SUB: INORGANIC CHEMISTRY
CODE: USO5CCHE22
UNIT-IV Inorganic Polymers

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Introduction

All the covalent macromolecules, which do not have carbon in their back bones, are considered to be inorganic polymers. Covalently-bonded crystals (e.g., oxides and halides), condensed phosphates etc., are the examples of inorganic polymers. These polymers possess distinctive physico-chemical characteristics and unique physical, mechanical and electrical properties. These polymers are of extensive utility in everyday life, particularly in the area of engineering and technology.

The important point of similarity between inorganic and organic polymers is, that both can be prepared by the addition and condensation methods. The former method is used when polymers of higher molecular weight and greater mechanical strength are needed.

Classification of inorganic polymers

There are different ways of classifying inorganic polymers.

1st classification. Depending on whether the polymer contains the atoms of only one element or of different elements in its backbone, the polymers are classified into the following two groups.

1. Homo-atomic polymers. These polymers contain the atoms of only one element in their back bones. Silicon, phosphorus, sulphur, germanium and tin form homo-atomic inorganic polymers. For example, sulphur has a tendency to form chain or rings in its elemental form (S_8) and in several compounds, like persulphides (H-S-S-H, H-S-S-S-H, H-S-S-S-S-H etc.), polythionic acids etc. Single bond strengths in homo-atomic inorganic polymers are 54 to 60 Kcal for sulphur, about 53 Kcal for silicon, 48-53 for phosphorus, about 45 for germanium and about 39 for tin.

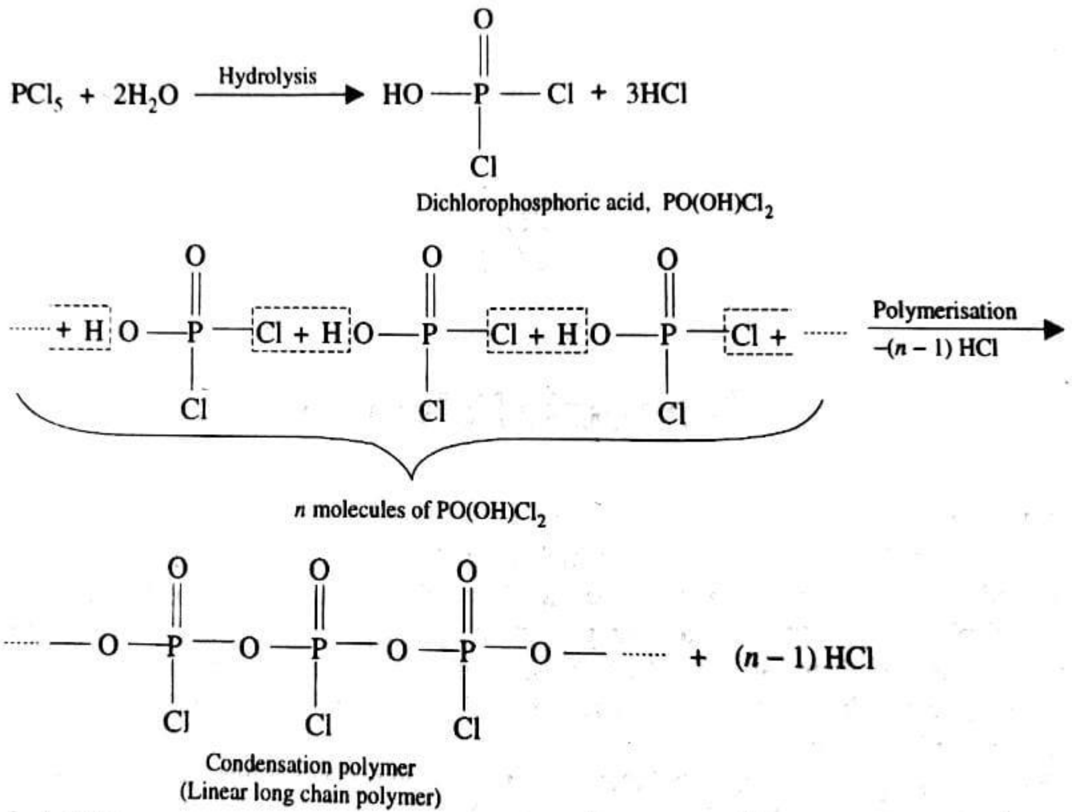
2. Hetero-atomic polymers. These contain the atoms of different elements in their backbones.

2nd classification. Inorganic polymers can also be classified in another way, which is based the type of reaction by which the polymers are formed. On this basis, inorganic polymers may be of the following types:

1. Condensation (polymerisation) polymers. Condensation polymers are those, which are formed by condensation (polymerisation) process. In this process, two or more simple molecules of the same substance polymerise together and form the condensation polymer. One or more H_2O, NH_3, H_2, HCl etc. molecules are also eliminated.

Examples. (a) Cross-linked silicone is obtained by the polymerisation of many $RSi(OH)_3$ molecules. Similarly, when many molecules of R_2 $Si(OH)_2$ undergo polymerisation, a straight chain (linear) or cyclic (ring) silicone is obtained. When two molecules of $R_3Si(OH)$ undergo polymerisation, a straight chain silicone (dimer) is obtained. For detail see "Silicones".

(b) When PCl_5, is partially hydrolysed by water, dichloro phosphoric acid, $PO(OH)Cl_2$ is obtained. When $PO(OH)Cl_2$ is heated, many molecules of this substance get polymerised and give to the formation of a condensation polymer. In this process HCl is eliminated.



2. Addition polymers. These polymers are obtained, when many simple molecules (monomers) combine together.

Examples. (a) Many molecules of sulphur trioxide may be polymerised by the addition of a small amount of water. This gives addition polymer.

(b) When SO_2 reacts with propylene, CH_3-CH = CH_2, in presence of benzoyl peroxide, an addition polymer is obtained.

3. Coordination polymers. These are formed by the addition of saturated molecules to each other or by combining a ligand with a metal atom. These polymers contain chelated metal atoms or ions.

Types of coordination polymers. (i) In these polymers, the chelated metal atom (ion) is an integral part of the polymer framework.

(ii) In these polymers the metal atom (ion) remains bound to a polymeric ligand, which has donor groups in its framework.

Preparation of coordination polymers. (i) This method involves the combination of molecule/ion (ligand) with the metal atom/ion.

(ii) In this method, the metal ions are fixed into a polymeric ligand, which has donor atom in its framework.

(ii) Coordination polymers can be prepared by condensation polymerisation, which requires appropriate monomers.

(iv) Coordination polymers can also be obtained by using elimination-addition reactions.

3rd classification. According to this classification, the inorganic polymers can be classified into the following catagories :

1. Polymers containing two bridging bonds per units, e.g., homo-atomic sulphur, selenium and teturium polymers.

2. The alternating silicone-oxygen polymers. Examples are silicones and related compounds.

3. The alternating phosphorus-nitrogen polymers. Examples are phosphonitrilic halides, $(NPX_2)_n$.

4. The alternating phosphorus-oxygen polymers. Examples are metaphosphates polyphosphates and cross-linked phosphates.

5. The alternating sulphur-nitrogen polymers. Examples are (i) polymeric nitrides of sulphur (e.g S_2N_2, S_4N_4, S_5N_2, etc.) (ii) thiazyl halides, [e.g., $(NSF)_3$, $(NSF)_4$, $(NSCl)_3$] (iii) imides sulphur (e.g., $S_7(NH)$, $S_6(NH)_2$, $S_5(NH)_3$, and $S_4(NH)_4$].

4th classification. This classification is based on the element which forms inorganic polymers.

Thus, we have:

1. *Polymers containing boron. Examples are: (a) Borazine,* $(BH)_3(NH)_3$ *or* $B_3N_3H_6$.

(b) substituted borazines like (i) B-trimethyl borazine, $[B(CH_3)_3 (NH)_3]$ (ii) Boroxine, $(BH)_3O_3$(iii) N-trimethyl borazine, $(BH)_3[N(CH_3)]_3$ (c) Boron nitride, $(BN)_n$.

2. Polymers containing silicon. These are called silicones.

3. Polymers containing phosphorus. Examples are: (a) Metaphosphates, (b) Polyphosphates, (c) Cross-linked phosphates, (d) Phosphonitrilic halides, $[PNX_2]_n$.

4. Polymeric compounds of sulphur. Examples are nitrides of sulphur, thiazyl halides imides of sulphur.

General properties of inorganic polymers

(i) Most of the inorganic polymers do not burn, but only soften or melt at high temperatures. Inorganic polymers, containing sulphur etc., are exceptions.

(ii) Inorganic polymers, having cross-linked structures with many covalent bonds, are generally stiffer and harder than the organic polymers.

(iii) Since most of the inorganic polymers are built up of highly polar repeat units, these polymers dissolve only in polar solvents. These polymers react with solvent molecules.

(iv) Inorganic polymers are generally less ductile than the organic polymers.

(v) Inorganic polymers have structures which are purely crystalline or purely amorphous while organic polymers have structures which are partly crystalline and parlty amorphous.

(vi) Inorganic polymers are generally stronger, harder and more brittle than the organic polymers.

Polymers containing boron

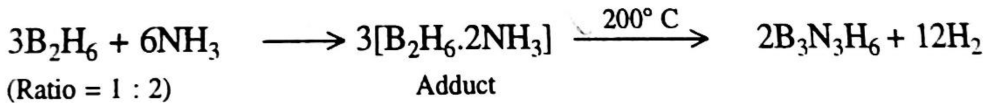
Borazine, substituted borazines and boron nitride are polymeric compounds of boron. Borazine is of special interest, because it is isoelectronic with benzene and some of its physical properties resemble those of benzene.

A. Borazine or borazole, $(BH)_3$ $(NH)_3$ or $B_3N_3H_6$

This compound is isoelectronic with benzene and hence has been called Inorganic Benzene by **Weberg**.

Preparation. Borazine can be prepared by the following methods :

(i) By Stock and Pohland's method (1926): Borazine was originally prepared by Stock and Pohland, in 1926, by the action of NH_3 on diborane (B_2H_6). The adduct, B_2H_6. $2NH_3$, is first formed Which then gets decomposed by heating in a closed tube at 200°C.



$$\underset{(\text{Ratio} = 1:2)}{3B_2H_6 + 6NH_3} \longrightarrow \underset{\text{Adduct}}{3[B_2H_6.2NH_3]} \xrightarrow{200^\circ\,C} 2B_3N_3H_6 + 12H_2$$

This method gives low yield of $B_3N_3H_6$ because of simultaneous formation of solid polymeric by-products.

(ii) By heating BCl_3 with NH_4Cl: When BCl_3 is heated with NH_4Cl in chlorobenzene (C_6H_5Cl) in the presence of Fe, Ni, or Co (used as catalyst) at about 140°C, B, B, B-trichloroborazine (one chloro group attached with each of the three B-atoms in $B_3N_3H_3$) is formed. This derivative, on being reduced by $LiBH_4$, in polyether, gives borazine, $B_3N_3H_6$.

$$3NH_4Cl + 3BCl_3 \xrightarrow[C_6H_5Cl\text{ and Fe)}]{140°C\text{ (In presence of}} \underset{\text{B, B, B-trichloroborazine}}{Cl_3B_3N_3H_3} + 9\,HCl$$

$$3Cl_3B_3N_3H_3 + 6LiBH_4 \xrightarrow{\text{Reduction}} 2B_3N_3H_6 + 6LiCl + 3B_2H_6$$

(ii) By heating a mixture of $LiBH_4$, and NH_4Cl (Laboratory method): $B_3N_3H_3$ can be prepared in the laboratory by heating a mixture of $LiBH_4$ and NH_4Cl in vacuum at 230°C.

$$3NH_4Cl + 3LiBH_4 \xrightarrow{230°C} B_3N_3H_6 + 3\,LiCl + 9H_2$$

This method gives 30% borazine.

Physical properties. (i) Barazine is a colourless mobile volatile liquid. It freezes at -58°C It's b.p. and m.p. are 64.5°C and -58°C respectively.

(ii) Decomposition: Borazine decomposes slowly on storage even at - 80°C and small quantities of a white solid are deposited over a period of several days. At room temperature, decomposition occurs much more rapidly and H_2, B_2H_6 and other volatile products are formed.

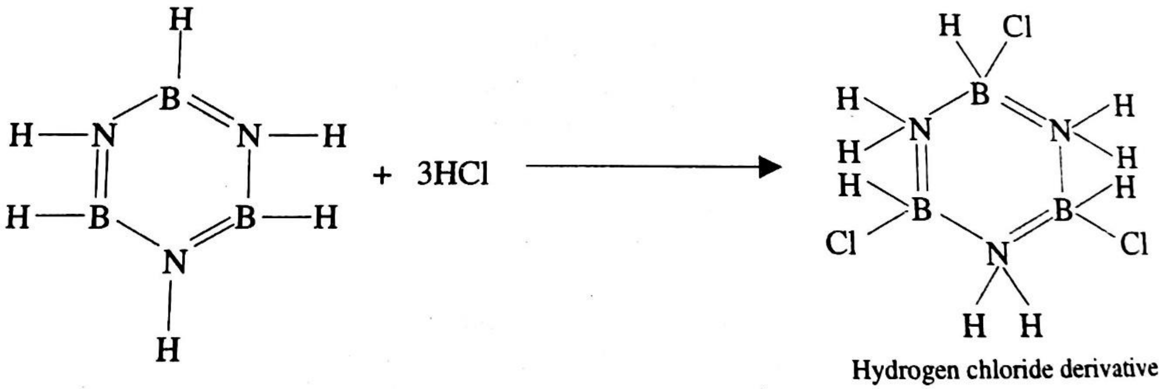
(iii) Similarities with benzene: Since borazine is isoelectronic with benzene, some of its physical properties are similar to those of benzene. This is shown below:

		Mol wt.	*M.pt.* (C°)	*B.pt.* (°C)	ΔH_{vap} (kJ mole^{-1})	*Trouton's constant*
Borazine ($B_3N_3H_6$)	:	80.6	– 58	64.5	39.3	21.4
Benzene (C_6H_6)	:	78.0	+ 6	80.0	31.0	21.0

This similarity of physical properties has unfortunately been over emphasised and hence borazine has been called **Inorganic Benzene**. However, the fact is that the properties of borazine and benzene are quite different.

Chemical properties. Main chemical properties of borazine are given below. These properties are not shown by benzene.

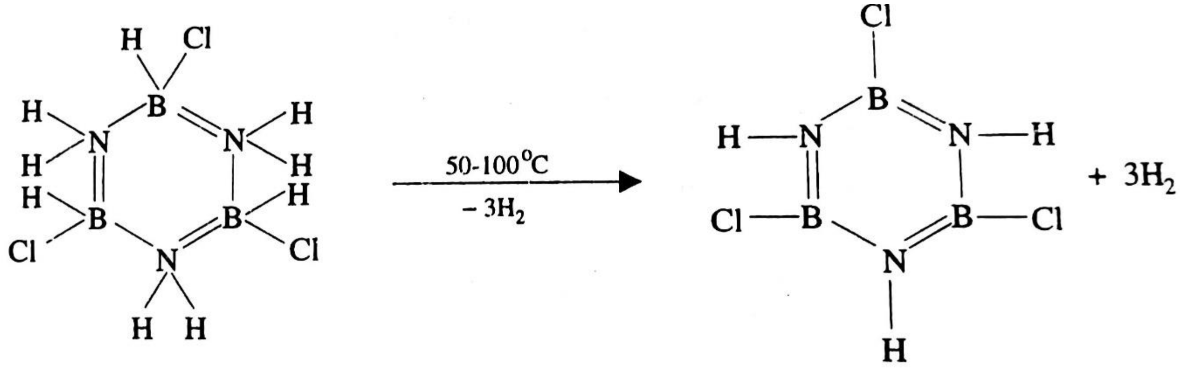
(i) Addition reactions: (a) One molecule of $B_3N_3H_6$, adds three molecules of HCl or HBr in the cold, without a catalyst. These molecules get attached with all the three B-atoms of $B_3N_3H_6$ molecule, since B-atom is more negative than N-atom in B-N or B = N bond and hydrogen chloride derivative ($B_3N_3H_9Cl_3$) is obtained. This addition reaction is not shown by benzene.



Hydrogen chloride derivative

$$\text{or} \quad B_3N_3H_6 + 3HCl \longrightarrow B_3N_3H_9Cl_3$$

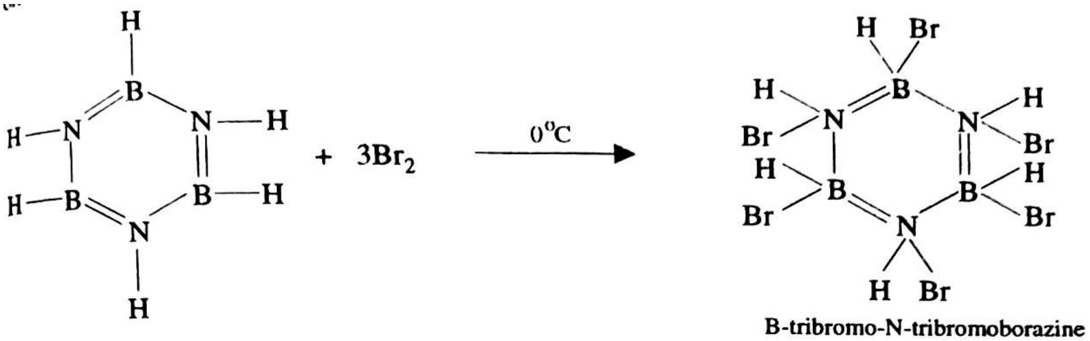
When this derivative is heated to 50-100°C, it loses three H_2 molecules, to give B,B,B-trichloroborazine, $B_3N_3H_3Cl_3$



B, B, B-trichloroborazine

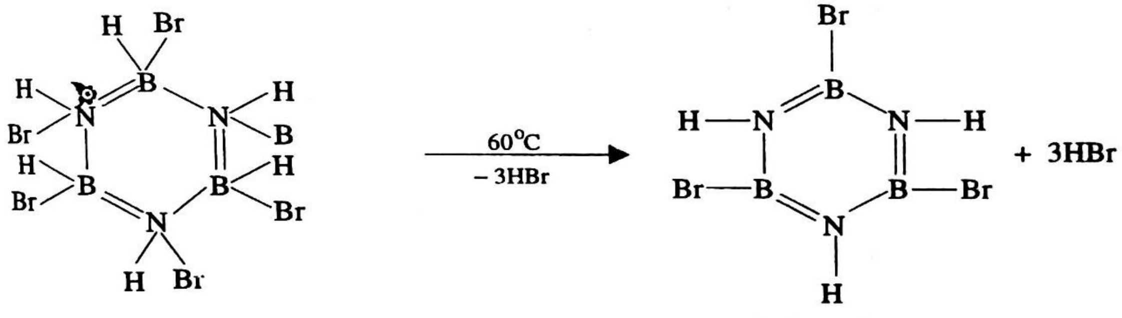
$$\text{or} \quad B_3N_3H_9Cl_3 \xrightarrow[-\,3H_2]{50\text{-}100^{\circ}C} B_3N_3H_3Cl_3 + 3H_2$$

(b) One molecule of borazine also adds three molecules of Br_2 at 0°C and gives B-tribromo –N- tribromoborazine which on being heated to 60° C, loses three molecules of HBr and forms B-tribromoborazine.



