosphoric acid	$P_2O_7^{4-}$ pyrophosphate	tetrabasic $pK_1 \sim 2$
HPO_3 Metaphosphoric	deliquescent solid	heat H_3PO_4 to 600 K		

Phosphorous Oxo/oxy-acids: (remember any parent , rest its derivatives only)



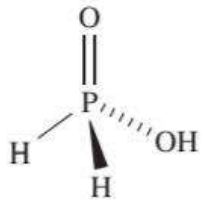
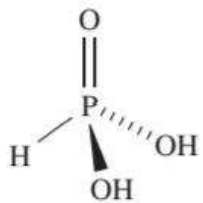
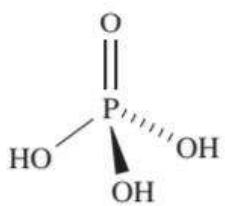
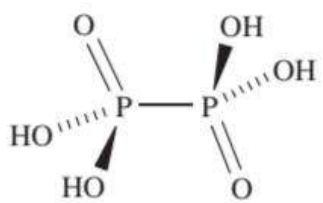
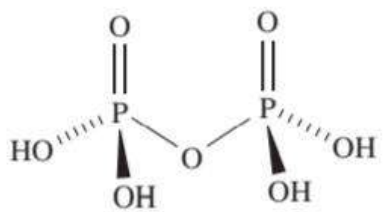
Phosphorous Oxoacids:

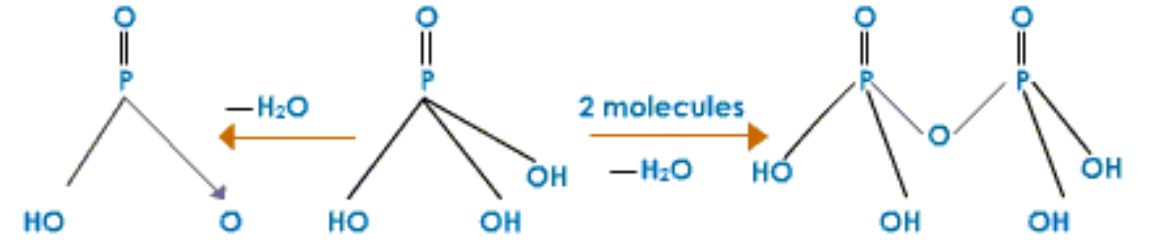
Characteristics :

- acids that contain O
- **P is sp^3 hybridised giving tetrahedral geometry around it**
- **all possess atleast one P=O and one P-OH bond**
- H attached to O have acidic character
- bond between P and non-hydroxylic O has predominant double bond character
- oxoacids where P oxidation state is less than +5 additionally contain P-P and P-H bonds as well
- P-H bonds induce reducing properties in these oxo-acids
- H in P-OH only ionizable but H in P-H is non-ionizable

Phosphorous Oxoacids:

Name	Formula	Oxidation state of P
Hypophosphorus acid	H_3PO_2	+1
Phosphorus acid	H_3PO_3	+3
Hypophosphoric acid	$H_4P_2O_6$	+4
Orthophosphoric acid	H_3PO_4	-
Diphosphoric acid (Pyrophosphoric acid)	$H_4P_2O_7$	+5
Metaphosphoric acid	HPO_3	+5
Peroxophosphoric acid	H_3PO_5	+7

Formula	Name	Structure	pK_a values
H_3PO_2	Phosphinic acid (hypophosphorous acid)		pK_a = 1.24
H_3PO_3	Phosphonic acid (phosphorous acid)		pK_a(1) = 2.00; pK_a(2) = 6.59
H_3PO_4	Phosphoric acid (orthophosphoric acid)		pK_a(1) = 2.21; pK_a(2) = 7.21; pK_a(3) = 12.67
$H_4P_2O_6$	Hypophosphoric acid		pK_a(1) = 2.2; pK_a(2) = 2.8; pK_a(3) = 7.3; pK_a(4) = 10.0
$H_4P_2O_7$	Diphosphoric acid (pyrophosphoric acid)		pK_a(1) = 0.85; pK_a(2) = 1.49; pK_a(3) = 5.77; pK_a(4) = 8.22



