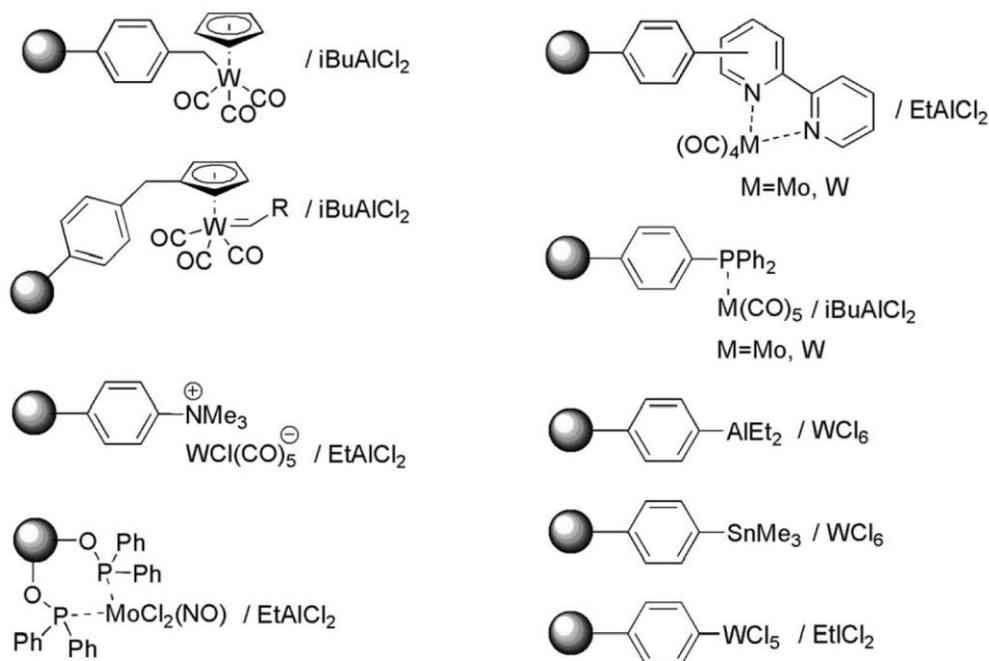


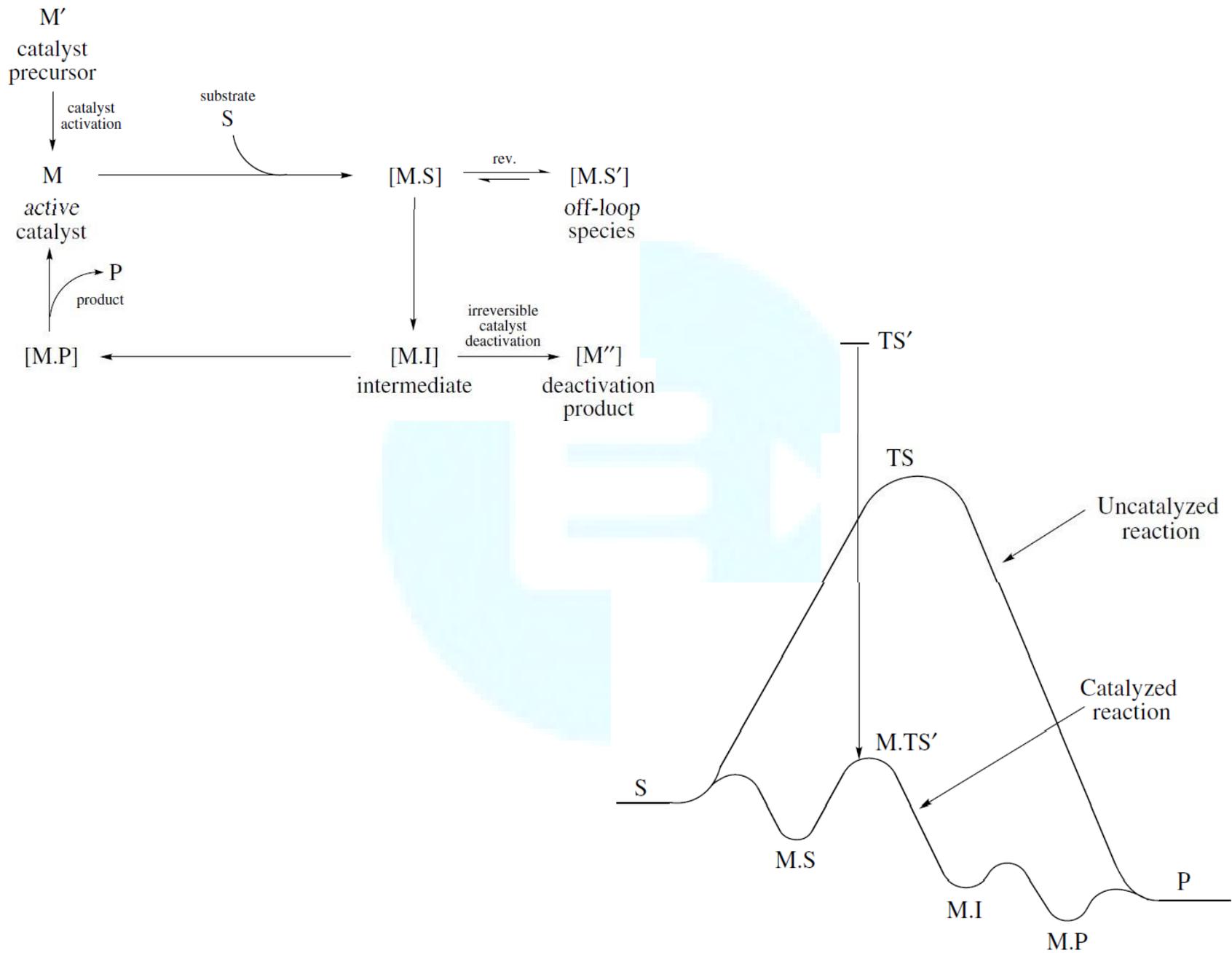
Organometallic Catalysis

- The catalysts we look at are soluble complexes, or *homogeneous catalysts*, as opposed to catalysts such as *palladium on carbon*, or *heterogeneous catalysts*.
- These terms are used because the catalyst and substrates for the reaction are in the same phase in the homogeneous, but not in the heterogeneous, type, where catalysis takes place at the surface of a solid catalyst.
- Catalytic mechanisms are considerably easier to study in homogeneous systems, where such powerful methods as NMR can be used to both assign structures and follow reaction kinetics.**
- Although the catalyst is now technically heterogeneous, it often retains the characteristic reactivity pattern that it showed as a homogeneous catalyst, and its properties are usually distinct from those of any of the classical heterogeneous catalysts—these are sometimes called “heterogenized” homogeneous catalysts.



Representative selection of polymer-bound binary metathesis catalysts.

- The mechanistic ideas developed in *homogeneous catalysis are also becoming more influential* in the field of classical heterogeneous catalysis by suggesting structures for intermediates and mechanisms for reaction steps.
- By bringing about a reaction at *lower temperature*, a catalyst can *save energy* in commercial applications. It often gives *higher selectivity* for the desired product, minimizing product separation problems and *avoiding the need to discard the undesired product as waste*.