B-tribromo-N-tribromoborazine

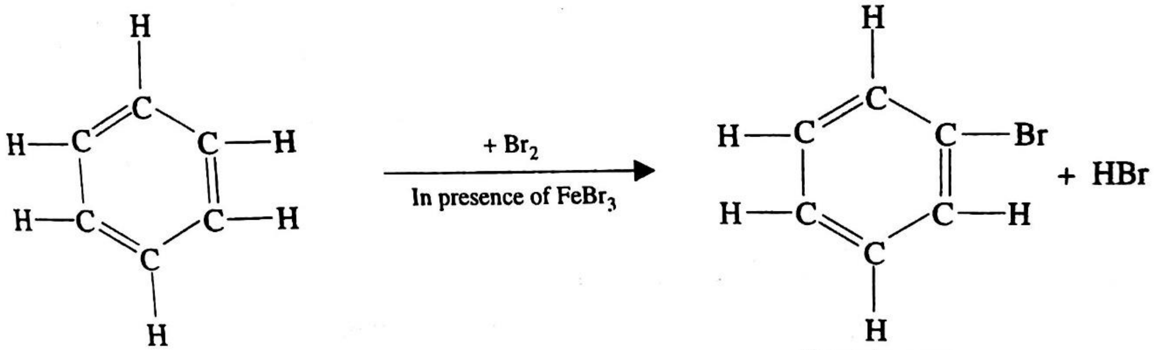
or $\underset{\text{Borazine}}{B_3N_3H_6} + 3Br_2 \xrightarrow{0^{\circ}C} B_3N_3H_6Br_6$



B-tribromoborazine

or $B_3N_3H_6Br_6 \xrightarrow[-\,3HBr]{60^{\circ}C} B_3N_3H_3Br_3 + 3HBr$

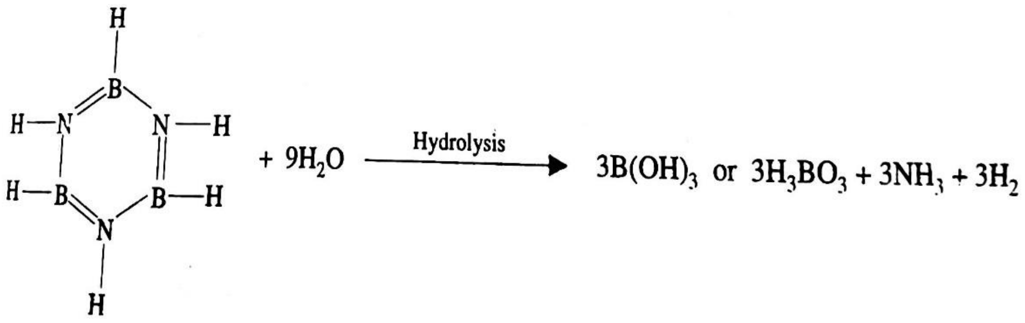
Benzene shows substitution reaction and give monobromobenzene, C_6H_5Br.



Bromobenzene

or $C_6H_6 \xrightarrow{+\,Br_2} C_6H_5\,Br + HBr$

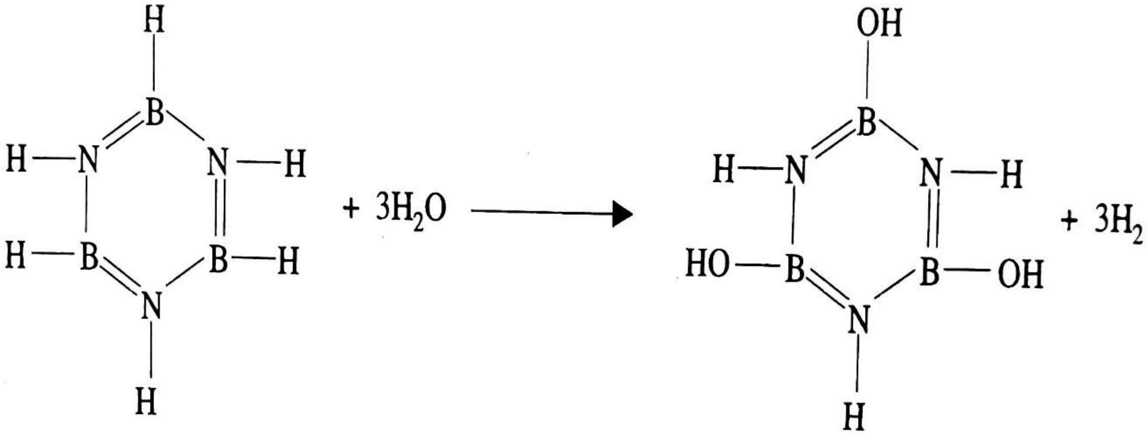
(ii) Hydrolysis. (a) Borazine gets slowly hydrolysed by water to produce boric acid [$B(OH)_3$ or H_3BO_3], NH_3 and H_2. Hydrolysis is favoured by the increase in temperature.



Or $B_3N_3H_6 + 9H_2O \longrightarrow 3B(OH)_3 + 3NH_3 + 3H_2$

C_6H_6 does not show this type of reaction.

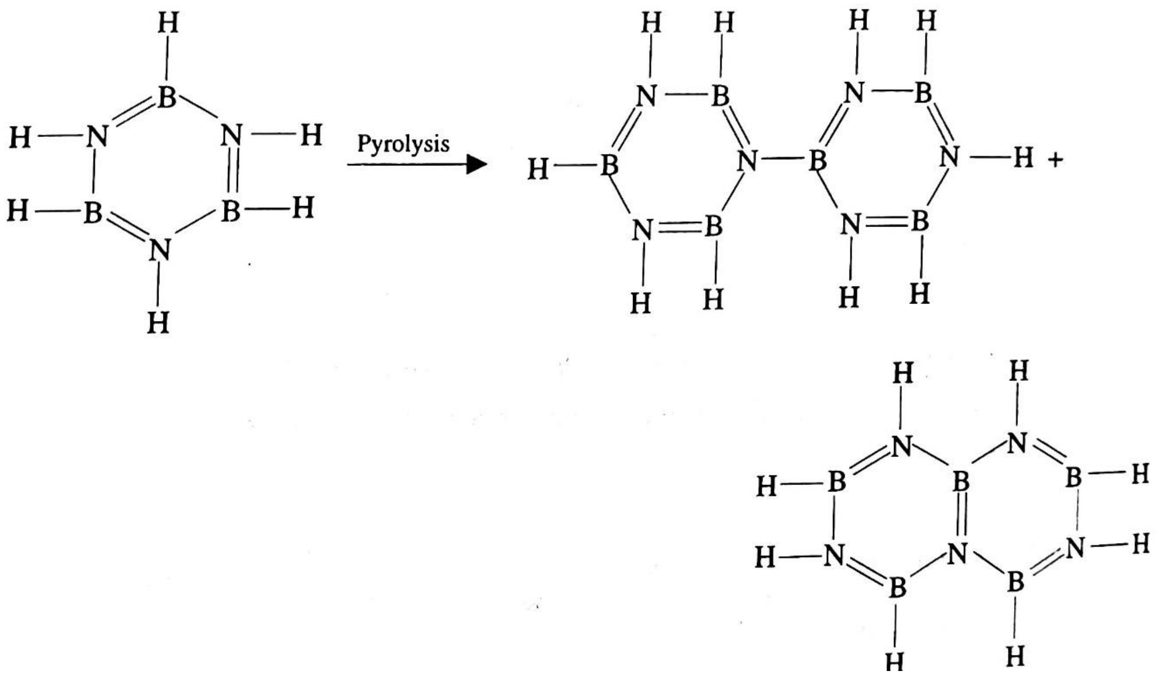
(b) It is reported that under proper conditions, borazine reacts with three molecules of water and gives B-trihydroxyl borazine, $B_3N_3H_3(OH)_3$ (substitution reaction).



B-trihydroxyl borazine

or $B_3N_3H_6 + 9H_2O \longrightarrow B_3N_3H_3(OH)_3 + 3H_2$

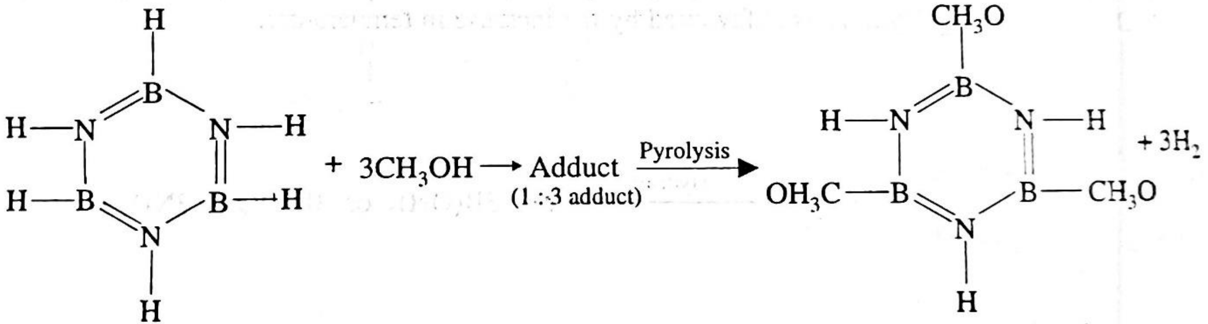
(iii) Pyrolysis: When borazine is pyrolysed above 340°C, $B_6N_6H_{10}$ and $B_5N_5H_8$ are produced. These products are boron-nitrogen analogues of diphenyl and naphthalene respectively.



Or $B_3N_3H_6 \xrightarrow{\text{Pyrolysis}} B_6N_6H_{10} + B_5N_5H_8$

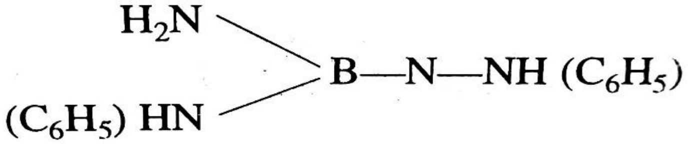
(iv) Hydrogenation: Hydrogenation of borazine produces polymeric materials of indefinite composition.

(v) Formation of adduct: Borazine forms an adduct with CH_3OH. This adduct undergoes pyrolysis with the elimination of H_2 and gives B-trimethoxy-borazine.



B-trimethoxy-borazine

(vi) Reaction with aniline: Borazine undergoes a strongly exothermic reaction with aniline, to produce tri-aminoborine,



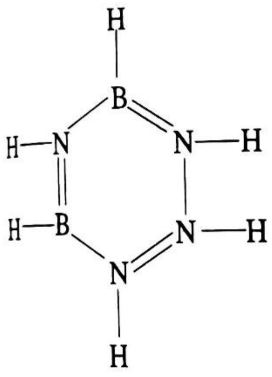
$$\begin{matrix}H_2N\\(C_6H_5)HN\end{matrix} > B\text{—}N\text{—}NH(C_6H_5)$$

Structure borazine molecule. Various chemical reactions and electron diffraction study of borazine molecule have shown, that this molecule is isoelectronic with benzene and hence its bure is the same as that of benzene. Thus, like benzene, borazine has a planar hexagonal structure containing six-membered ring, in which B and N atoms are arranged alternately. It is because of the similarity between the structures of borazine and benzene that borazine is called **Inorganic benzene**.

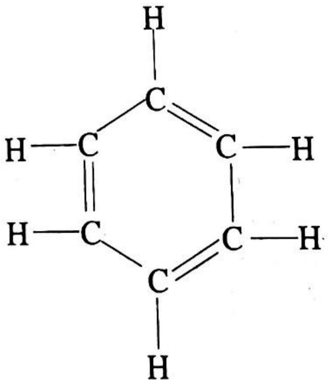
In the structure of borazine, both B and N atoms are sp^2 hybridised. Each N-atom has one lone of electrons, while each B-atom has an empty *p*-orbital. (B-N) π-bond in borazine is a dative bond, which arises from the sidewise overlap, between the filled *p*-orbitals of N-atom and empty *p*-orbitals of B-atom.

Since borazine is isoelectronic with benzene, both the compounds have aromatic π-electron cloud (electrons in π-orbitals). Due to greater difference in the electronegativity values of B and N-atoms, the π-electron cloud in B_3N_3 ring of borazine molecule is partially delocalised, while in case of benzene ring, the π-electron cloud is completely delocalised. In fact, complete delocalisation of π-electron cloud in B_3N_3 ring in borazine molecule, cannot be expected, since N - π orbitals are of lower energy than the B - π orbitals. Molecular orbital calculations have indicated that π-electron drift from N to B is less than the σ-electron drift from B to N, due to greater electronegativity of N-atom. In C_6H_6 molecule, C = C bonds are nonpolar, while in case of $B_3N_3H_6$ molecule, due to the difference in electronegativities between B and N atoms, B-N bond is polar.

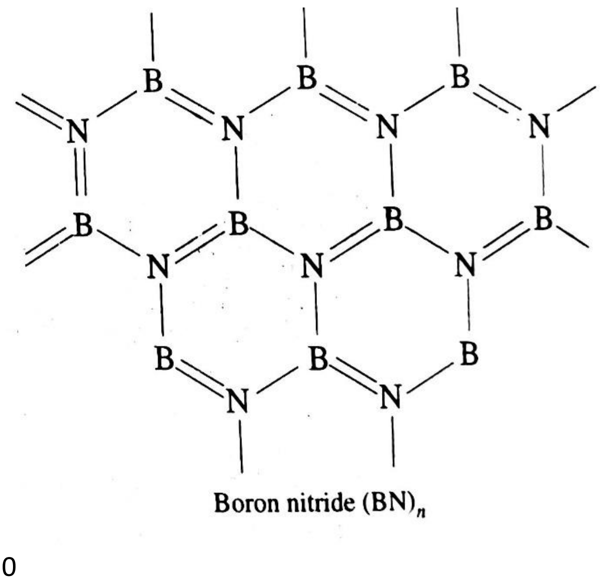
The ring structure of borazine molecule is the same as the layer lattice structure of boron nitride, $(BN)_n$.



Borazine, $B_3N_3H_6$



Benzene, C_6H_6



Boron nitride $(BN)_n$

It is due to the partial delocalization of the π-electron cloud that π-bonding in B_3N_3 ring is weakened. In addition, N-atom retains some of its basicity and boron atom retains some of its acidity. Polar species like HCl, therefore, attack the double bond between N and B. Thus, borazine, in contrast to C_6H_6, readily undergoes addition reactions.

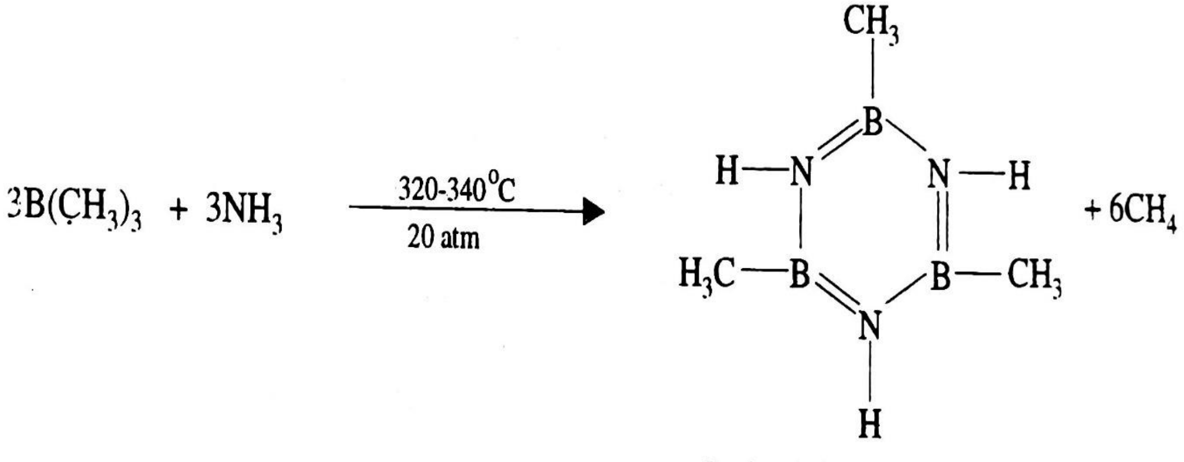
In these reactions, more electronegative atom (e.g., Cl in HCl molecule) is generally attached with B-atom, which is less electronegative than N in B-N bond.

In borazine, B-N bond length is equal to 1.44 Å, which is between the calculated single B-N bond (= 1 54 Å) and double bond, B = N (= 1.36 Å) distances. The angles are equal to 120°. In benzene C-C bond length is equal to 1.42 Å.

B. Substituted borazines

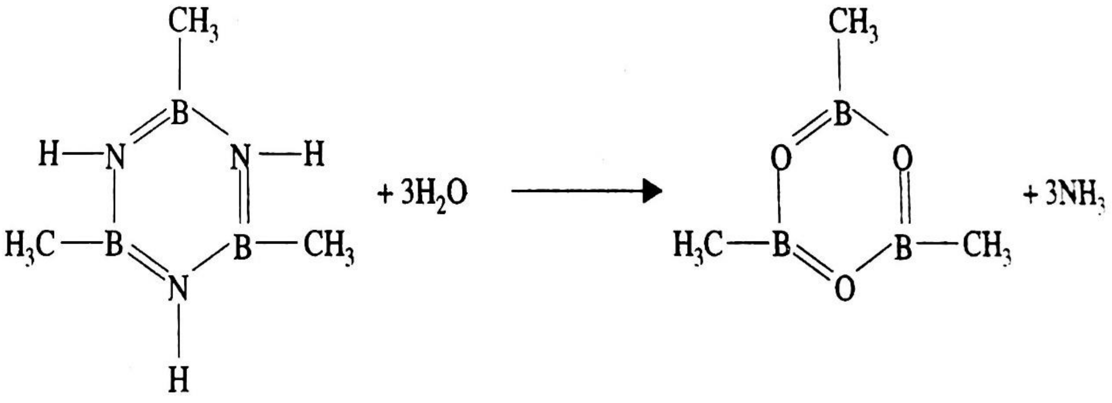
Here, we shall discuss the following substituted borazines.

1. **B-trimethyl borazine, $[B(CH_3)]_3(NH)_3$.** It is prepared by heating $B(CH_3)_2$ with NH_3 at 320-340° at 20 atm. for 2 hours.



B-trimethyl borazine, $[B(CH_3)]_3(NH)_3$

At room temperature, this compound exists as colourless crystals. Its m.pt. and b.p. are 31.8° and 127°C respectively. It is stable in vacuum upto 350°C. It is sensitive towards moisture, but insoluble in water. It is soluble in many organic solvents. At 100°C, water replaces the NH groups by O-atoms and gives B-trimethyl boroxine, $[B(CH_3)]_3O_3$.