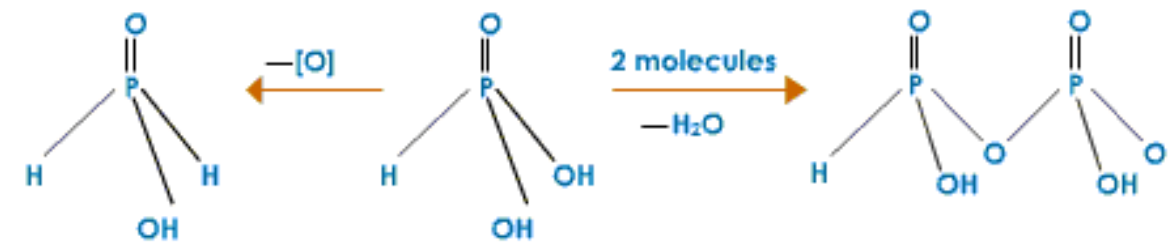
Metaphosphoric acid
HPO_3 (P = +5)
(Monobasic)

Orthophosphoric acid
H_3PO_4 (P = +5)
(Tribasic)

Diphosphoric acid
(or Pyrophosphoric acid)
$H_4P_2O_7$ (P = +5)
(Tetrabasic)

Peroxomonophosphoric acid
H_3PO_5 (P = +7)
(Tribasic)

Hypophosphoric acid
$H_4P_2O_6$ (P= +4)
(Tetrabasic)

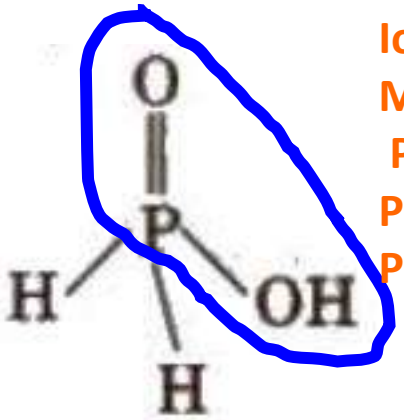


Hypophosphorus acid
H_3PO_2 (P= + 1)
(Monobasic)

Phosphorus acid
H_3PO_3(P= + 3)
(Monobasic)

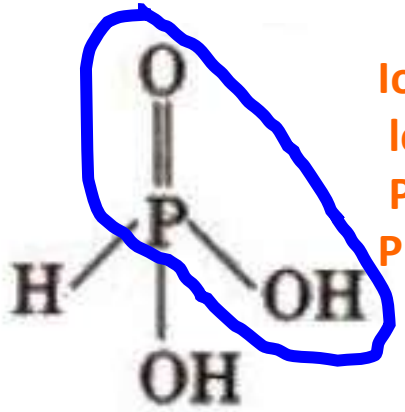
Pyrophosphorus acid
$H_4P_2O_5$(P= + 3)
(Dibasic)

Phosphorous Oxoacids:



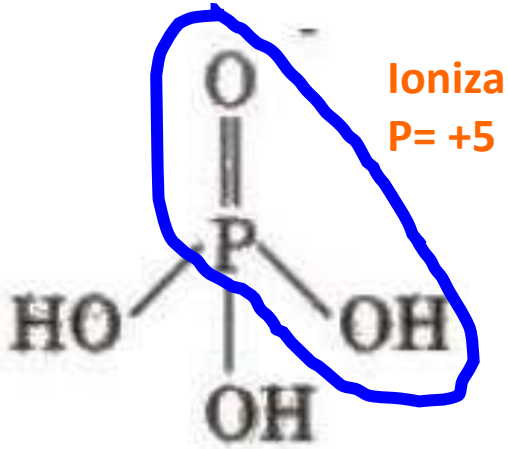
Ionizable H = 1
Most reducing
P-H bonds
P = +1
Phosphinic acid

hypophosphorous acid
(H_3PO_2)