- Environmental concerns have promoted the idea of *atom economy*, which values a process most highly when all the atoms in the reagents are used to form the product, minimizing waste.
- The selectivity can be changed by altering the ligands, allowing synthesis of products not formed in the un-catalyzed process.
- With growing regulatory pressure to synthesize drugs in enantiopure form, asymmetric catalysis has come to the fore, along with enzyme catalysis, as the only practical way to make such products on a large scale.
- A catalyst may be defined by its *Turnover Number (TN)*. Each time the complete catalyst cycle occurs we consider one catalytic occurs, turnover to have been completed (one mole of product formed per mole of catalyst).
- The catalytic rate can be conveniently given in terms of the **Turnover Frequency (TOF)** measured in turnovers per unit time (often per hour).
- The *lifetime of the catalyst* before deactivation is measured in terms of total turnovers.
- For most transition metal catalysts, the catalyzed pathway is completely changed from the pathway of the uncatalyzed reaction. Instead of passing by way of the high-energy uncatalyzed transition state TS, the catalyzed reaction normally goes by a multistep mechanism in which the metal stabilizes intermediates that are stable only when bound to the metal.
- Normally, the catalyst only increases the rate of a process but *does not alter its position of equilibrium*, which is decided by the relative thermodynamic stabilities of substrate and products.
- For example, if the substrate S is slightly less stable than the product P, so the reaction will eventually reach an equilibrium favoring P.