B-trimethyl borazine, $[B(CH_3)]_3(NH)_3$ B-trimethyl boroxine, $[B(CH_3)]_3O_3$

2. Boroxine, $(BH)_3O_3$. This compound is isoelectronic with borazine, $B_3N_3H_6$ ($B_3O_3H_3$) = 3 x 3 + 3 x 6 + 3 x 1 = 30, $B_3N_3H_6$ = 3 x 3 + 5 x 3 + 6 x 1 = 30). It is produced by the explosive oxidation of B_2H_6 or B_5H_9. This compound decomposes at room temperature to diborane (B_2H_6) and boron trioxide (B_2O_3).

$$2B_3O_3H_3 \rightarrow 2B_2O_3 + B_2H_6$$

Boroxine exhibits aromatic properties of benzene. $B_3O_3H_3$ molecule has six-membered planar structure, as shown in Fig. Boroxine is even less stable and presumably has less π-delocalization than borazine. In this molecule, B - O bond distance is equal to 1.38 Å. The characteristic Roman frequency of the ring is at 807 cm^{-1}. B = O, double bond present in the structure is due to the donation of a lone pair of electrons from O-atom to boron atom. This results in the development of a formal negative charge on B-atom and equal formal positive charge on O-atom. These charges have not been shown in the Fig.

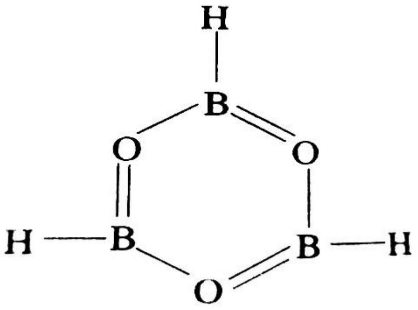
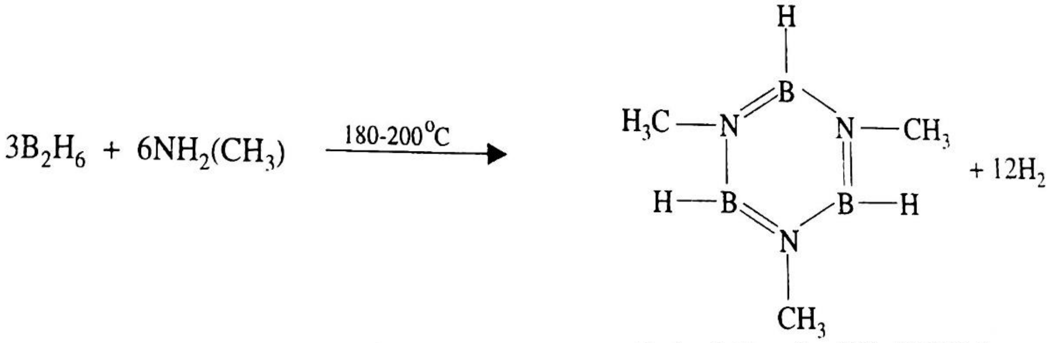


Fig.: six-membered planar structure Boroxine molecule, $(BH)_3O_3$

3. N-trimethyl borazine, $(BH)_3$ $[N(CH_3)]_3$ It is obtained in 90% yield by heating mixture of B_2H_6 and $NH_2.(CH_3)$ in the correct proportions at 180-200°C for 2 hours.

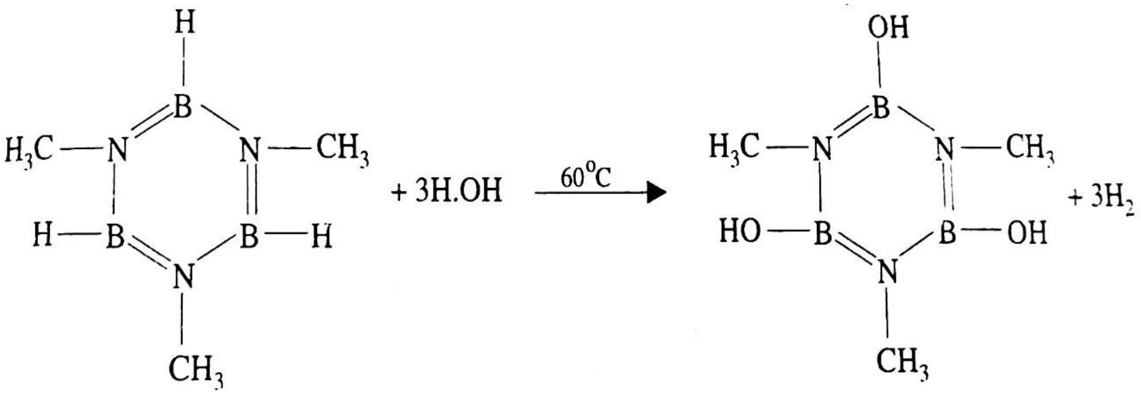


N-trimethyl borazine, $(BH)_3$ $[N(CH_3)_3]$

This compound can also be prepared by reducing monomethyl ammonium chloride, $(CH_3)NH_3$ Cl with lithium borohydride, $LiBH_4$

$$3(CH_3)NH_3Cl + 3LiBH_4 \rightarrow (BH)_3[N(CH_3)]_3 + 3LiCl + 9H_2$$

It is a colourless mobile liquid having m.pt. = -9 °C and b.p. = 132 °C. It is stable upto 500°C. At 60 °C, H-atom attached with B-atom is replaced by OH group.



C. Boron nitride, BN:

Preparation: It is prepared by following methods:

(i) by heating boron to a white heat, in an atmosphere of nitrogen, NO or NH_3.

$$2B + N_2 \rightarrow 2BN; \qquad 5B + 3NO \rightarrow 3BN + B_2O_3$$

$$2B + 2NH_3 \rightarrow 2BN + 3H_2$$

(ii) by heating B_2O_3 with $Hg(CN)_2$, KCN or NH_4Cl.

$$B_2O_3 + Hg(CN)_2 \rightarrow 2BN + CO + CO_2 + Hg$$

$$B_2O_3 + 2KCN \rightarrow 2BN + K_2O + 2CO$$

$$B_2O_3 + 2NH_4Cl \rightarrow 2BN + 3H_2O + 2HCl$$

(iii) when perfectly anhydrous borax ($Na_2B_4O_7$) is heated with dry NH_4Cl to a red heat in a Platinum crucible.

$$Na_2B_4O_7 + 2NH_4Cl \rightarrow 2BN + 2NaCl + B_2O_3 + 2H_2O$$

The resulted mass is treated with dil. HCl which dissolves B_2O_3 and NaCl, leaving behind BN. It is repeatedly washed with water and dried.

(iv) Pure. BN is best prepared by heating boron amide, $B(NH_2)_3$ or boron imide, $B_2(NH)_3$ or by the action of NH_3 on BCl_3.

$$2B(NH_2)_3 \xrightarrow{\Delta} 2BN + 4NH_3; \quad B_2(NH)_3 \xrightarrow{\Delta} 2BN + NH_3$$

$$2BCl_3 + 8NH_3 \rightarrow 2BN + 6NH_4Cl$$

(v) BN can also be prepared by passing N_2 gas through a mixture of B_2O_3 and carbon heated in an electric furnace.

$$B_2O_3 + 3C + N_2 \rightarrow 2BN + 3CO\uparrow$$

(vi) When diborane (B_2H_6) reacts with excess of NH_3 at high temperature, BN is obtained.

$$B_2H_6 + 2NH_3 \text{ (excess)} \rightarrow 2BN + 6H_2$$

Properties:

(i) Boron nitride is white powder of density 2.34. It melts under pressure at 3000 ^{0}C. It is very stable and unreactive substance. It remains unaffected by mineral acids, solution of alkalies and Cl_2 at red heat.

(ii) Decomposition: (a) It gets decomposed when heated in steam, evolving NH_3.

$$BN + 3H_2O \rightarrow B(OH)_3 \text{ or } H_3BO_3 + NH_3$$

(b) It is decomposed, but slowly, by HF, forming ammonium borofluoride, NH_4BF_4.

$$BN + 4HF \rightarrow NH_4BF_4$$

(c) It is also decomposed when fused with KOH.

$$BN + 3KOH \rightarrow K_3BO_3 + NH_3\uparrow$$

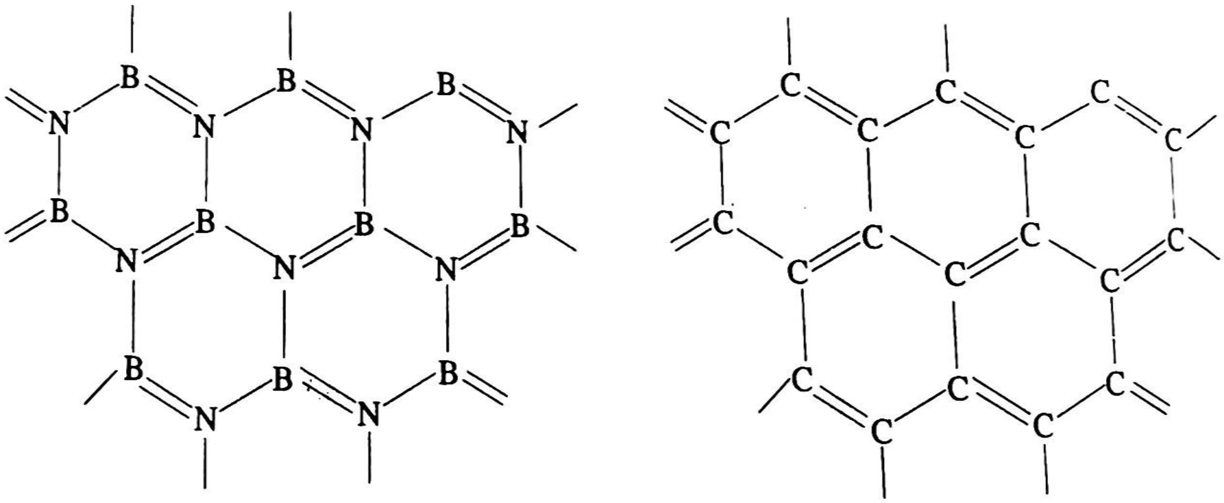
(iii) Reaction with K_2CO_3: When BN is fused with K_2CO_3, potassium cyanate (KCNO) and potassium metaborate (KBO_2) are obtained.

$$BN + K_2CO_3 \rightarrow KCNO + KBO_2$$

Uses: BN possesses same hardness as diamond and can withstand temperature of more than 300 ^{0}C. Due to this property it is used for coating crucible linings.

Structure: The lattice of boron nitride consists of different layers. Each layer has a hexagonal arrangement of B and N atoms. Different layers are arranged in such a manner that B-atoms in one layer are immediately above the N-atoms in the adjascent layer. The (B-N) distances are equal to 1.45 Å and the distance between the two layers is 8.33 Å. The (B-N) bonds in boron nitride are formed by the overlapping of sp^2 hybrid orbitals of boron and nitrogen atoms. The remaining electrons form π-bonds.

BN molecule is iso-electronic with two adjascent C-atoms in graphite (BN=3+5=8, C_2 =4+4=8) and hence the structure of $(BN)_n$ is similar to that of graphite, C_n. In graphite π-electrons are completely delocalized over all the C-atoms of the lattice while in boron nitride the π-electrons are only partially delocalized over B-atoms, leading to unequal (B-N) bond lengths. Boron nitride, like graphite, is able to act as host, i.e., it is able to occlude oxides, sulphides, oxy-halides and chlorides in the same way as graphite does. Boron nitride, when heated to 3000 ^{0}C at 70,000 atm pressure gives a cubic form of boron nitride which has diamond like structure in which all the B and N-atoms attain tetrahedral (four) coordination. This cubic form is superior to diamond, in its mechanical strength and hardness, and suffers only superficial oxidation in air at high temperatures.



Boron nitride, $(BN)_n$

Graphite, C_n

Fig.: Similarity between the structures of boron nitride and graphite.

Silicones: Polymers containing silicon

What are silicones?

Silicons are organo-silicon polymers containing -----O--Si-O----- linkages. These may be linear silicones cyclic silicones and cross-linked silicones.

Preparation of silicones

These are prepared by the hydrolysis of alkyl or aryl derivatives of $SiCl_4$ like $RSiCl_3$, R $SiCl_2$ and R_3SiCl and polymerisation of alkyl or aryl hydroxy-derivatives obtained by hydrolysis. Thus, this method consists of the following steps:

(i) To prepare alkyl or aryl derivatives of silicon tetrachloride:
Examples of such derivatives are $RSiCl_3$, R_2SiCl_2 and R_3SiCl_2 where R is an alkyl (e.g., CH_3, C_2H_5 etc.) or aryl (e.g., C_6H_5) group.

These derivatives are prepared by the following methods:

(a) Methyl chlorosilanes like $(CH_3)SiCl_3$, $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$ are prepared by heating methyl chloride, $(CH_3)Cl$ with Si, catalyzed by Cu, at 300°C. This reaction gives a mixture of methyl chlorosilanes.

$$2CH_3Cl + Si \xrightarrow[300^\circ C]{Cu} \underbrace{(CH_3)SiCl_3 + (CH_3)_2SiCl_2 + (CH_3)_3SiCl}_{\text{Mixture of methyl chlorosilanes}} + \text{Other compounds}$$

The yield of $(CH_3)_2SiCl_2$ (b.p. = 69.6°C) is over 50%. Careful fractionation is used to separate $(CH_3)_2SiCl_2$, from $(CH_3)SiCl_3$ (b.p. = 66.9°C) and $(CH_3)_3SiCl$ (b.p. = 87.7°C).

It a mixture of CH_3Cl and HCl is heated with Si, catalysed by Cu, at 300°C, then $(CH_3)SiCl_3$ is obtained as the main product.

$$CH_3Cl + 2HCl + Si \xrightarrow[300^\circ C]{Cu} (CH_3)SiCl_3 + H_2$$

(b) Alkyl chlorosilanes can also be obtained by the action of Grignard reagent on $Sici_4$.

$$RMgCl\ (\text{Grignard reagent}) + SiCl_4 \rightarrow RSiCl_3 + MgCl_2$$

$$2RMgCl + SiCl_4 \rightarrow R_2SiCl_2 + 2MgCl_2$$

$$3RMgCl + SiCl_4 \rightarrow R_3SiCl + 3MgCl_2$$

(c) Phenyl chlorosilane, (C_6H_5) $SiCl_3$ is obtained by heating C_6H_6 with $HSiCl_3$ at 230-300°C in presence of a catalyst like BF_3, BCl_3 or $AlCl_3$.

$$C_6H_6 + HSiCl_3 \xrightarrow[\text{Catalyst}]{\Delta} (C_6H_5)SiCl_3 + H_2$$

(ii) To prepare alkyl or aryl hydroxy derivatives of silicon tetrachloride (called silanols or silandiols): Examples of such silanols are R Si $(OH)_3$, $R_2Si(OH)_2$ and $R_3Si(OH)$. These silanols are obtained by the hydrolysis of $RSiCl_3$, R_2SiCl_2 and R_3SiCl respectively.

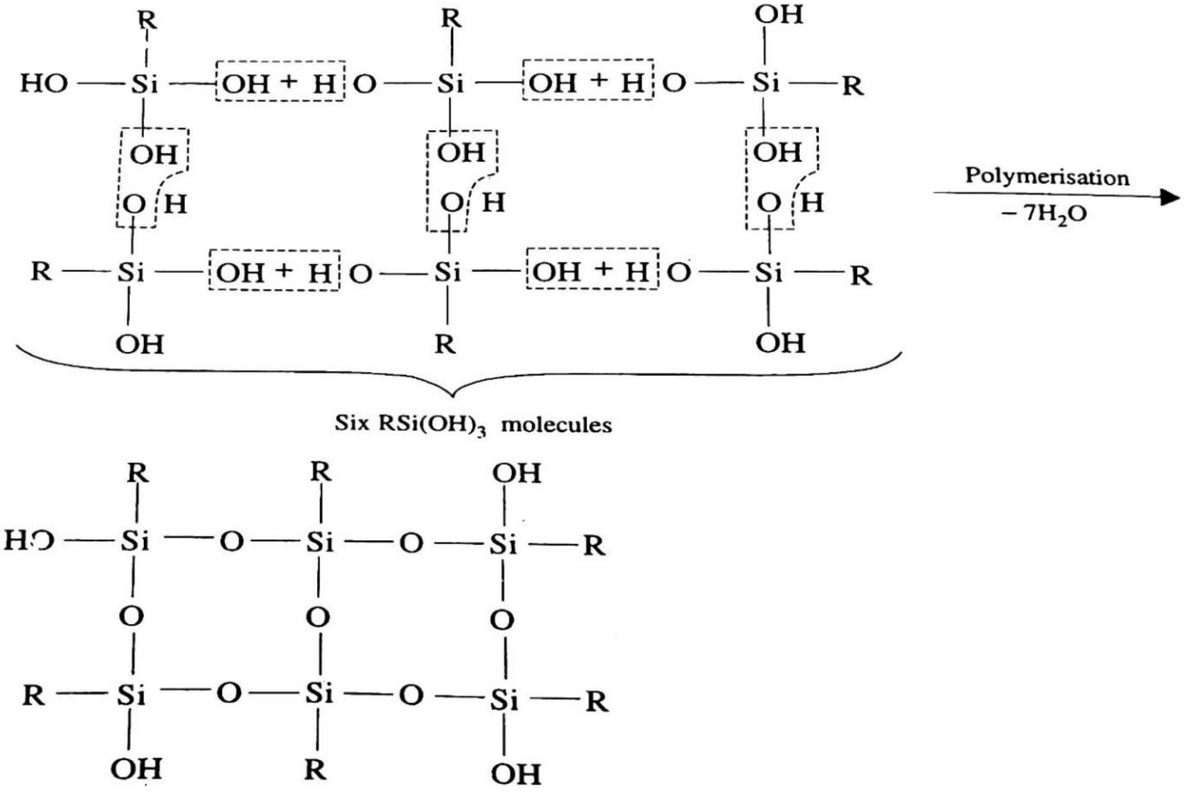
$$\begin{array}{lcl}
RSiCl_3 + 3H.OH & \xrightarrow{\text{Hydrolysis}} & RSi(OH)_3 + 3HCl \\
R_2SiCl_2 + 2H.OH & \xrightarrow{\text{Hydrolysis}} & R_2Si(OH)_2 + 2HCl \\
R_3SiCl + H.OH & \xrightarrow{\text{Hydrolysis}} & R_3Si(OH) + HCl \\
\textbf{Chlorosilanes} & & \textbf{Silanols}
\end{array}$$

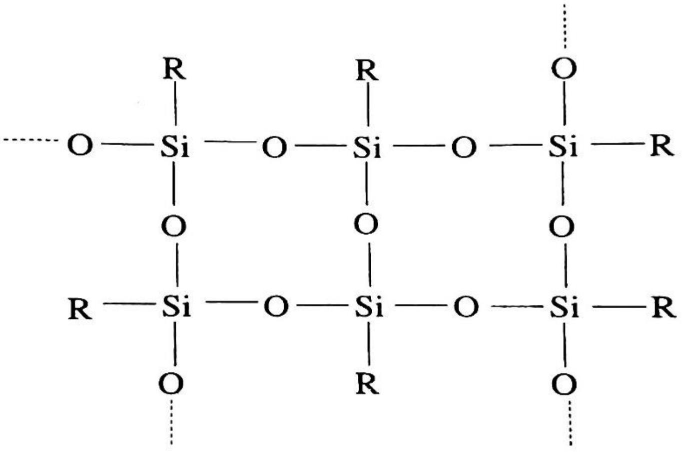
The general equation representing the hydrolysis reaction can be written as:

$$\text{Clorosilane} + \text{Water} \xrightarrow{\text{hydrolysis}} \text{Silanols} + \text{HCl}$$

(iii) To allow the alkyl or aryl hydroxy derivatives to undergo polymerization: Polymerisation process involves removal of some H_2O molecules and leads to the formation of different types of silicones. The type of silicone obtained depends on the nature of alkyl or aryl hydroxyderivative and the way in which the hydroxy-derivative undergoes polymerisation. For example:

(a) When many molecules of alkyl trihydroxy-silane, $RSi(OH)_3$ undergoes polymerisation, a cross-linked two dimensional silicone is obtained.