Ionizable H = 2 (dibasic)
less reducing
P= +3
Phosphonic acid

orthophosphorous acid
(H_3PO_3)

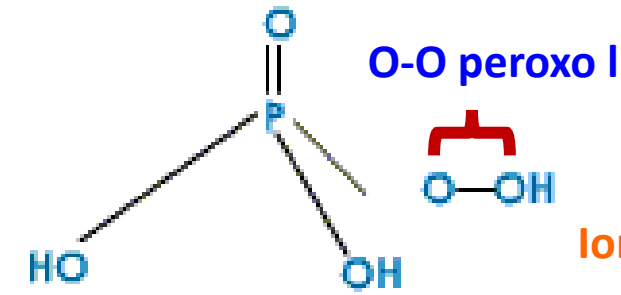


Ionizable H = 3
P= +5

orthophosphoric acid
(H_3PO_4)

peroxophosphoric acid

H_3PO_5



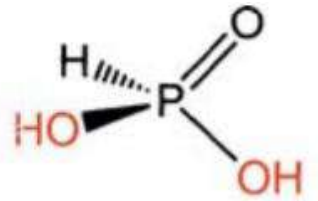
O-O peroxo linkage

Ionizable H = 3

Peroxomonophosphoric acid
H_3PO_5 (P = +7)
(Tribasic)

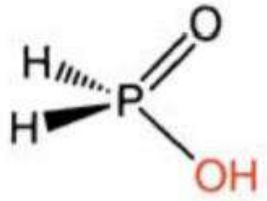
Phosphorous Oxoacids:

+3 acids



Phosphonic acid
(Phosphorous acid)
$HP(O)(OH)_2$

Dibasic



Phosphinic acid
(Hypophosphorous acid)
$H_2P(O)OH$

Monobasic

- ✓ Phosphinic acid and its salts are reducing agents. $NaH_2PO_2.H_2O$ is used industrially in a non-electrochemical reductive process which plates nickel onto steel
- ✓ Pure H_3PO_3 forms colourless, deliquescent crystals
- ✓

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

$$H_3PO_2 + H_2O \rightleftharpoons [H_3O]^+ + [H_2PO_2]^-$$

$$4H_2PO_2^- \rightarrow 2PH_3 + 2HPO_4^{2-}$$

$$3H_3PO_2 \xrightarrow{\Delta} PH_3 + 2H_3PO_3$$

or

$$2H_3PO_2 \xrightarrow{\Delta} PH_3 + H_3PO_4$$

$$H_3PO_3(aq) + H_2O \rightleftharpoons [H_3O]^+ + [H_2PO_3]^-$$

$$[H_2PO_3]^-(aq) + H_2O \rightleftharpoons [H_3O]^+ + [HPO_3]^{2-}$$

$$4H_3PO_3 \xrightarrow{470\ K} PH_3 + 3H_3PO_4$$

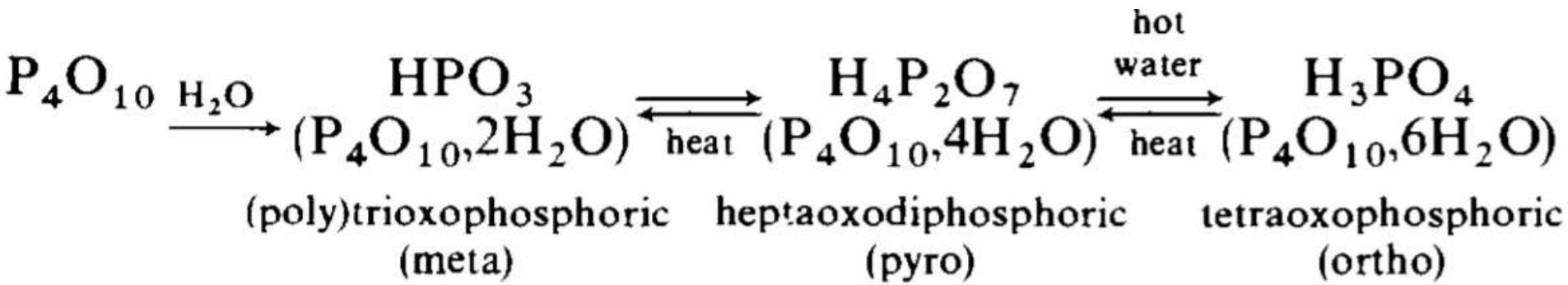
H_3PO_3 ionization

$$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^-; \quad H_2PO_3^- \rightleftharpoons H^+ + HPO_3^{2-}$$

Phosphorous Oxoacids:

+5 acids

The important phosphoric acids and their relation to the anhydride P_4O_{10} are:



Tetraoxophosphoric acid, H_3PO_4:

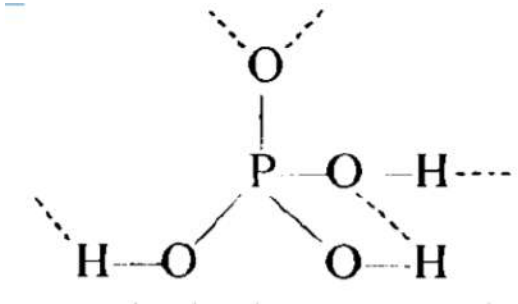
- Tetraoxophosphoric acid is a colourless solid, very soluble in water
- It is tribasic, giving the ions

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} \rightleftharpoons PO_4^{3-}$$

(tetrahedral)

decreasing hydrogen ion concentration
decreasing solubility of salts

- In anhydrous phosphoric(V) acid, tetrahedral PO_4^{3-} groups are connected by hydrogen bonds



- The dotted lines represent the hydrogen bonds and it is these bonds which are responsible for the syrupy nature of the acid.

- Organic phosphates(V) are of great importance in biological processes, for example photosynthesis.

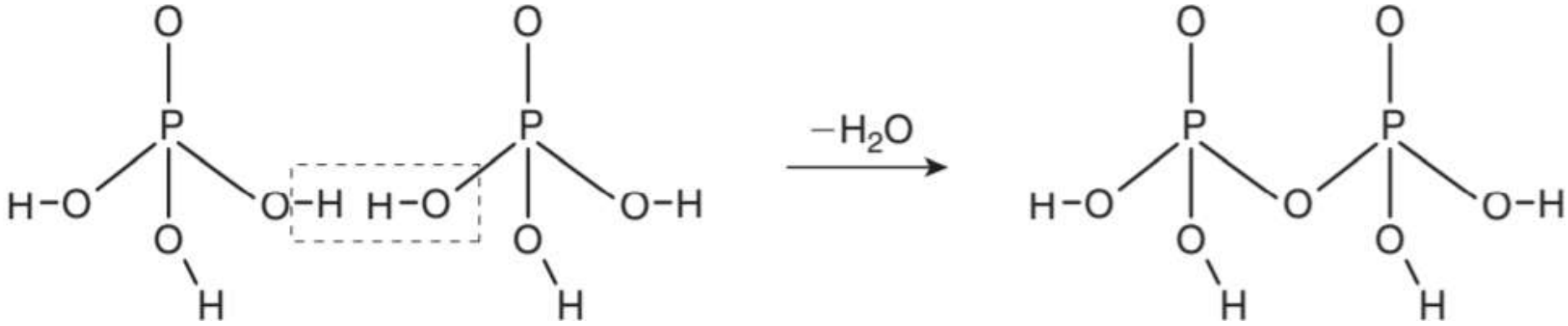
Phosphorous Oxoacids:

+5 acids

Heptaoxodiphosphoric acid, $H_4P_2O_7$

When H_3PO_4 is heated at 510 K, it is dehydrated to diphosphoric acid

$$2H_3PO_4 \xrightarrow{\Delta} H_4P_2O_7 + H_2O$$

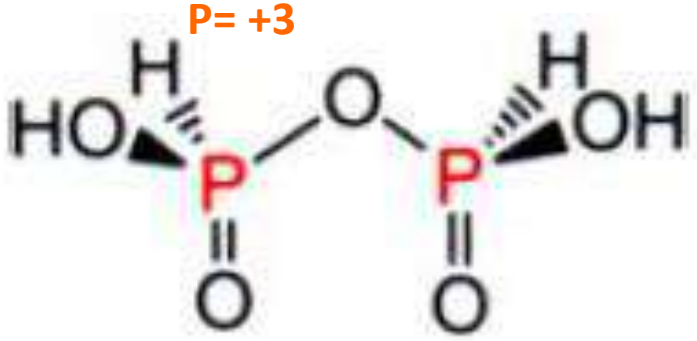


$$H_4P_2O_7 + H_2O \rightarrow 2H_3PO_4$$

Phosphorous Oxoacids: (two P)

Ionizable H = 2 (dibasic) + reducing agent

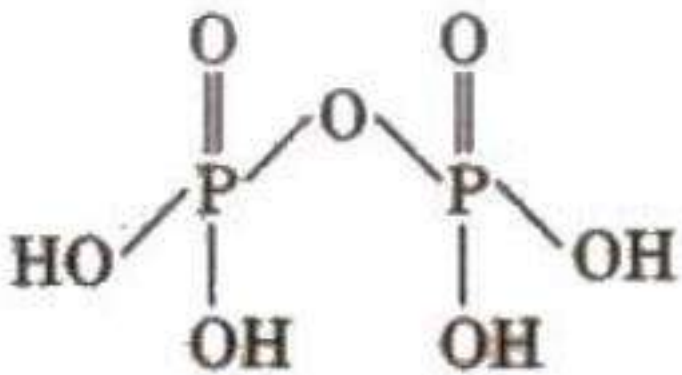
P= +3



$H_4P_2O_5$

pyrophosphorous acid

- must have P-O-P linkage
- Link two P with one O
- second on P it must have P=O and P-OH
- Then remaining to be filled



pyrophosphoric acid ($H_4P_2O_7$)

Ionizable H = 4 (tetrabasic)