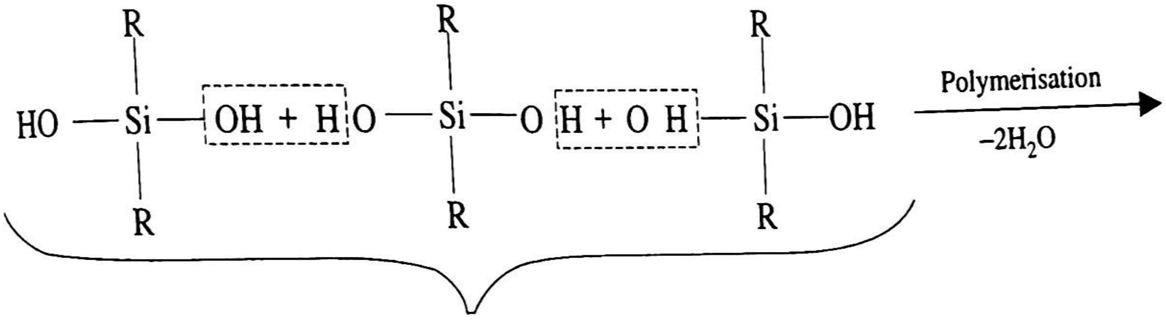




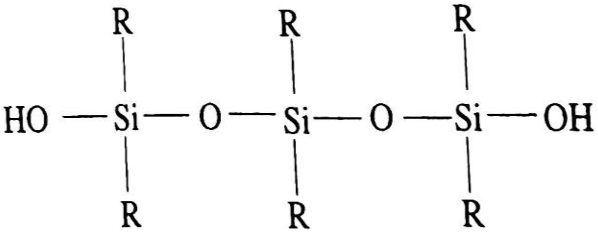
Two dimensional cross-linked silicone

Since an active OH group is present at each end of the chain, polymerisation continues on both the ends and hence the length of the chain increases. The increase in the length of the chain produces cross-linked silicone as shown below:

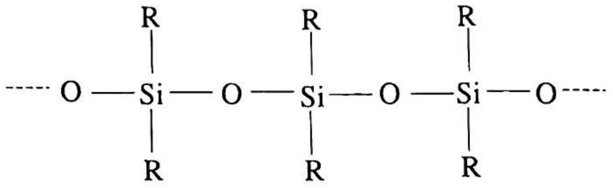
(b) When many molecules of dialkyl dihydroxy-silane, $R_2Si(OH)_2$ undergo polymerisation, a straight chain (linear) or cyclic (ring) silicone is obtained.



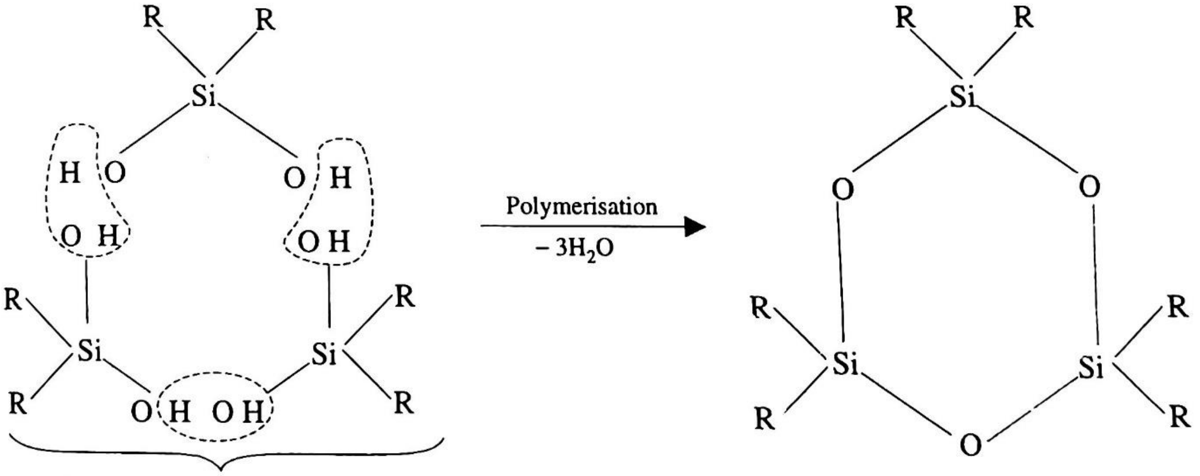
Three molecules of $R_2Si(OH)_2$



Since an active OH group is present at each end of the chain, polymerisation continues and hence the length of the chain increases and gives rise to the formation of long chain silicon, as shown below:



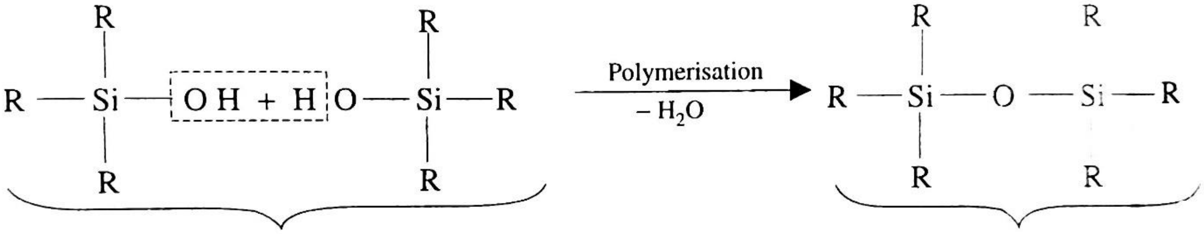
Linear or straight chain silicone (Thermoplastic polymer) (siloxane)



Three molecules of $R_2Si(OH)_2$

Cyclic trimer

(c) When two molecules of trialkyl monohydroxy-silane, $R_3Si(OH)$ undergo polymerisation, a straight chain silicone (dimer) is obtained.



Two molecules of $R_3Si(OH)$

Straight chain $R_3Si\text{-}O\text{-}SiR_3$ (dimer)
((It is a Siloxane)

Properties and uses of silicones

The following properties and uses are common to all types of silicones :

(i) They have high thermal stability in the absence of air and withstand temperature upto 250-300°C.

(ii) They remain unaffected by most of the chemical reagents, such as weak acids, alkalies and salt solutions. Thus, silicones are chemically inert.

(iii) Many of low molecular weight silicones dissolve in solvents like C_6H_6, ether and CCl_4.

(iv) They do not become too viscous on cooling and are, therefore, used for low-temperature, lubrication.

(v) They are water repellent, i.e., they are not wetted by water and are, therefore used in making waterproof cloth and paper by exposing cloth or paper to the silicone vapours.

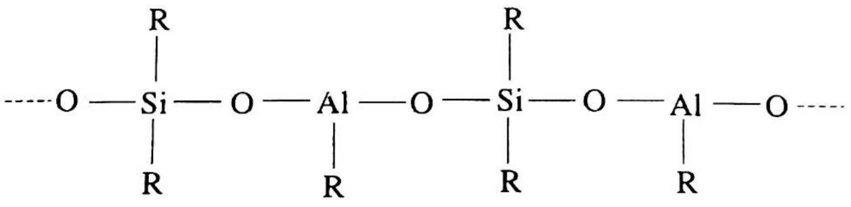
(vi) All silicones have good insulating properties and can withstand high temperature without charring. It is due to these properties that silicones are used as insulating materials for electric motors and other electric appliances.

(vii) They are non-toxic.

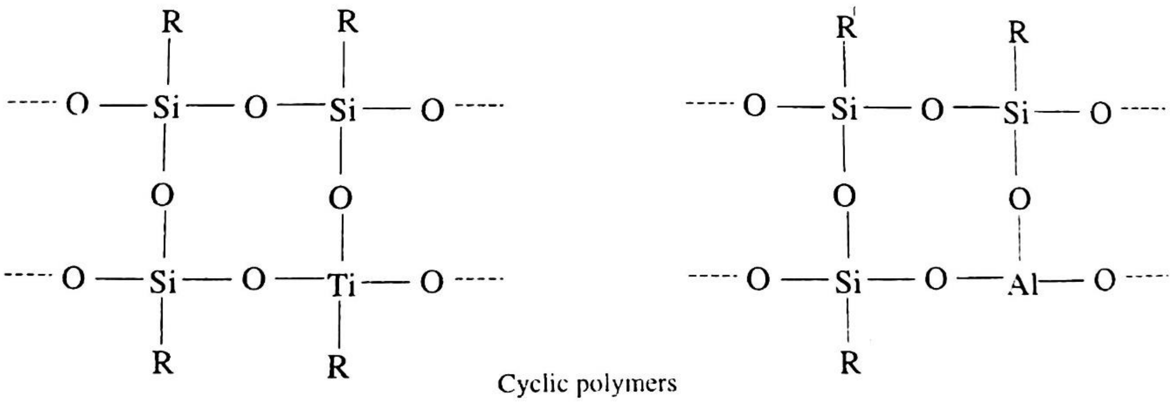
Types of silicones: Their preparation, properties and uses

Depending on the degree of polymerisation undergone by the alkyl or aryl hydroxy-derivatives of $SiCl_4$, the length of the straight chain in cross-linked silicones and the nature of the alkyl or aryl groups attached with Si-atom in silicones, silicones can be obtained in the form of oils, viscous fluids, resins or rubber-like solids. Thus, silicones can be classified into the following types:

1. High thermal silicones: When hydrolysis of an organo silicon halide is carried out in presence of the halides or alkoxides of Al or Ti, two-dimensional linear or cyclic silicone polymer is obtained. In this polymer, some Si-atoms are replaced by Al or Ti atoms.



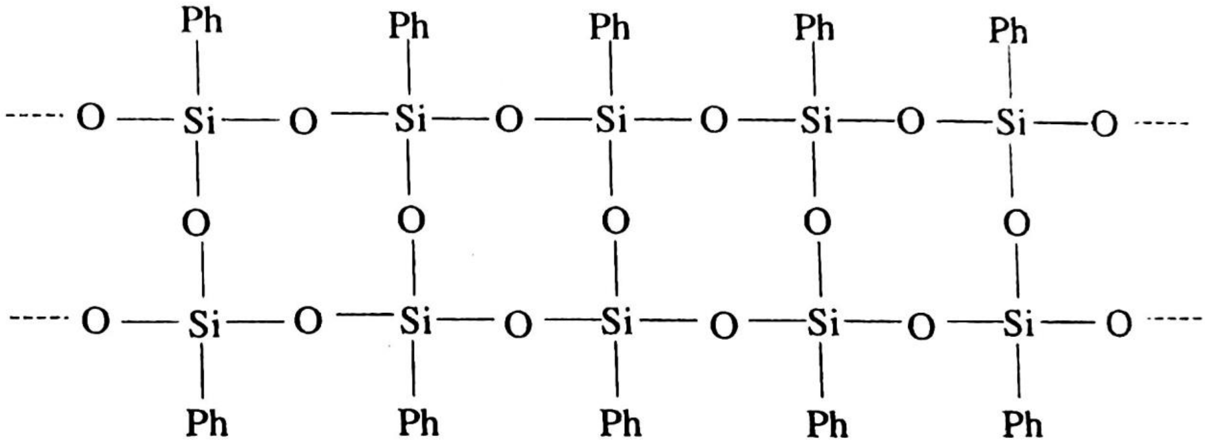
Linear polymer



Cyclic polymers

High thermal silicones have exceptionally high thermal stability and remain unchanged, even in contact with a white-hot electrically-heated wire. The presence of Al and Ti atoms in the structure of the polymers increases the thermal stability of the polymers.

In 1960, Brown *et al* reported the synthesis of a linear polymer. This polymer has exceptionally high thermal stability. Its structure can be represented as:

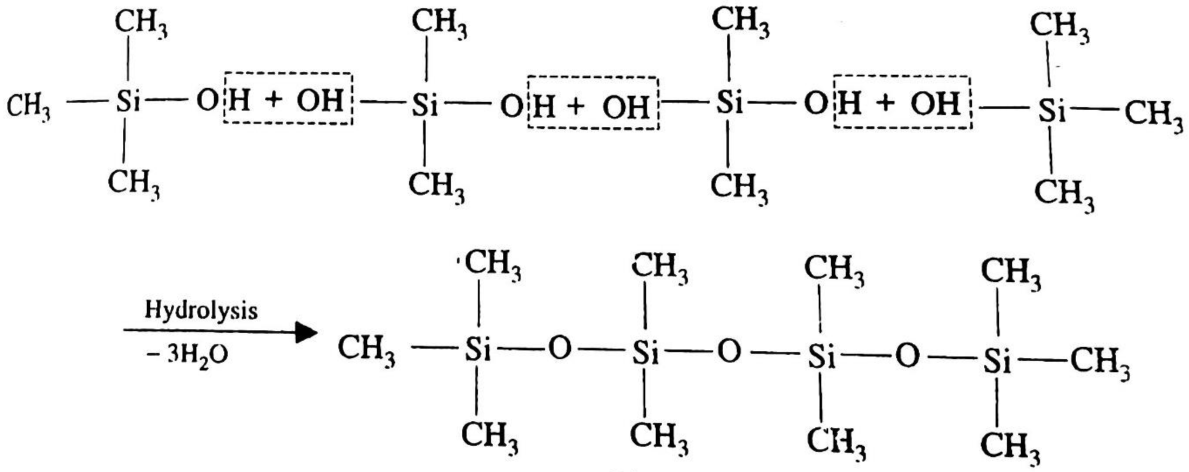


2. Silicone resins: Silicone resin is obtained by blending silicone with organic resin, such acrylic ester. If the hydrolysis of $(CH_3)_2SiCl_3$ is carried out in presence of $(CH_3)SiCl_3$ and then polymerisation is allowed, a rigid silicone is obtained. This silicone is called silicone resin. These are of many types, like coating resins, laminating resins, release resins, water-repellent resins, molding resins and electrical resins. These are stable to heat, water-repellent and have good electrical conductivity chemical inertness and weather resistance. To develop best properties in them, baking or heat treatment is given to them. These can withstand temperature as high as 250°C and coating made up of silicone resin plus organic resins and Al can withstand temperature upto 500°C.

Release resins are baked on metal surfaces, to prevent materials from sticking to these surfaces. Silicone resin solutions are mixed in paints, pigments and enamels, to make them resistant to the effects of high temperatures, sunlight, chemicals and damp. Silicone resin, mixed with the pigment like Al-flakes, can withstand 400°C. Silicone resins, having TiO_2 (TiO_2, is a pigment) resist dissociation, due to heat and weathering. These silicone resins are not affected by soap and fruit juices.

3. Silicone fluids or oils: A silicone fluid is a mixture of equal proportions of linear and cyclic polymers. These have low temperature-coefficient of viscosity, which makes them valuable hydraulic fluids. They have good insulating properties and high thermal stability. It is due to these properties that silicone fluids are used as dielectric fluids.

Emulsions of silicone fluids in water are made for convenience in applying small amounts to silicone textiles, paper or other surfaces. Silicone oils are highly stable and non-volatile, even on heating. They are therefore, used for high temperature oil baths, high vacuum pumps and low temperature lubrication. Variation in the length of the chain gives silicone oils varying viscosities. The viscosity of silicone oils remains constant, even with the change of temperature and as such these silicones do not thicken in cold weather. Generally, low molecular weight silicones are oily liquids.



Dimethyl silicone oil

Preparation of dimethyl silicone oil: If a mixture containing $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$, in proper ratio, is hydrolysed and the hydroxy-derivatives, thus obtained, are polymerised, then dimethyl silicone oil is obtained. This compound contains CH_3 group at each end of the chain. It is a linear silicone.

4. Silicone rubbers: These are long chain polymers, with some cross-linking between the chains. They are made by the hydrolysis of $(CH_3)_2$ $SiCl_2$ or $[(CH_3)_2$ $SiO]_4$ followed by polymerisation. $(CH_3)_3$ Si–O—Si $(CH_3)_3$ may be added to the reaction mixture to control the chain length of the polymer. Silicone rubbers consist of cross-linked type silicones with SiO_2 or ZnO as filler and vulcanizer, such as benzoyl peroxide.

Silicone rubbers are especially valuable, since they retain their elasticity over a range of temperatures and are resistant to oils. Silicone rubbers, which can withstand temperature upto 400°C for 200 hours and upto 540 °C for 90 hours, have also been prepared. Their resistance to heat is much higher than that of many organic rubbers. It is due to their property to withstand high temperatures, that they are used in sealing joints and seams of jet aircraft and insulating electrical parts like transistors, which cannot be heated.

Silicone rubber retains its shape and elasticity permanently, even after vulcanization and has, therefore, been used in a number of ways. High molecular weight silicones, containing long chain or ring structure, are generally waxy or rubber-like solids.

5. Silicone greases: These are made by adding carbon black, special soaps or finely dispersed SiO_2 to silicone oils. Silicone grease, prepared from medium phenyl oil and lithium soap, is used for ball bearings operating at high speed and high temperature. Silicone greases are Vaseline-like, these are used as lubricants in aeroplanes, since they do not freeze at as low temperature as - 40°C and do not melt at 200°C.

Polymers containing phosphorus

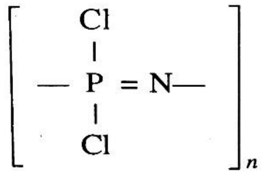
Depending on the type of bonding existing between their atoms, these polymers can be of the following two types:

1. Chain polymers: These polymers include (i) polyphosphazines, $[NPR_2]_n$ in which R = Cl, OCH_3 or OC_2H_5. Polyphosphazines may be of three types namely (a) polyphosphonitrilic chlorides, $[NPCl_2]_n$ (b) polydimethoxy-phosphazines, $[NP(OCH_3)_2]_n$ (c) poly diethoxy-phosphazines, $[NP(OC_2H_3)_2]_n$ (ii) polyphosphoryl chlorides, $P_n\ O_{2n-1}$, Cl_{n+2} (iii) vitreous polyphosphates (phosphate glasses) (iv) crystalline polymetaphosphates. Examples are Maddrell's and Kuroll's salts (v) platicised and flexible phosphates (vi) polyphosphoric acids.