P= +5

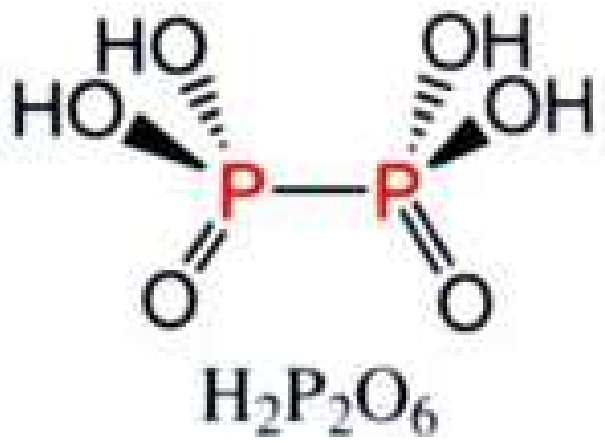
Stronger acid than H_3PO_4

P-O(term) = 1.52 Å

P-O(bridging) = 1.61 Å

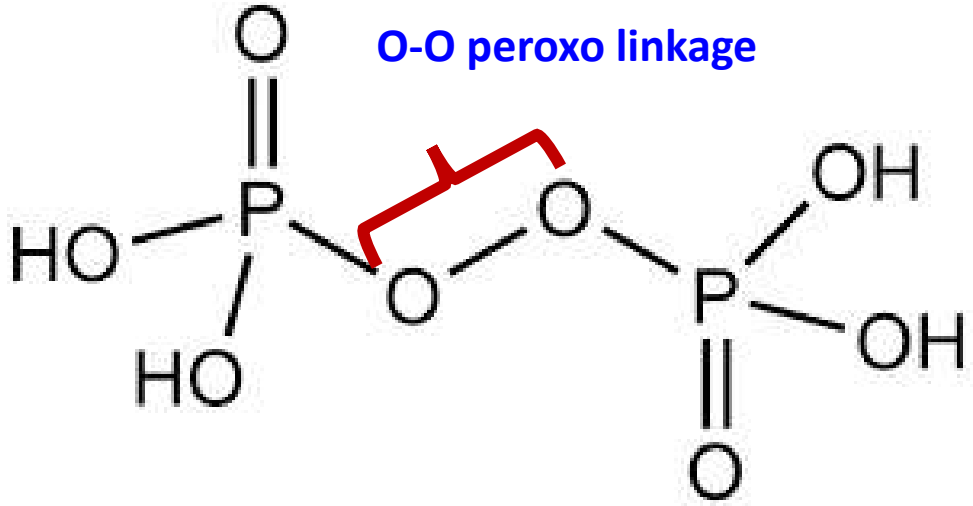
P-O-P = 130°

Phosphorous Oxoacids: (two P)



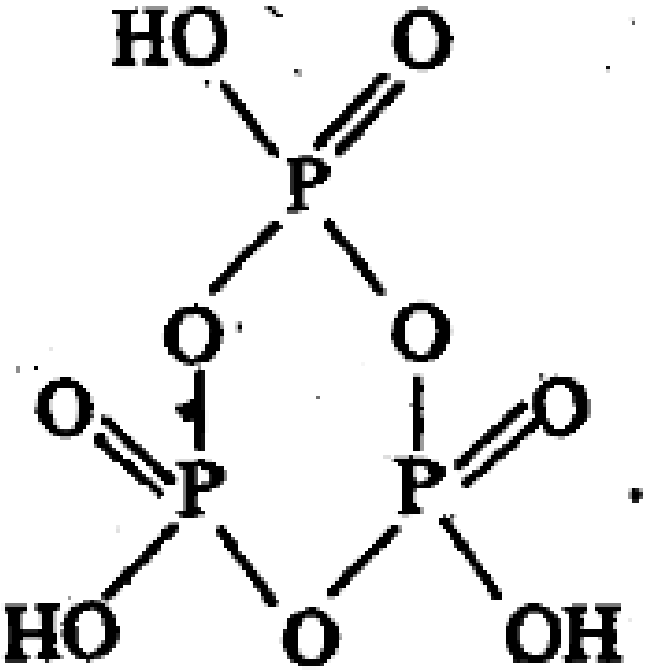
Hypophosphoric acid

- **tetrabasic**



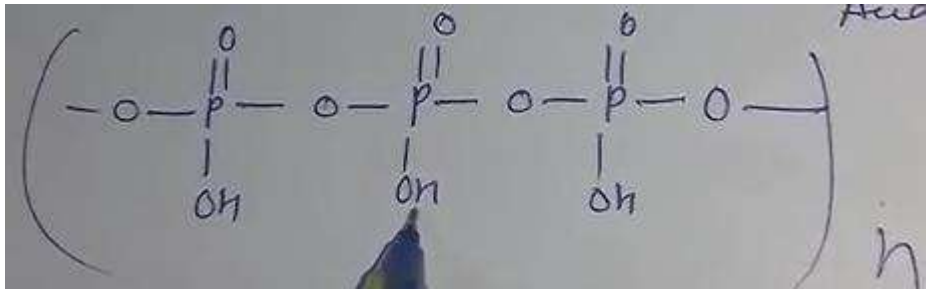
peroxydisphosphoric acid

- **tetrabasic**



Cyclo-triphosphoric acid

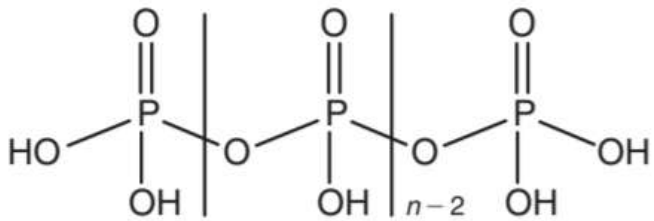
cyclotrimetaphosphoric acid $(HPO_3)_3$
• in ring form
• P-O-P-O linkage