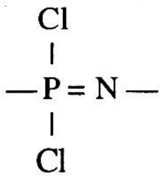
2. Network polymers: These polymers include (i) polymeric phosphorus pentoxide (ii) polymeric boron orthophosphates, $[BPO_4)_n$ (iii) polymeric aluminium orthophosphates $[AlPO_4]_n$ (iv) polymeric silver orthophosphate, $[Ag_3PO_4]_n$, (v) polymeric ferrous orthophosphate, $[Fe_3(PO_4)_2.8H_2O)_n$ (vi) sulphur-phosphorus polymers (vii) ultraphosphate glasses (viii) boron phosphate glasses.

Polyphosphonitrilic chlorides, $[PNCl_2]_n$ (n = 3 to 7) :

These polymers are also called **inorganic rubbers**. These compounds can be represented by the general structure,



$$\left[-\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{P}}}}=N- \right]_n$$

Thus, these compounds contain  $-\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{P}}}}=N-$ as a repeating unit.

Examples of polyphosphonitric chlorides are triphosphonitrilic chloride, $[PNCl_2]_3$; *tetraphos*phonitrilic chloride, $[PNCl_2]_4$ etc.

Preparation. The following methods have been used for the preparation of these compounds:

(i) $(NPCl)_3$ and $(NPCl_2)_4$ can be prepared by the ammonolysis of PCl_5.

$$3PCl_5 + 3NH_3 \rightarrow (NPCl_2)_3 + 9HCl \ ; \ 4PCl_5 + 4NH_3 \rightarrow (NPCl_2)_4 + 12HCl$$

(ii) These compounds can be prepared by the reaction between PCl_5 and NH_4Cl in presence of $C_2H_4Cl_2$ or C_6H_5Cl or by heating PCl_5 with solid NH_4Cl at 145-160° C.

$$nPCl_5 + nNH_4Cl \xrightarrow[\text{or } C_6H_5Cl]{C_2H_4Cl_2} (NPCl_2)_n + 4nHCl$$

$$nPCl_5 + nNH_4Cl\ (s) \xrightarrow{145-160^\circ} (NPCl_2)_n + 4nHCl$$

Both the above reactions produce a mixture of various phosphonitrilic chlorides, but under controlled conditions, high yields of $(NPCl_2)_3$ and $(NPCl_2)_4$ can be obtained. These two compounds can be separated from each other by using the fact that $(NPCl_2)_3$ sublimes in vacuum at 50°C as a white crystalline solid whereas $(NPCl_2)_4$ does not do so under these conditions.

The formation of $(NPCl_2)_n$ takes place through the following steps :

(*a*) $NH_4Cl + PCl_5 \longrightarrow NH_4\ PCl_6$ (*Ammonium hexachlorophosphate—an unstable compound*)

(*b*) $NH_4\ PCl_6 \xrightarrow{\text{Decomposition}} HN.\ PCl_3 + 3HCl$

(*c*) $nHN.\ PCl_3 \xrightarrow[(-nHCl)]{\text{Condensation}} (NPCl_2)_n + nHCl$

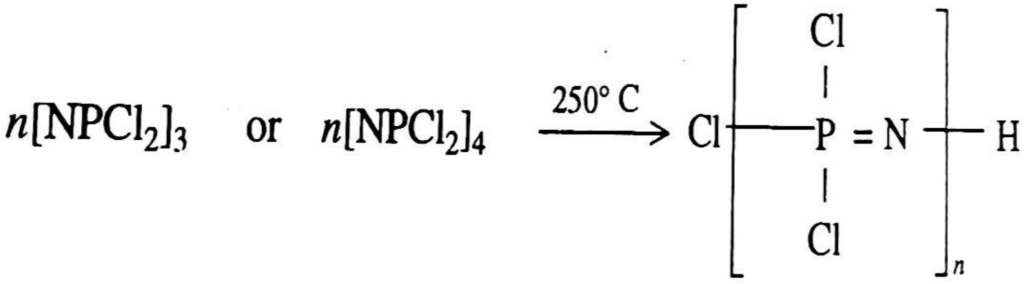
(*iii*) S_4N_4 reacts with $SOCl_2$ in PCl_3 to give $(NPCl_3)_2$.

$$S_4N_4 + 6SOCl_2 + 12PCl_3 \longrightarrow 4(NPCl_2)_3 + 10\ S + 3O_2 + 12Cl_2$$

Properties. (1) $(NPCl_2)_3$; melts at 114° C, boils at 256°C at 1 atm pressure and is readily soluble in benzene, ether and carbon tetrachloride. $(NPCl_2)_4$ melts at 123.5°C, boils at 328.5°C and has a lower solubility in benzene, ether and carbon tetrachloride than $(NPCl_2)_3$.

(2) $(NPCl_2)_3$ and $(NPCl_2)_4$ are irritating and somewhat toxic also.

(3) Cyclic trimer. $[NPCl_2]_3$ or tetramer, $[NPCl_2]_4$, when heated in vacuum at 250°C gives a chain polymer.



$$n[NPCl_2]_3 \quad \text{or} \quad n[NPCl_2]_4 \xrightarrow{250^\circ C} Cl\left[\overset{\overset{\textstyle Cl}{|}}{\underset{\underset{\textstyle Cl}{|}}{P}} = N\right]_n H$$

chain polymer

Chain polymer obtained in this way is somewhat cross-linked and hence has low solubility in organic solvents.

(4) Reactions involving replacement of Cl-atom of P-Cl bond: Cl-atom in P-Cl bond in fairly reactive and can be replaced by many nucleophiles. The mechanism of this replacement is not well understood. However, it appears to involve S_N2 attack on P-atom. The following reactions illustrate the replacement of Cl-atom.

(*i*) $(NPCl_2)_3 + 6NaF \xrightarrow{\text{Acetonitrile}} (NPF_2)_3 + 6\,NaCl$

(*ii*) $[NPCl_2]_3 + 2NaOCH_3 \longrightarrow [NP\,(OCH_3)_2]_3 + 2NaCl$

Tri (dimethoxy) phosphazine

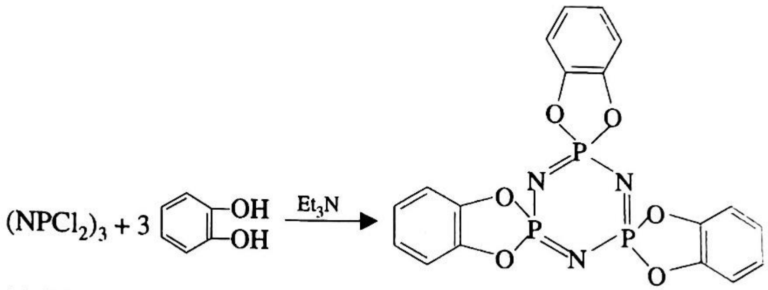
$[NPCl_2]_3 + 2NaC_2H_5 \longrightarrow [NP\,(OC_2H_5)_2]_3 + 2NaCl$

Tri (diethoxy) phosphazine

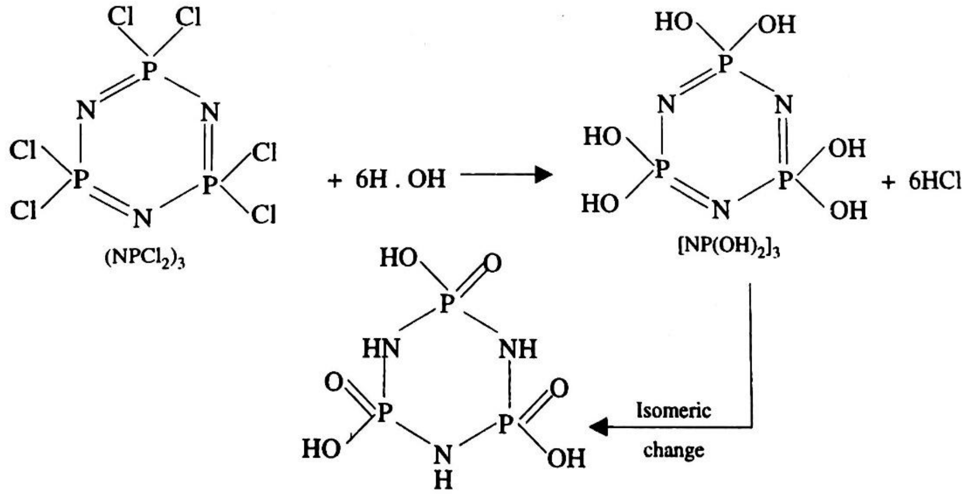
(*iii*) $[NPCl_2]_3 + \underset{\text{Grignard reagent}}{6C_6H_5MgBr} \xrightarrow[\text{toluene}]{\text{Boiling}} [NP\,(C_6H_5)_2]_3 + 3MgCl_2 + 3MgBr_2$

(*iv*) $[NPCl_2]_3 + \underset{\text{1, 2-phenol}}{3C_6H_4(OH)_2} \xrightarrow{Et_3\,N} [NP\,(C_6H_4O_2)]_3 + 6HCl$

or

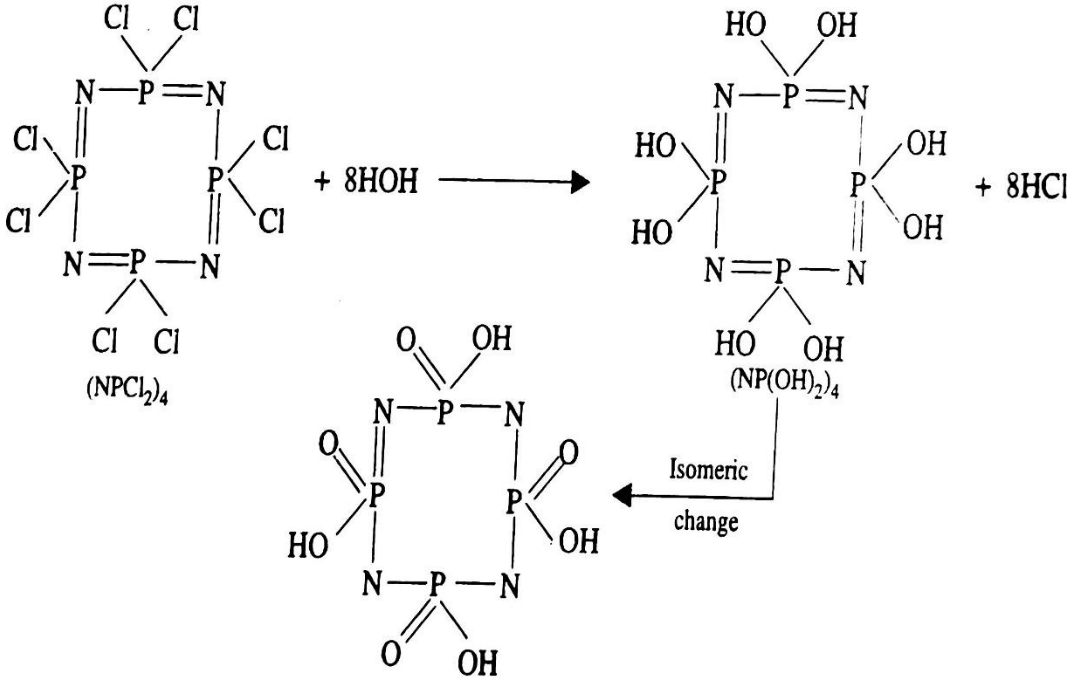


(*v*) *Hydrolysis.* (*a*) When $(NPCl_2)_3$ reacts with H_2O (aqueous ether), all Cl-atoms are replaced by OH groups.

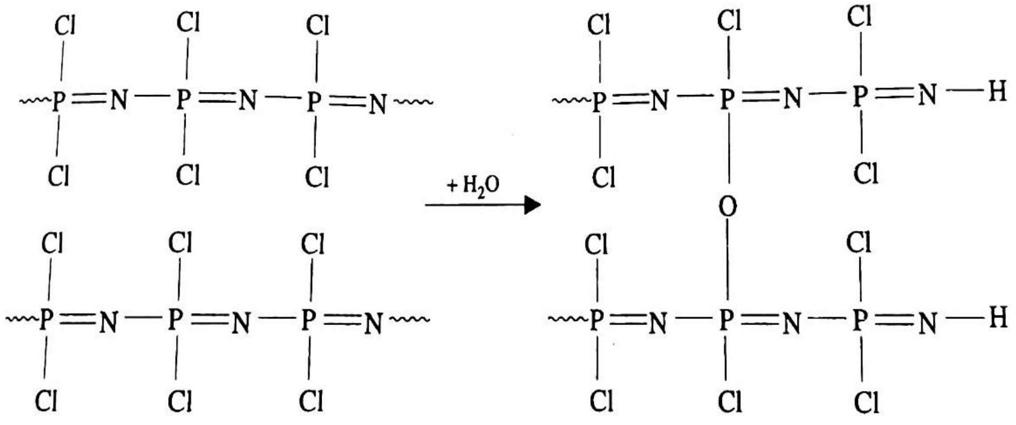


$(NPCl_2)_3$ in acid solution is hydrolysed to H_3PO_4 and NH_3.

(b) Hydrolysis of $(NPCl_2)_4$ in boiling water is rapid and a stable product is obtained.

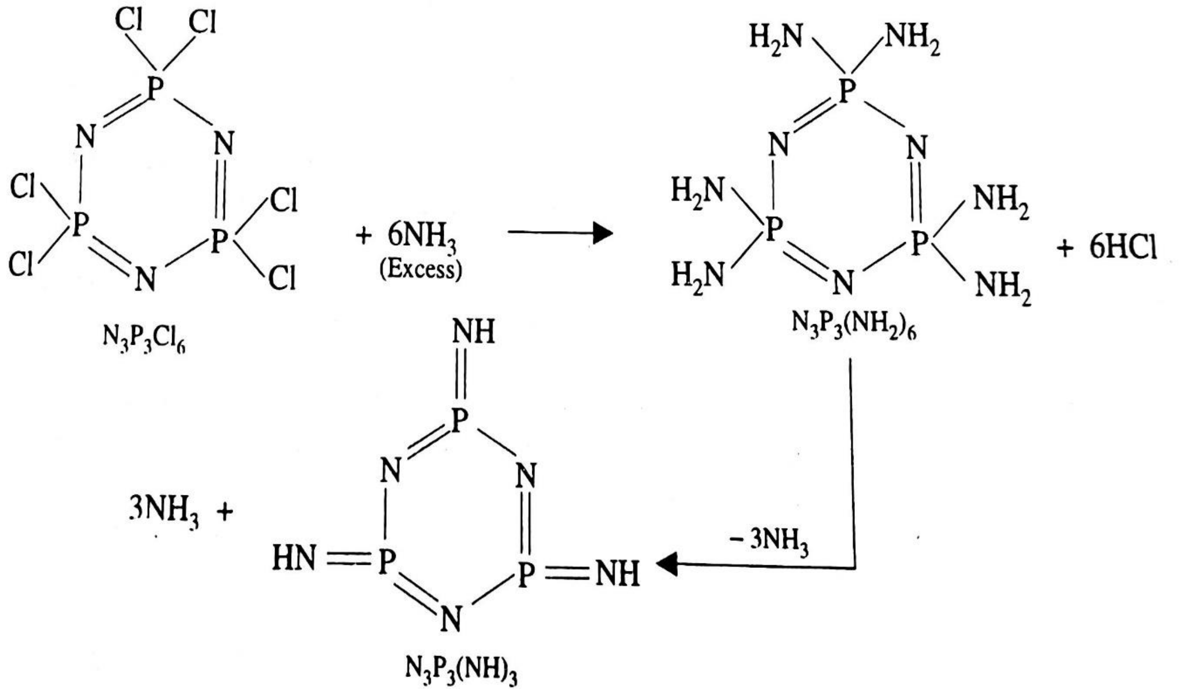


(c) When $[NPCl_2]_n$ polymers are stored in air, they become brittle. This is due to the action of H_2O which forms O-bridges between P-atoms.

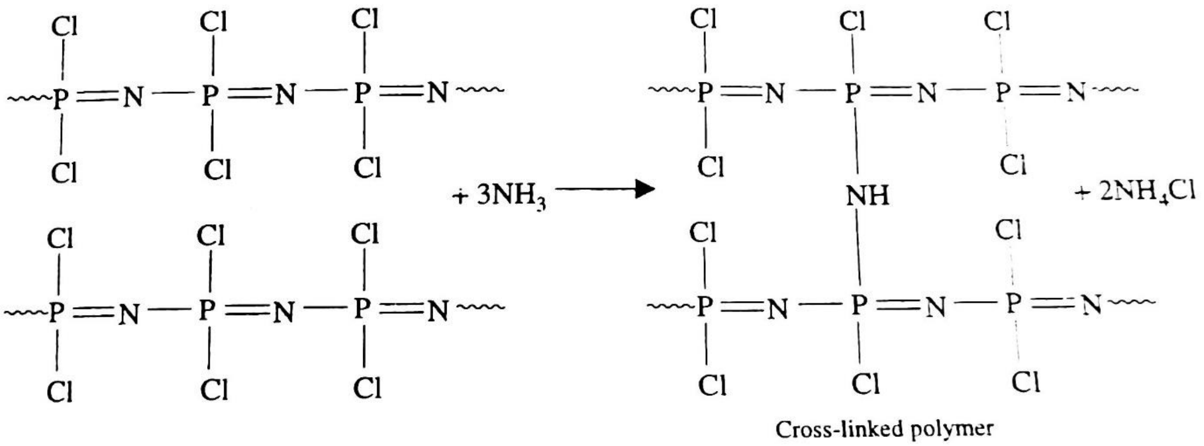


(vi) Reaction with NH_3:

(a) When $[NPCl_2]_3$ reacts with excess of NH_3 all the six Cl-atoms are replaced by NH_2 groups and $N_3P_3(NH_2)_6$, is produced. This compound loses $3NH_3$ molecules, forming phospham, $N_3P_3(NH)_3[NPCl_2]_4$ undergoes similar reaction with excess of NH_3.



(b) When $[PNC_2]_n$ reacts with NH_3 (not excess) and amines, cross-linked polymers are produced.



(vii) Reaction with benzene, C_6H_6 (Friedel-crafts reaction): C_6H_6 reacts with $N_3P_3Cl_6$ in presence of $AlCl_3$ (Friedal-Crafts reaction) to form diphenyl derivative $N_3P_3Cl_4 (C_6H_5)_2$.

$$N_3P_3Cl_6 \quad + \quad 2C_6H_6 \quad \xrightarrow{AlCl_3} \quad N_3P_3Cl_4 (C_6H_5)_2 \quad + \quad 2HCl$$

(viii) PbF_2 fluorinates $N_3P_3Cl_6$ (trimer), giving ultimately $N_3P_3F_6$.

$$N_3P_3F_6 \; + \; 3PbF_2 \quad \longrightarrow \quad N_3P_3F_6 \; + \; 3PbCl_2$$

Some of the trimer ($N_3P_3Cl_3$) is also converted into the derivatives of the tetramer

($N_4P_4Cl_8$) such as $N_4P_4Cl_4F_4$ and $N_4P_4Cl_2F_6$.

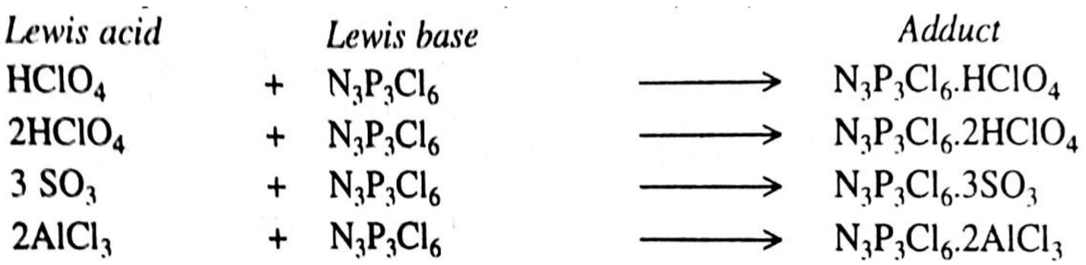
$$N_5P_3Cl_6 \; + \; PbF_2 \; \rightarrow \; N_4P_4Cl_4F_4 \; + \; N_4P_4Cl_4 F_4$$

(ix) When $(NPCl_2)_3$ and $(NPCl_2)_4$, react with potassium fluorosulphite (KSO_2F), fluoro trimer and fluorotetramer are obtained.

$$(NPCl_2)_3 \; + \; 6\,KSO_2F \; \rightarrow \; (NPF_2)_3 \; + \; 6KCl \; + \; 5SO_2$$

$$(NPCl_2)_4 \; + \; 8\,KSO_2F \; \rightarrow \; (NPF_2)_4 \; + \; 8KCl \; + \; 8SO_2$$

(5) Basic properties of $N_3P_3Cl_5$: Formation of addition compounds: The lone pair of electrons present on each N-atom in $N_3P_3Cl_6$ molecule makes it basic and hence this molecule forms adducts (addition compounds) with Lewis acids, like $HClO_4$, SO_3, $AlCl_3$, etc.

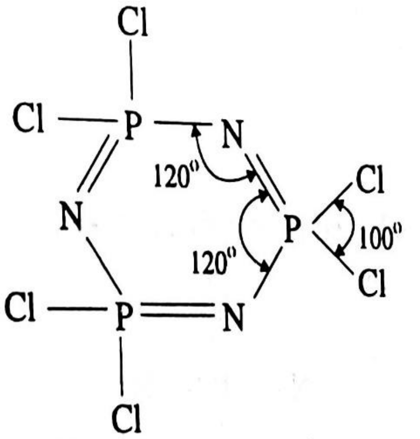


Lewis acid		*Lewis base*		*Adduct*
$HClO_4$	+	$N_3P_3Cl_6$	$\longrightarrow$	$N_3P_3Cl_6.HClO_4$
$2HClO_4$	+	$N_3P_3Cl_6$	$\longrightarrow$	$N_3P_3Cl_6.2HClO_4$
$3\,SO_3$	+	$N_3P_3Cl_6$	$\longrightarrow$	$N_3P_3Cl_6.3SO_3$
$2AlCl_3$	+	$N_3P_3Cl_6$	$\longrightarrow$	$N_3P_3Cl_6.2AlCl_3$

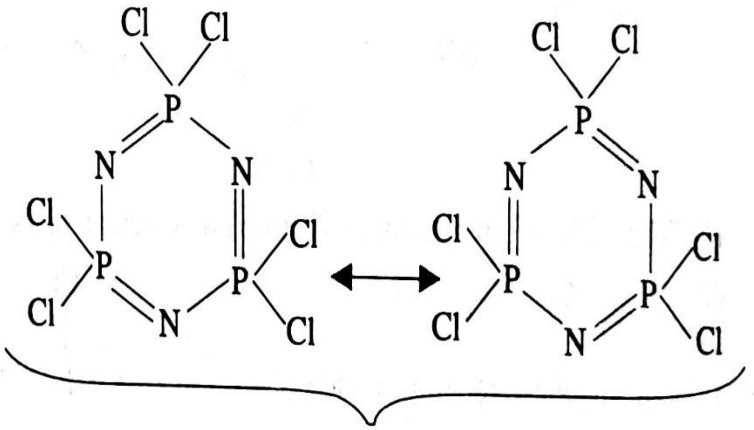
(6) Freshly-prepared $(NPCl_2]_n$ polymers are soluble in chloroform but insoluble in petroleum ether. When their solution is allowed to stand, $(NPCl_2]_n$ get cross-linked and slowly gel.

(7) These polymers exhibit high elasticity and can be stretched several-fold with almost complete recovery. However, they undergo degradation under normal atmospheric conditions more rapidly than do the organic rubbers. Hence these polymers do not find much commercial use.

Structure of $(NPCl_2)_3$ molecule: X-ray analysis has shown that $(NPCl_2)_3$ molecule has a planar six-membered ring structure (Structure I) in which each N-atom is *sp^2* hybridised and each P-atom is *sp^3* hybridised. The lone pair of electrons on each N-atom resides in one of the three *sp^2* hybrid orbitals. It is this lone pair of electrons on which makes $(NPCl_2)_3$ molecule to show basic properties. The bond angles are as shown in the structure. Resonance structures can also be drawn, as in case of C_6H_6 molecule, indicating aromaticity in the ring.

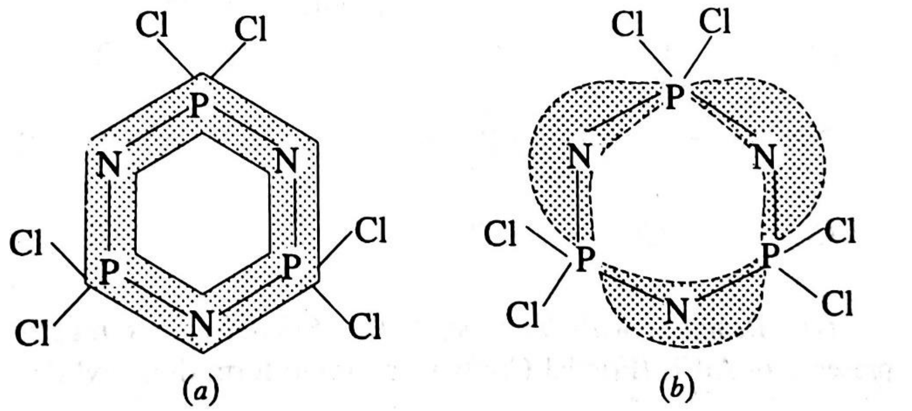


Planar ring structures of $(NPCl_2)_3$ molecule (I)



Two resonating structures of $(NPCl_2)_3$ molecule

Unlike benzene which involves extensive (pπ - pπ) bonding, $(N_3P_3Cl_6)$ molecule involves (dπ - pπ) bonding. The extent of (dπ - pπ) bonding appears to be quite appreciable as the N-P distance (- 1.6 Å) is considerably shorter than the N-P single bond distance (1.75 -1.80 Å). Whether there is complete delocalisation of π-electron charge cloud on all the ring atoms as in C_6H_6 molecule or there are intensely-localised *islands of the* electron cloud within the PNP segments cannot be answered with certainty.



(a) Structure of $(NPCl_2)_3$ molecule having complete delocalisation of π-electron charge cloud on all the ring atoms (b) structure of $(NPCl_2)_3$ molecule having intensely-localised islands of π-electron charge cloud within the PNP segments.

Structure of $(NPCl_2)_4$ molecule: This molecule has a tube-like puckered structure *that has a been shown in fig.*

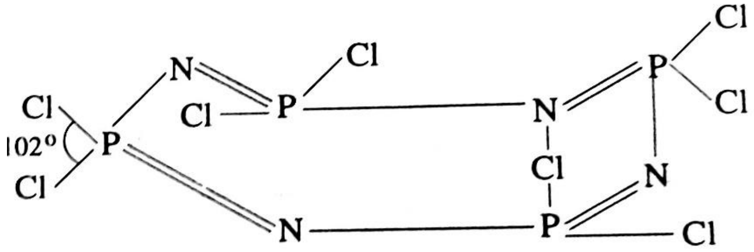
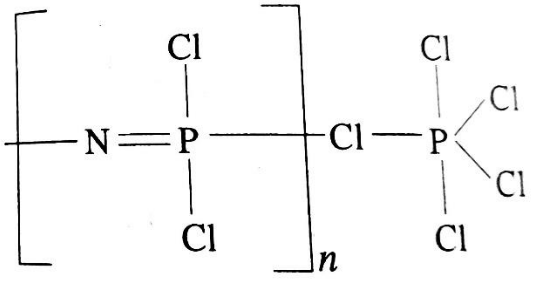


Fig.: tube-like puckered structure of $(NPCl_2)_4$ molecule

Linear phosphonitrilic halides or inorganic rubber: When PCl_5 and NH_4Cl are heated together in a refluxing S-tetrachloroethane, a product is obtained. Some portion of this product is insoluble in petroleum ether and has the composition, $[NPCl_2]_n$. PCl_5, where n =10 to 15. This product is rubber-like and hence is called **inorganic rubber**. The structure of this compound can be represented as shown below.



Structure of $[NPCl_2]_n$. PCl_5

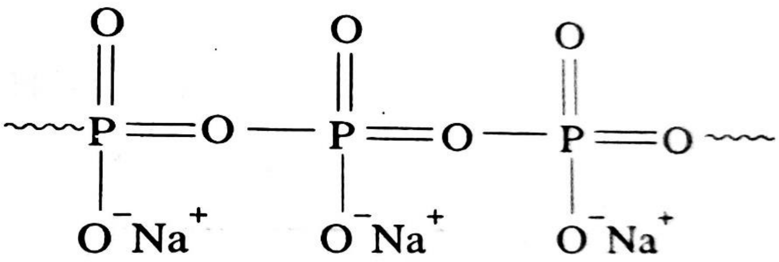
This structure has been confirmed by the fact that ^{31}P n.m.r. spectrum of this compound has two peaks.

A similar product is formed when $(NPCl_2)_3$ is heated in a sealed tube at 350° with PCl_5. If inorganic rubber is kept in air for several hours, it becomes brittle due to hydrolytic condensation by atmospheric moisture and hence a chain-to-chai cross-linking through O-atoms takes place.

Uses of phosphonitrilic halides. These compounds find uses in flame-proofing of fabrics, as plasticisers and as catalysts in the manufacture of silicones.

Vitreous polyphosphates: Phosphate glasses

In these polymers, the negative charges present on the polyphosphate anions are balanced by the positive charges present on the cations like Na^+, K^+ etc., as shown below:



The polyphosphate anions present these polymers have long straight chains, but one P-atom out of 1000 P-atoms forms a cross-linked between the chains. These cross-links disappear within 12 hours when the polymer is dissolved in water or in a neutral aqueous salt solution.

Vitreous sodium polyphosphate can be obtained by heating $Na_4P_2O_7$, or Na_3PO_4, with P_2O_5.

The short chain vitreous polyphosphate polymers are used for deflocculation of proteins. The long chain vitreous sodium phosphate polymers are used in food processing industry. Their use in this industry is based on the interaction of phosphates with proteins.

Crystalline polymetaphosphates:

polymetaphosphates are the salts of polymetaphosphoric acids. These acids are represented by general formula $H_nP_nO_{3n}$ or $(HPO_3)_n$ and can be regarded as having been obtained by eliminating n moles of H_2O from n moles of H_3PO_4. Thus:

$$nH_3PO_4 \xrightarrow{nH_2O} H_nP_nO_{3n} \quad \text{or} \quad (HPO_3)_n \quad + \quad nH_2O$$

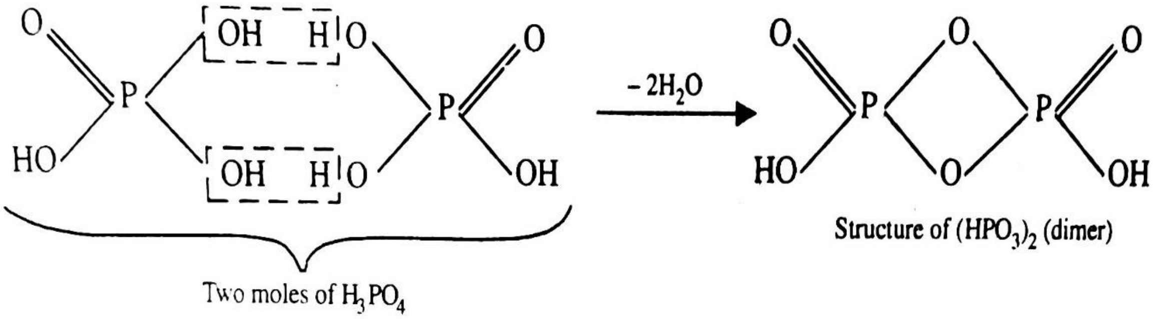
The above discussion shows that $H_2P_2O_6$ or $(HPO_3)_2$, $H_3P_3O_9$, or $(HPO_3)_3$ and $H_4P_4O_{12}$ or $(HPO_3)_4$ can be obtained as:

$2H_3PO_4 \xrightarrow{-2\,H_2O} H_2P_2O_6$ or $(HPO_3)_2$ (*dimetaphosphoric acid*) (*dimer*)

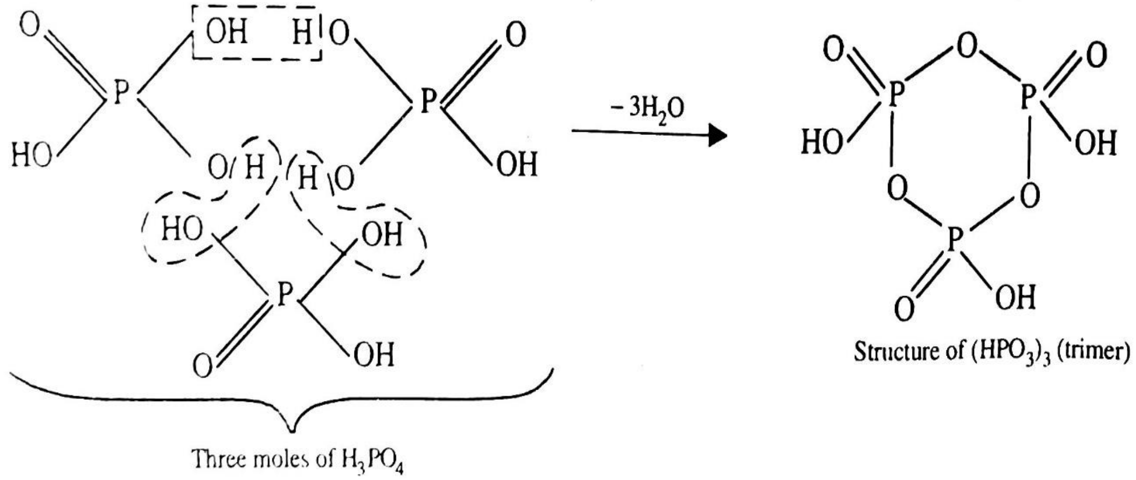
$3H_3PO_4 \xrightarrow{-3\,H_2O} H_3P_3O_9$ or $(HPO_3)_3$ (*trimetaphosphoric acid*) (*trimer*)

$4H_3PO_4 \xrightarrow{-4\,H_2O} H_4P_4O_{12}$ or $(HPO_3)_4$ (*tetrametaphosphoric acid*) (*tetramer*)

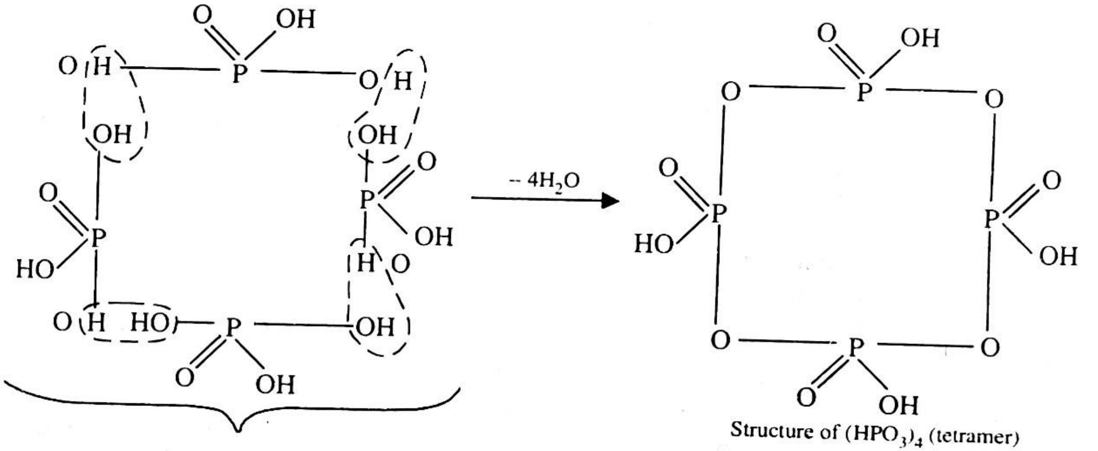
Polymetaphosphoric acids and polymetaphosphates have cyclic structure. The structures of $(HPO_3)_2$ (dimer), $(HPO_3)_3$ (trimer) and $(HPO_3)_4$ (tetramer) are shown below in Fig.



Structure of $(HPO_3)_2$ (dimer)



Structure of $(HPO_3)_3$ (trimer)

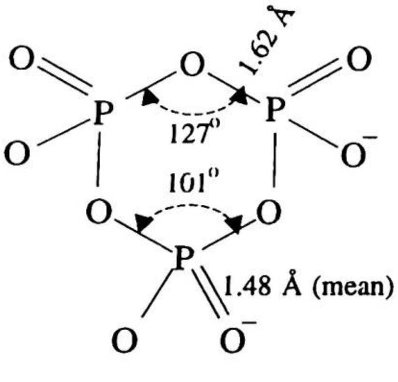


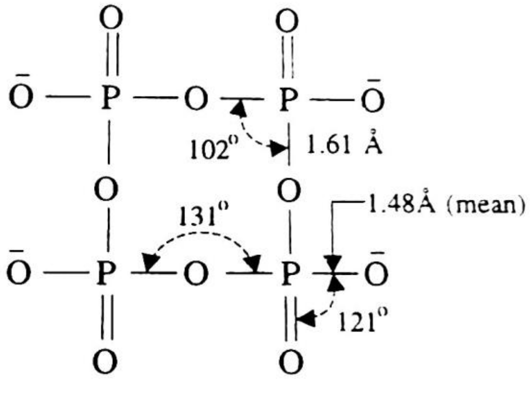
4 moles of H_3PO_4

Structure of $(HPO_3)_4$ (tetramer)

The structure of trimetaphosphate ion, $[(PO_3)_3]^{3-}$ or $P_3O_9{}^{3-}$ has been shown below in Fig. The ring strucutre of $[(PO_3)_3]^{3-}$ ion has been established by the X-ray analysis and 31P n.m.r. spectrum of the trimetaphosphates of several cations. The ^{31}P n.m.r. spectrum shows a single peak which is splitted into a triplet by two neighbouring phosphorus atoms in the ring, thereby showing that the three P-atoms are equivalent.