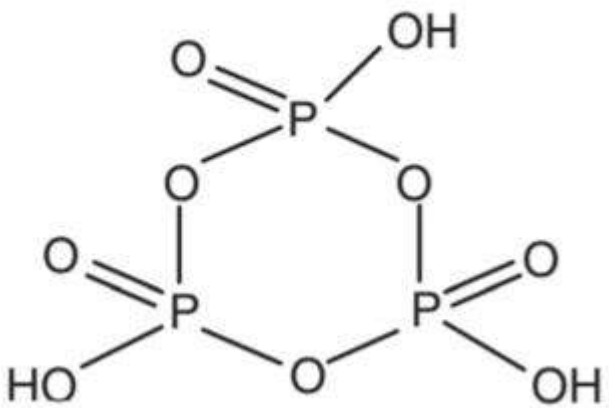
Linear polymetaphosphoric acid $(HPO_3)_n$
• in ring form
• P-O-P-O linkage

•This phosphate P-O-P linkage crucial in biological systems
• as prime storage of energy

Other condensed polyphosphoric acids have the general formula $H_{n+2}P_nO_{3n+1}$, and they are formally produced by the elimination of water between the $(n-1)$ acid and a molecule of H_3PO_4. The general structure can be represented as



Another " phosphoric acid, " trimetaphosphoric acid, is a trimer of HPO_3 representing the H_2O/P_2O_5

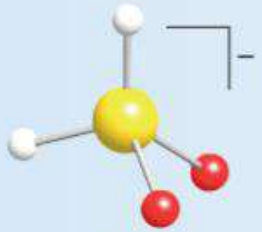
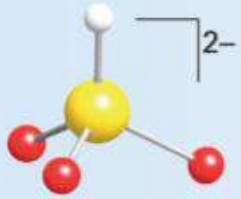
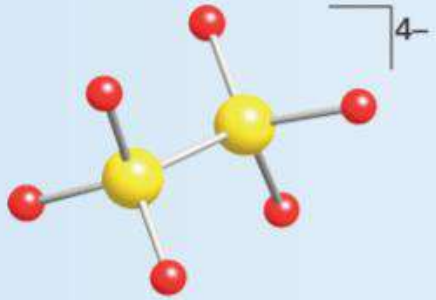
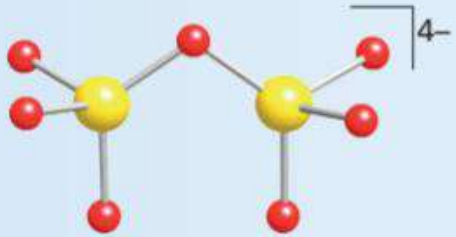


$H_3P_3O_9$

P

O

H

Oxidation number	Formula	Name	Structure	Comments
+1	$H_2PO_2^-$	Hypophosphite (dihydrodioxophosphate)		Facile reducing agent
+3	HPO_3^{2-}	Phosphite		Facile reducing agent
+4	$P_2O_6^{4-}$	Hypophosphate		Basic
+5	PO_4^{3-}	Phosphate		Strongly basic
+5	$P_2O_7^{4-}$	Diphosphate		Basic; longer chain

Refs: Inorganic Chemistry books by following authors

- R. Sarkar (Vol-2)
- James E. House
- J. D. Lee
- Chambers, Holliday
- Housecroft, Sharpe
- Shriver, Atkins

Thank you