The structure of tetrametaphosphate ion, $[(PO_3)_4]_{4-}$ or $P_4O_{12}{}^{4-}$ can be obtained by removing 4OH-atoms from 4OH groups present in $(HPO_3)_4$ molecule. Thus $[(PO_3)_4]^{4-}$. ion has the structure which has been shown below in Fig. It has been shown by X-ray diffraction study and ^{31}P n.m.r. spectrum of $Na_4P_4O_{12}$ that $P_4O_{12}{}^{4-}$ ion has a puckered eight-membered ring structure with O and P-atoms in alternate positions. Each P-atom is attached with more two O-atoms. $P_4O^{4-}{}_{12}$ ion can exist in both boat and chair forms.





The above discussion shows that polymetaphosphate ions, $[(PO_3)_n]^{n-}$ have cyclic (ring) structures in which three or more PO_4 tetrahedra are linked together through two O-atoms to form a ring. The value of n varies from 3 to 8.

It is due to the cyclic structure of the metaphosphoric acids that these acids are also called cyclic polymetaphosporic acids.

Insoluble crystalline sodium or potassium polymetaphosphates have been prepared by the condensation of $Na_2H_2P_2O_7$ or $K_2H_2P_2O_7$. By using different condensation conditions, a number of polymetaphosphates having the same general formula, MPO_3 (M = Na or K) but different properties have been obtained. Important polymetaphosphates obtained in this way are Na (or K) PO_3-II, Na (or K) PO_3 - III (both these metaphosphates are called **Maddrell's salts)** and Na (or K) PO_3-IV (called **Kuroll's salt).** These metaphosphates are actually polymeric and hence are represented by the general formula, $[Na\ (or\ K)\ PO_3]_n$.

Sodium Maddrell's salts (i.e., $NaPO_3$-II and $NaPO_3$-III) have negligible solubility in water and in saline solutions at room temperature. At higher temperatures and in the presence of salts of alkali metal ions (other than Na^+ ions) and NH_4^+ ions in solution, these salts dissolve at a higher rate. $NaPO_3$-II, dissolves more readily than $NaPO_3$-III. Under these conditions, Potassium Maddrell's salts (i.e., KPO_3-II and KPO_3-III) also show similar behaviour.

Kuroll's salts, Na (or K) PO_3-IV are somewhat more soluble in pure water than the corresponding Maddrell's salt. When a Kuroll's salt is kept in ice-cold distilled water for a few days or in hot water for a few hours, its crystals swell and become gummy. The solubility of sodium Kroll's salt is increased by the presence of salts having cations other than Na^+ ions. Potassium Kuroll's salt also shows similar behaviour.

The process of dissolution of Kuroll's and Maddrell's salt, in solutions of simple salts containing cations other than Na^+ and K^+ ions, is an exchange process, taking place between cations of the salt and Na^+ or K^+ ions, present in Kuroll's and Maddrell's salts.

X-ray study of sodium Maddrell's salt, $NaPO_3$-II has shown that this polymer has long -P-O-P- chains which are composed of interconnected PO_4 groups. The pattern repeats itself after every three units and the chains do not spiral.

Sodium Maddrell's salt is used as a polishing agent in dental surgery while potassium Kuroll's salt is employed in the manufacture of sausages to prevent water loss.

Polyortophosphoric acids (also called polyphosphoric acids):

Polyphosphoric acids can be regarded as having been obtained by eliminating (n-1) moles of H_2O from n moles of H_3PO_4.

$$nH_3PO_4 \xrightarrow{-(n-1)H_2O} H_{n+1}P_n O_{3n+1} + (n-1)H_2O$$

Thus, these acids can be represented by the general formula, $H_{n+2} P_n O_{3n+1}$

The above discussion shows that $H_4P_2O_7$, $H_5P_3O_{10}$, H_6 P_4O_{13} etc., can be obtained as:

$$2H_3PO_4 \xrightarrow{-H_2O} H_4P_2O_7 \quad [\textit{di (or pyro) phosphoric acid}]$$

$$3H_3PO_4 \xrightarrow{-2\,H_2O} H_5P_3O_{10} \quad (\textit{triphosphoric acid})$$

$$4H_3PO_4 \xrightarrow{-3\,H_2O} H_6P_4O_{13} \quad (\textit{tetraphosphoric acid})$$

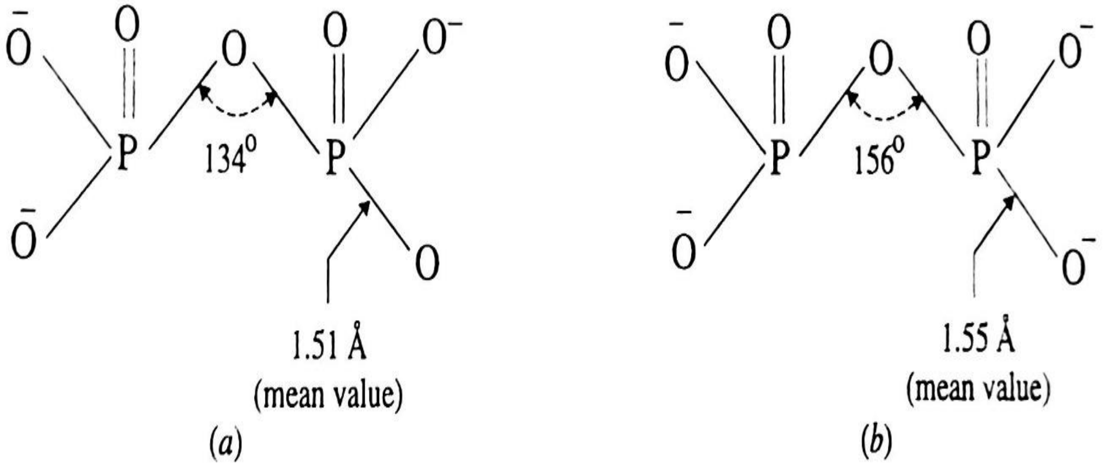


Fig.: Bond parameters of $P_2O_7^{4-}$ ion found in Na_4. $P_2O_7.10H_2O$ [shown at (a)] and in α- $Mg_2P_2O_7$ [shown at (b)]

Polyphosphoric acids have linear chains and hence are also called linear polyphosphoric acids. In the structure of polyphosphate ion, $[P_nO_{3n+1}]^{-(n+2)}$ the linear chains are obtained by uniting PO_4 tetrahedrons together through one, two or more O-atoms. The structures of the ions are obtained by joining PO_4 tetrahedrons in such a way that one O-atom is common between two fun tetrahedrons. The structure of pyrophosphate ion, $P_2O_7^{2-}$ found in Na_4. $P_2O_7.10H_2O$ and in $\alpha -$ $Mg_2P_2O_7$, salts are shown below in Fig.

The structures of $H_5P_3O_{13}$ and $H_6P_4O_{13}$ molecules and the anions derived from them are given below in Figs.

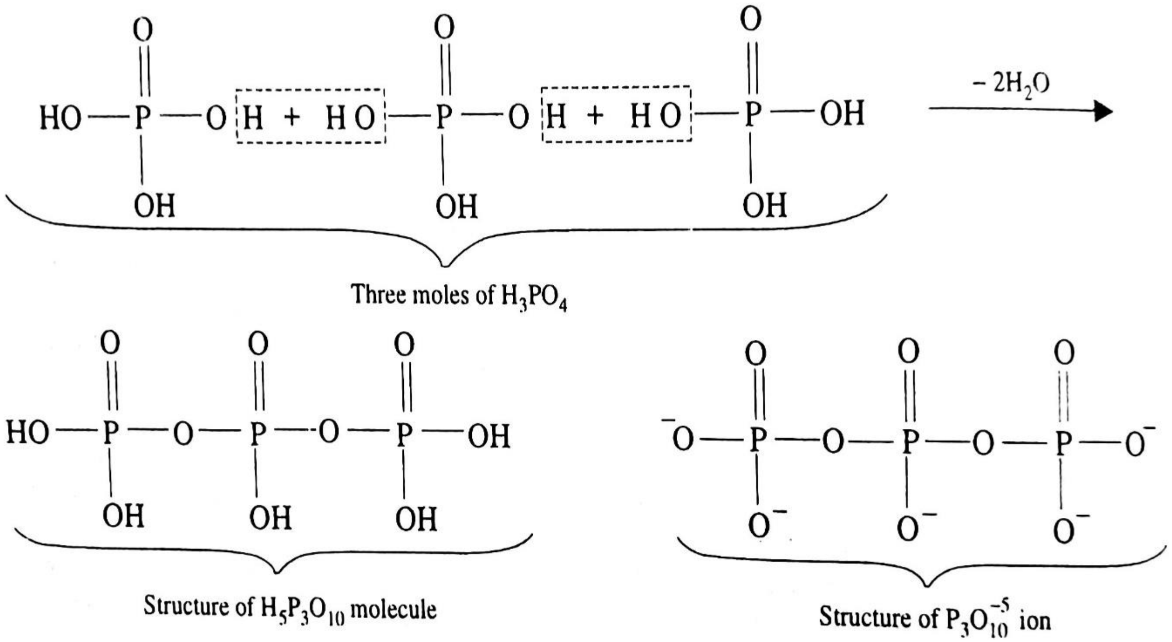


Fig.: Structure of $H_5P_3O_{10}$ molecule and $P_3O_{10}^{5-}$ ion

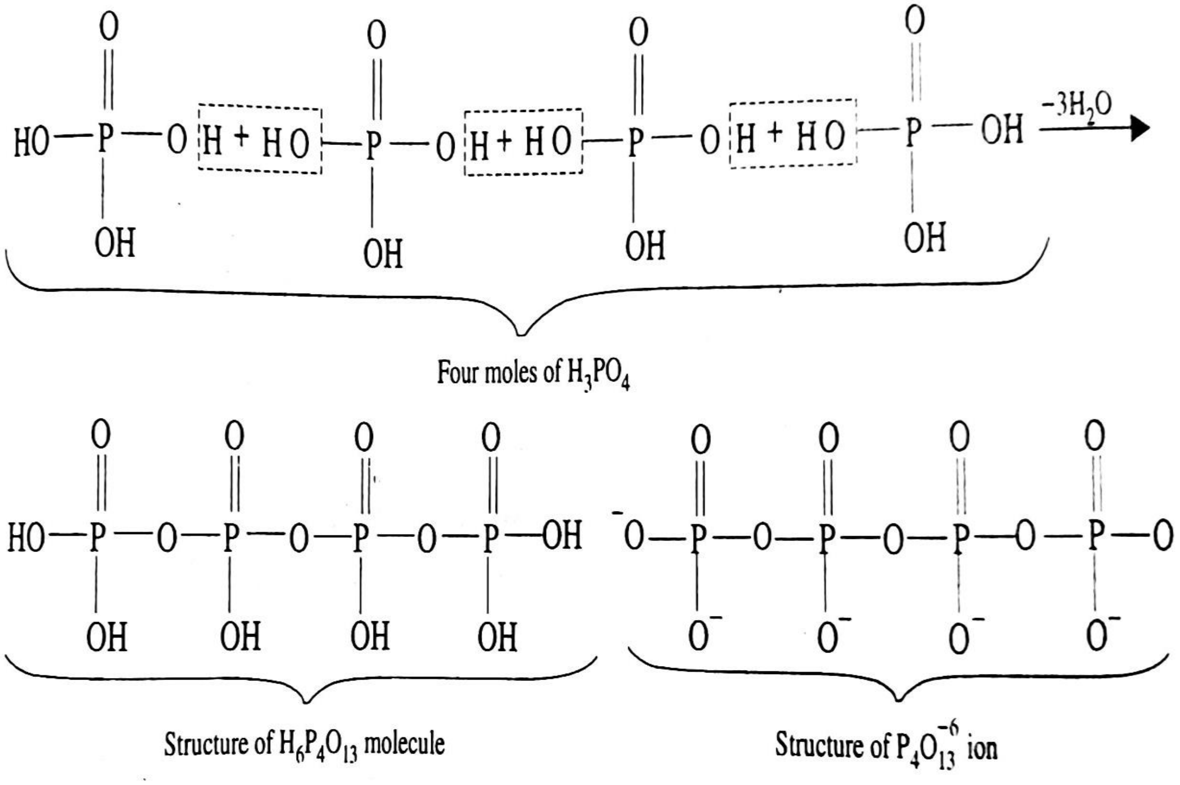
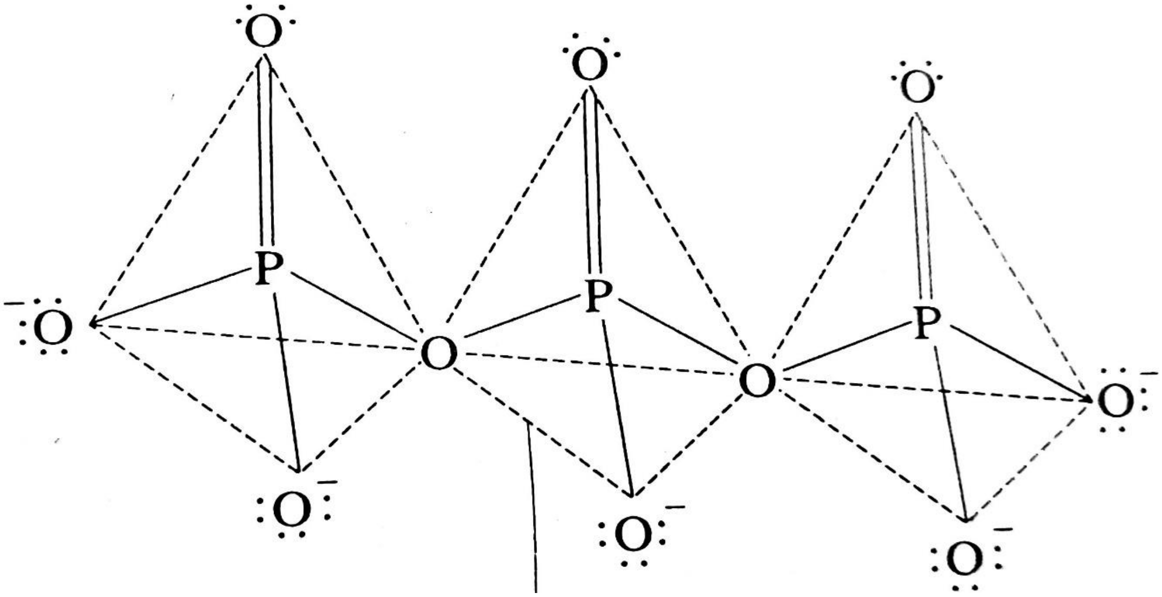


Fig.: Structure of $H_6P_4O_{10}$ molecule and $P_4O_{13}^{6-}$ ion

The linking of three PO_4 tetrahedrons through three O-atoms, to get the Structure of $P_3O^{-5}_{10}$, ion has been shown below in Fig.



The structures of polyphosphate molecules and ions, as given above each structure is *sp*^{3} hybridised.

Borophosphate glasses:

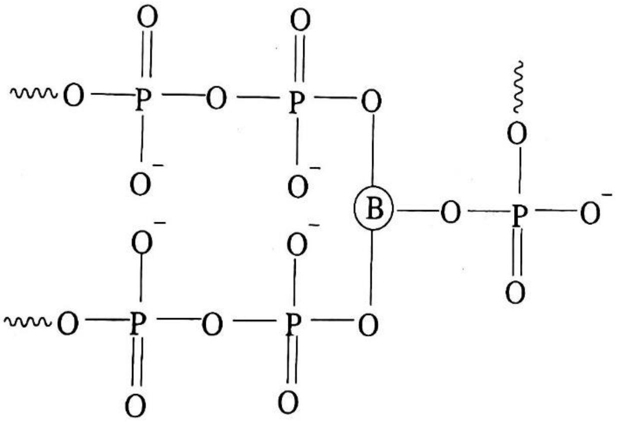
These are formed by heating H_3PO_4, B_2O_3 and alkali metal carbonates or oxides at 700°C.Borophosphate glasses are of the following three types:

(i) Those which contain excess of alkali over P_2O_5. In this variety all the B-atoms are present as trigonal BO_3 groups.

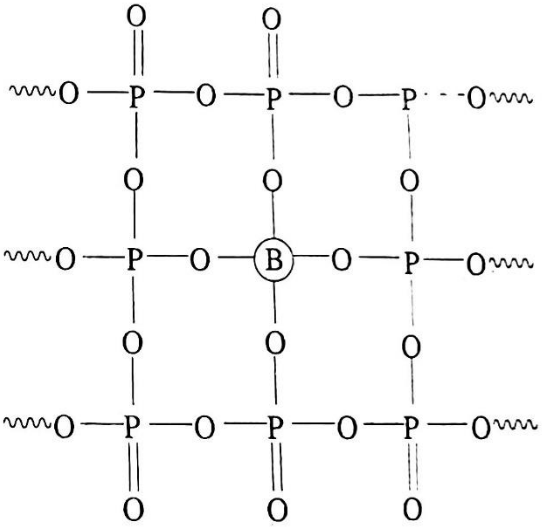
(ii) Those which contain excess of P_2O_5 over alkali. These borophosphate glasses are called acidic borophosphate glasses. If there is less than 10 mole percent of B_2O_3, all B-atoms are four coordinated.

(iii) Those which contain P_2O_5 and alkali in equivalent proportions. The number of 4-coordinated B-atoms decreases steadily with the increase in the content of B_2O_3 and becomes almost zero at about 47 mole per cent of B_2O_3.

Structures of borophosphate glass having three- and four-coordinated B-atoms are shown below in Fig.



(*a*) Borophosphate glass having 3-coordinated B-atom.



(*b*) Borophosphate glass having 4-coordinated B-atom.

P_2O_5 -80 mole % and B_2O_3 -5 mole %, dissolve easily in water. Their solubility decreases with the increase in the percentage of four-coordinated B-atoms. Borophosphate glasses, having both alkali and alkaline earth metal cations, are more durable than simple ultraphosphate glasses, having similar composition. When 5 mole percent B_2O_3, is added to an ultraphosphate polymer having the composition, Li_2O 10 mole percent, Na_2O 10 mole percent and BaO 5 mole percent, a new polymer is obtained. The durability of new polymer is increased towards running water.

Borophosphate glasses have an ability to resist surface contamination. Water vapours on the ordinary silica glass condense in the form of water droplets, while on the borophosphate glass water vapours condense in the form of a thin layer and not in the form of water droplets. This is the reason why borophosphate glasses are used in the manufacture of spectacle and other lenses.

Polymeric compounds of Sulphur:

Sulphur forms a number of compounds which are polymeric in nature. Such compounds can be classified into the following three groups:

I. Nitrides of Sulphur:

Since sulphur has lower electronegativity than nitrogen (S = 2.5, N = 3.0), compounds of sulphur with nitrogen are correctly called nitrides of sulphur. Sulphur forms many nitrides which are polymeric compounds. These are covalent compounds and have industrial and technical importance. Following are important nitrides of sulphur.

II. Tetrasulphur tetranitride, S_4N_4 or $(SN)_4$:

This tetramer is the starting material for the preparation of many compounds containing S-N bonds.

Preparation.

(i) When sulphur monochloride, S_2Cl_2 reacts with NH_3 (ammonolysis of S_2Cl_2) either in solution in an inert solvent or is heated over solid NH_4Cl, S_4N_4 is obtained.

$$6S_2Cl_2 + 16\,NH_3 \xrightarrow{CCl_4} S_4N_4 + S_8 + 12NH_4Cl$$

(ii) When anhydrous NH_3 reacts with sulphur, S_4N_4 is obtained.

$$10S + 4NH_3 \rightleftharpoons 6H_2S + S_4N_4$$

Since the reaction is reversible, AgI is added to remove H_2S. AgI is readily soluble in anhydrous NH_3 while Ag_2S is not and hence Ag_2S is removed from the reaction.

$$H_2S + 2AgI \longrightarrow Ag_2S + 2HI$$

(iii) When trithiazyl trichloride, $(NS)_3Cl_3$ is heated with tetrasulphur tetraimide, $S_4(NH)_4$ in presence of pyridine, $(NS)_3Cl_3$ undergoes reduction and tetrasulphur tetranitride (S_4N_4) is obtained.

$$4(NS)_3Cl_3 + 3S_4(NH)_4 \xrightarrow[\text{Pyridine}]{\Delta} 6S_4N_4 + 12\,HCl$$

Pyridine used in the reaction absorbs HCl.

Properties. (i) It is an oragne-yellow crystalline solid which melts and boils with decomposition at about 443 K. It is strongly exothermic and explodes on heating. It may explode even on impact or if submitted to friction (e.g., when removing stopper from a bottle).

(ii) It is diamagnetic.

(iii) It is insoluble in H_2O but soluble in many organic solvents.

(iv) Action of heat: S_4N_4 is stable only at low temperature. If the temperature is raised to room temperature, it polymerises to a coloured solid which is polymeric and insoluble in organic solvents. On heating to about 575 K in a high vacuum (pyrolysis) or on silver wool (catalyst), it gives disulphur dinitride (S_2N_2).

(v) Action of a boiling alkali: S_4N_4 undergoes hydrolysis readily by a boiling alkali. In the reaction all nitrogen of S_4N_4 is converted into NH_3.

$$2S_4N_4 + 6OH^- + 9H_2O \longrightarrow \underset{\text{Trithionate}}{2S_3O_6^{2-}} + \underset{\text{Thiosulphate}}{S_2O_3^{2-}} + 8NH_3$$

(vi) Fluorination: Fluorination of S_4N_2 by AgF_2 gives tetrathiazyl tetrafluoride, $(NS)_4F4$ or $N_4S_4F_4$.

$$S_4N_4 + AgF_2 \rightarrow (NS)_4F_4 + 4AgF$$

(vii) Reduction: Reduction of S_4N_4 with $SnCl_2$, in ethanol gives tetrasulphur tetraimide, $S_4(NH)_4$ or $S_4N_4H_4$ which is a colourless compound.

$$S_4N_4 + 4H \xrightarrow{\text{Reduction by } SnCl_2 \text{ in } C_2H_5OH} S_4(NH)_4$$

(viii) Oxidation: Oxidation of S_4N_4 with Cl_2 gives trithiazyl trichloride, $(NS)_3Cl_3$.

$$3S_4N_4 + 6Cl_2 \rightarrow 4(NS)_3Cl_3$$

(iv) Bromination: When S_4N_4 is brominated in a solvent, a bronze – coloured crystalline compound having the formula, NSBr is obtained. This compound is polymeric.

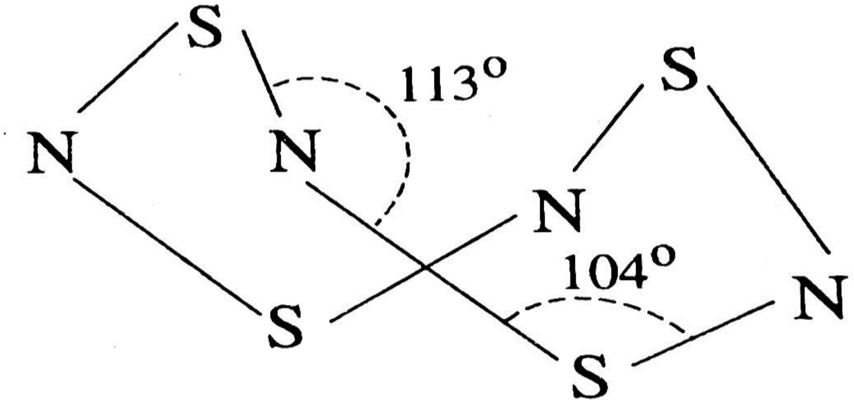
(v) Reaction with S_2Cl_2: When S_4N_4 is boiled with S_2Cl_2 in CCl_4 solution, thiotrithiazyl chloride, $[S(NS)_3]^+ Cl^-$ or $[N_3S_4]^+$ is obtained. As is evident, it is an ionic compound.

$$3S_4N_4 + 2S_2Cl_2 \xrightarrow[\text{Pyridine}]{\text{Boil}} 4[S(NS)_3]^+ Cl^-$$

(xi) Formation of adducts: Due to the presence of lone pairs of electrons on its N-atom, S_4N_4 acts as a Lewis base and hence forms adducts with several metal halides (Lewis acids). The adducts may be of S_4N_4 A (A = $SbCl_5$, $MoCl_5$, BF_3, WCl_4) or S_4N_4 2A (A = $SnCl_4$) type.

(xii) Reaction with PCl_3: S_4N_4, reacts with PCl_3 and forms an ionic compound whose formula is $[Cl_3P.N.PCl_2.N.PCl_3]^+ [PCl_6]^-$.

Structure. Electron diffraction and X-ray measurements have shown that S_4N_4 molecule has an eight-membered cradle ring (cyclic) structure in which all the N-S bond lengths are equal to 1.62 Å. NSN bond angle = 104° and SNS bond angle = 113°.



2. Disulphur dinitride, S_2N_2: As already stated, when S_4N_4 is heated to about 575 K in a high vacuum or on silver wood, S_2N_2 is obtained. This compound forms highly volatile colourless crystals which explode when struck, rubbed or heated to about 303 K. They are soluble in organic solvents like benzene. On keeping, these crystals change to a dark blue polymer.

3. Pentasulphur dinitride, S_5N_2: When S_4N_4 is heated in solution, S_5N_2, is obtained. It is a somewhat less stable than S_4N_4. and is a deep red oil which freezes to a grey solid at 284 K.

II. Thiazyl halidesonide:

Thiazyl halides can be represented by the general formula $(NS)_n X_n$ or $(NSX)_n$ (X = F, Cl, Br, n = 3, 4 etc.). Examples of such compounds are trithiazyl trifluoride [$(NSF)_3$], tetrathiazyl tetrafluoride [$(NSF)_4$] and trithiazyl trichloride [$(NSCl)_3$].

1. Trithiazyl trifluoride, $(NS)_3F_3$ or $(NSF)_3$: It is prepared:

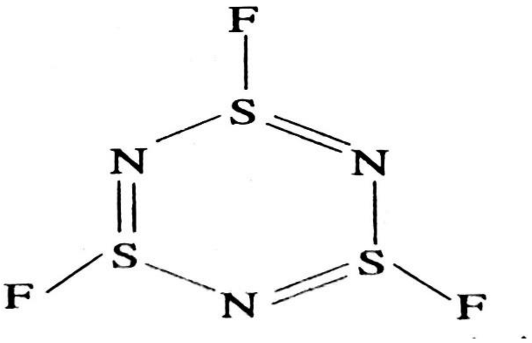
(i) by fluorinating trichloride, $(NSCl)_3$ with AgF_2 in CCl_4.

$$(NSCl)_3 \xrightarrow{AgF_2 \ in \ CCl_4} (NSF)_3$$

(ii) by heating tetrathiazyl tetrafluoride, $(NSF)_4$ at 200-250 ^{0}C which dissociates into NSF, followed by polymerization.

$$(NSF)_4 \xrightarrow[200-250° \ C]{\text{Dissociation}} 4NSF; \quad 3NSF \xrightarrow{\text{Polymerisation}} (NSF)_3$$

The structure of $(NSF)_3$ molecule is not known with certainty, However, n.m.r. spectrum of this molecule indicates that all F-atoms are equivalent. $(NSF)_3$ molecule has a six-membered ring structure which is almost planar with all the F-atoms on one side of the ring in axial positions. All N-S distances are equal to 1.60 Å



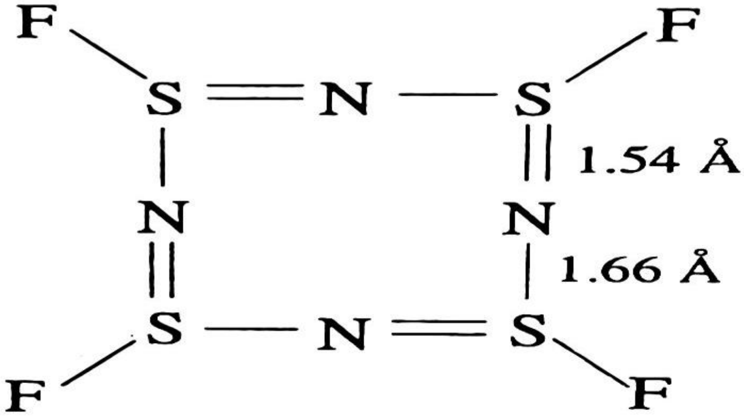
2. Tetrathaizyl tetrafluoride, $(NSF)_4$: It is prepared by fluorinating S_4N_4 with AgF_2

$$S_4N_4 + 4AgF_2 \rightarrow (NSF)_4 + 4AgF$$

It is a white sensitive solid. It dissociates at 200-250 ^{0}C into NSF, which polymerises to trimer, $(NSF)_3$.

$$(NSF)_4 \xrightarrow{200\text{–}250°\ C} 4NSF\ ;\ 3NSF \longrightarrow (NSF)_3$$

The ^{19}F n.m.r spectrum of tetramer, $(NSF)_4$ gives a single resonance peak which indicates that all the F-atoms are equivalent. $(NSF)_4$ molecule has a 8-membered puckered ring structure, with alternating S-N distances of 1.66 Å ^{and} 1.59 Å .



3. Trithiazyl trichloride, $(NSCl)_3$:

Preparation. It is prepared by oxidising tetrasulphur tetranitride (S_4N_4) by Cl_2.

$$3S_4N_4 + 6Cl_2 \longrightarrow 4\,(NSCl)_3$$

Properties. (i) When $(NSCl)_3$, is heated with tetrasulphur tetraimide, $S_4(NH)_4$ in presence of pyridine, $(NSCl)_3$ undergoes reduction and tetrasulphur tetranitride (S_4N_4) is obtained.

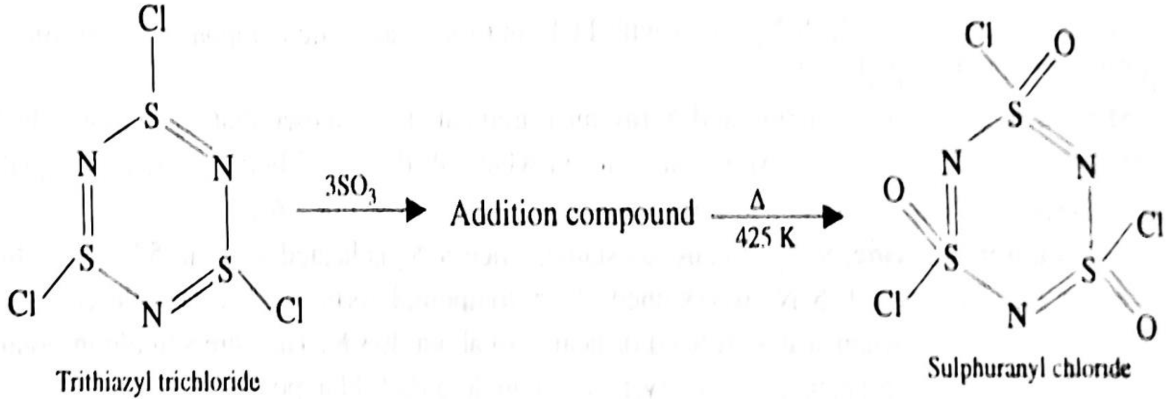
$$4(NSCl)_3 + 3S_4(NH)_4 \xrightarrow[\text{Pyridine}]{\Delta} 6S_4N_4 + 12HCl$$

Pyridine used in the above reaction absorbs HCl.

(i) $(NSCl)_3$ is converted into $(NSF)_3$ by fluorinating it with AgF_2 in CCl_4

$$(NSCl)_3 \xrightarrow{AgF_2 \text{ in } CCl_4} (NSF)_3$$

(iii) This compound forms an addition compound with three molecules of SO_3. The addition compound, on being heated to 425 K, gives sulphuranyl chloride.



Structure: $(NSCl)_3$ molecule has the same structure as $(NSF)_3$ molecule has.

III. Imides of Sulphur:

These compounds may be regarded as having been obtained by replacing one or more S-atom in S_8 by imide group (NH). These compounds can be represented by the general formula, $S_n(NH)_{8-n}$. The compounds having two or more NH groups exist as isomers. Examples of such compounds are $S_7(NH)$ 1, 3-S_6 $(NH)_2$; 1, 4-S_6 $(NH)_2$; 1, 5-S_6 $(NH)_2$; 1, 3,5- S_5 $(NH)_3$; 1,3,6-$S_5(NH)_3$; $S_4(NH)_4$ etc. The numbering system is based on S_8 ring.

Preparation: When S_2Cl_2 reacts with NH, (ammonolysis of S_2Cl_2) in dimethyl formide, S_7 (NH), 1, 3-$S_6(NH)_2$, 1, 4-S_6 $(NH)_2$, 1, 5, S_6 $(NH)_2$, 1, 3, 5-S_5 $(NH)_3$, 1, 3, 6-S_5 $(NH)_3$, etc., are obtained. These products are separated from each other by chromatography and fractional crystalllisation.

Tetrasulphur tetraimide, $S_4(NH)_4$ is prepared by reducing S_4N_4 with $SnCl_2$ in C_2H_5OH.

$$S_4N_4 + 4H \xrightarrow{\text{Reduction by } SnCl_2 \text{ in } C_2H_5OH} S_4(NH)_4$$

Properties of $S_7(NH)$:

(i) The reaction of $S_7(NH)$ with C_6H_5Na gives $S_7(NNa)$.

$$S_7(NH) + C_6H_5Na \longrightarrow S_7(N\,Na) + C_6H_6$$

(ii) N - H bonds in $S_7(NH)$ can be acetylated and benzoylated.

(iii) The reaction of $S_7(NH)$ with the salts of Hg (II) and Hg (I) in non-aqueous solvents gives $Hg(NS_7)_2$ and $Hg_2(NS_7)_2$ respectively.

Properties of $S_4(NH)_4$:

(i) It is a colourless compound and reacts with C_6H_5Na to form $S_4(NNa)_4$.

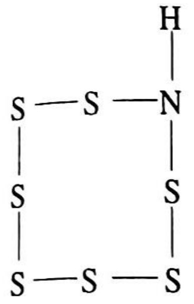
$$S_4(NH)_4 + 4C_6H_5Na \dashrightarrow S_4(NNa)_4 + 4C_6H_6$$

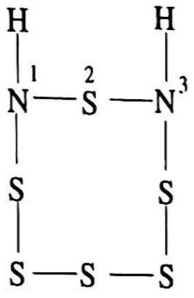
(ii) N-H bonds in $S_4(NH)_4$ molecule can be acetylated and benzoylated.

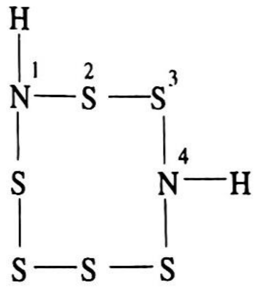
(iii) Air oxidation of S_4 $(NH)_4$ at 100°C gives a tetrameric thionyl imide,

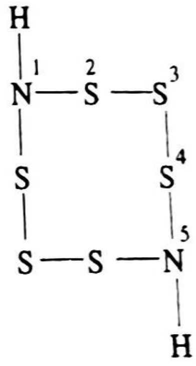
$(OS)_4$ $(NH)_4$ or $(OSNH)_4$

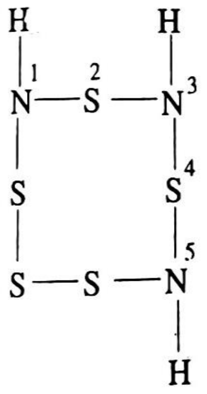
Structure of imides of Sulphur: None of the imides has N-N bonds. The structures of some imides are given below in Fig. $S_7(NH)$ does not have any isomer and hence, it is represented by the structure shown in the figure.

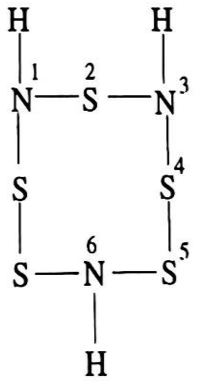

S_7 (NH).

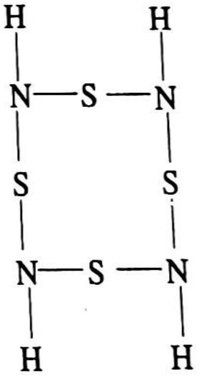

1, 3 - S_6 $(NH)_2$

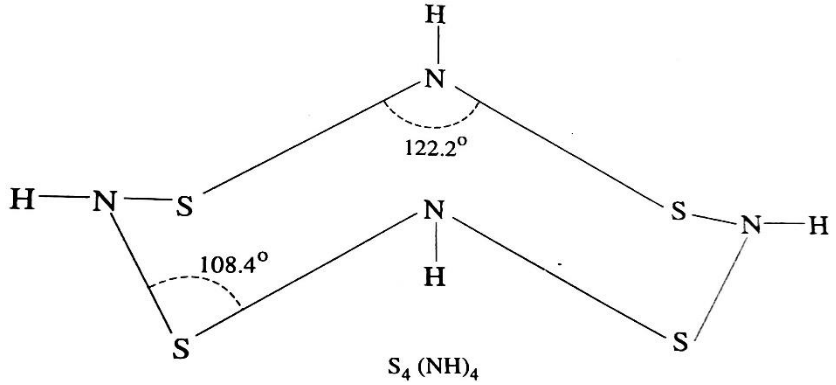

1, 4 - S_6 $(NH)_2$


1, 5 - S_6 $(NH)_2$


1, 3, 5 - S_5 $(NH)_3$


1, 3, 6 - S_5 $(NH)_3$


S_4 $(NH)_4$



S_4 $(NH)_4$

It has one N-H bond. $S_6(NH)_2$ has three isomers namely 1, 3; 1,4 and 1,5 while $S_5(NH)_3$ exists in two isomeric forms which are 1, 3, 5 and 1, 3, 6. The structure of each isomer of $S_6(NH)_2$ and $S_5(NH)_3$ has been shown in the figure. The structure of $S_4(NH)_4$ is the same as that S_8. NSN and SNS bond angles are 108.4° and 122.2°. Note that SSS bond angle in S_8 is 107.8. All N-S bond lengths in S_4 $(NH)_4$ are the same (= 1.67 A^0). $S_4(NH)_4$ cannot be reduced to hydrazine. This shows no two N-atoms are directly linked to each other in $S_4(NH)_4$ molecule, i.e., $S_4(NH)_4$ does not have any N-H bonds. $S_4(NH)_4$ molecule does not have any isomer and hence is represented by a single structure.

THE END