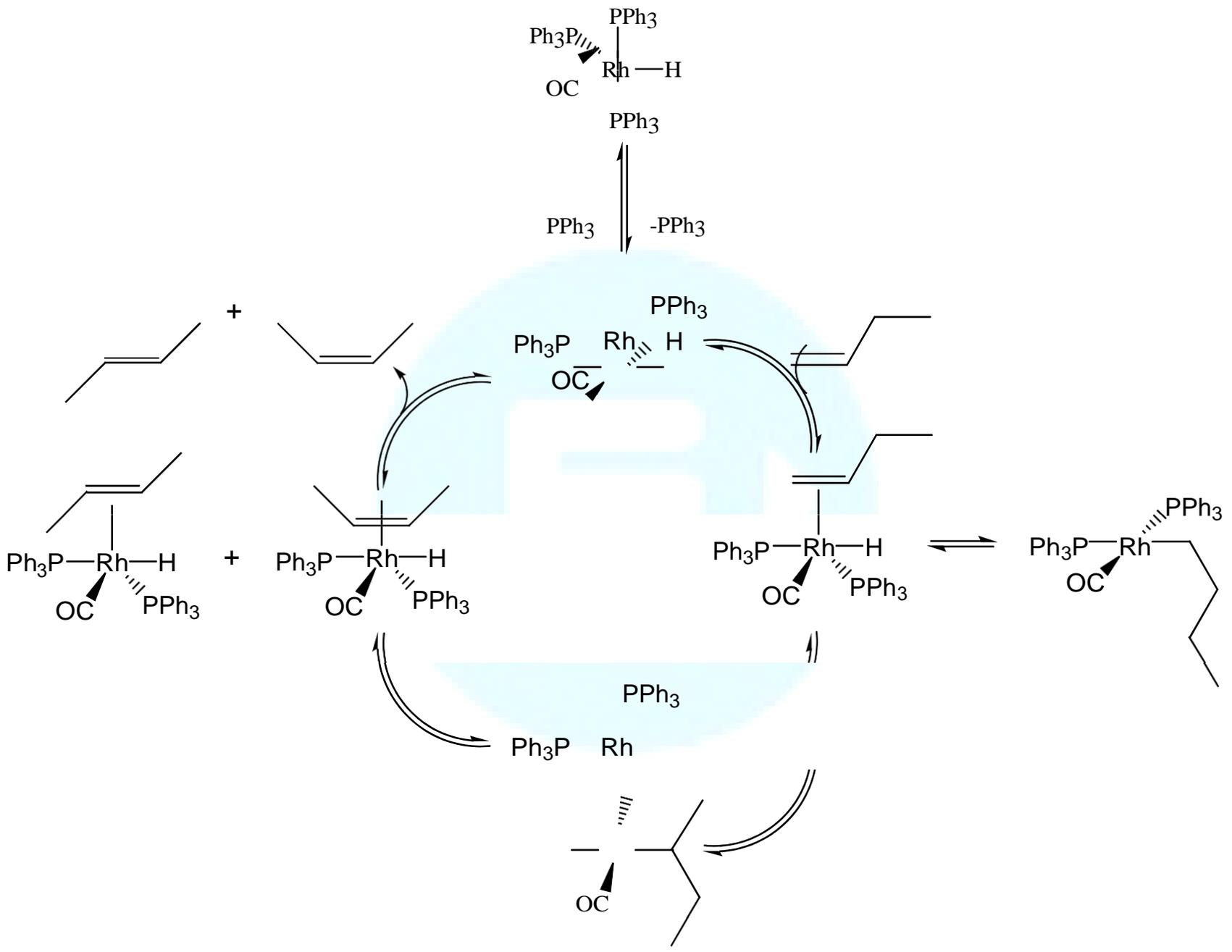
- The TS structure in the absence of the metal would be extremely unstable, but the energy of binding is so high that M.TS is now much more favorable than TS and the reaction all passes through the catalyzed route.
- Different metal species may be able to stabilize other transition states TS—which may lead to entirely different products—hence different catalysts can give different products from the same starting materials.
- The slow step in a catalytic process is called the *turnover limiting step*. **Any change that lowers the barrier for this step will increase the turnover frequency (TOF).**
- Changes in other barriers will not affect the TOF. For a high TOF, we require that none of the intermediates be bound too strongly (otherwise they may be too stable and not react further) and that none of the transition states be prohibitively high in energy.
- Indeed, the whole reaction profile must not stray from a rather narrow range of free energies, accessible at the reaction temperature. Even if all this is arranged, a catalyst may undergo a catalytic cycle only a few times and then “die.”
- This happens if undesired deactivation reactions are faster than the productive reactions of the catalytic cycle itself.

Alkene Isomerization

- Many transition metal complexes are capable of catalyzing the 1,3-migration of hydrogen substituents in alkenes, a reaction that has the net effect of moving the C=C group along the chain of the molecule.
- This is often a side reaction in other types of catalytic alkene reactions, desired or not according to circumstances.
- Two mechanisms are most commonly found:
 1. via alkyl intermediates.
 2. via η^3 -allyl intermediates.
- Note that in each cycle, all the steps are reversible, so that the substrates and products are in equilibrium, and therefore although a non-thermodynamic ratio of alkenes can be formed at early reaction times, the thermodynamic ratio is eventually formed if the catalyst remains active long enough.

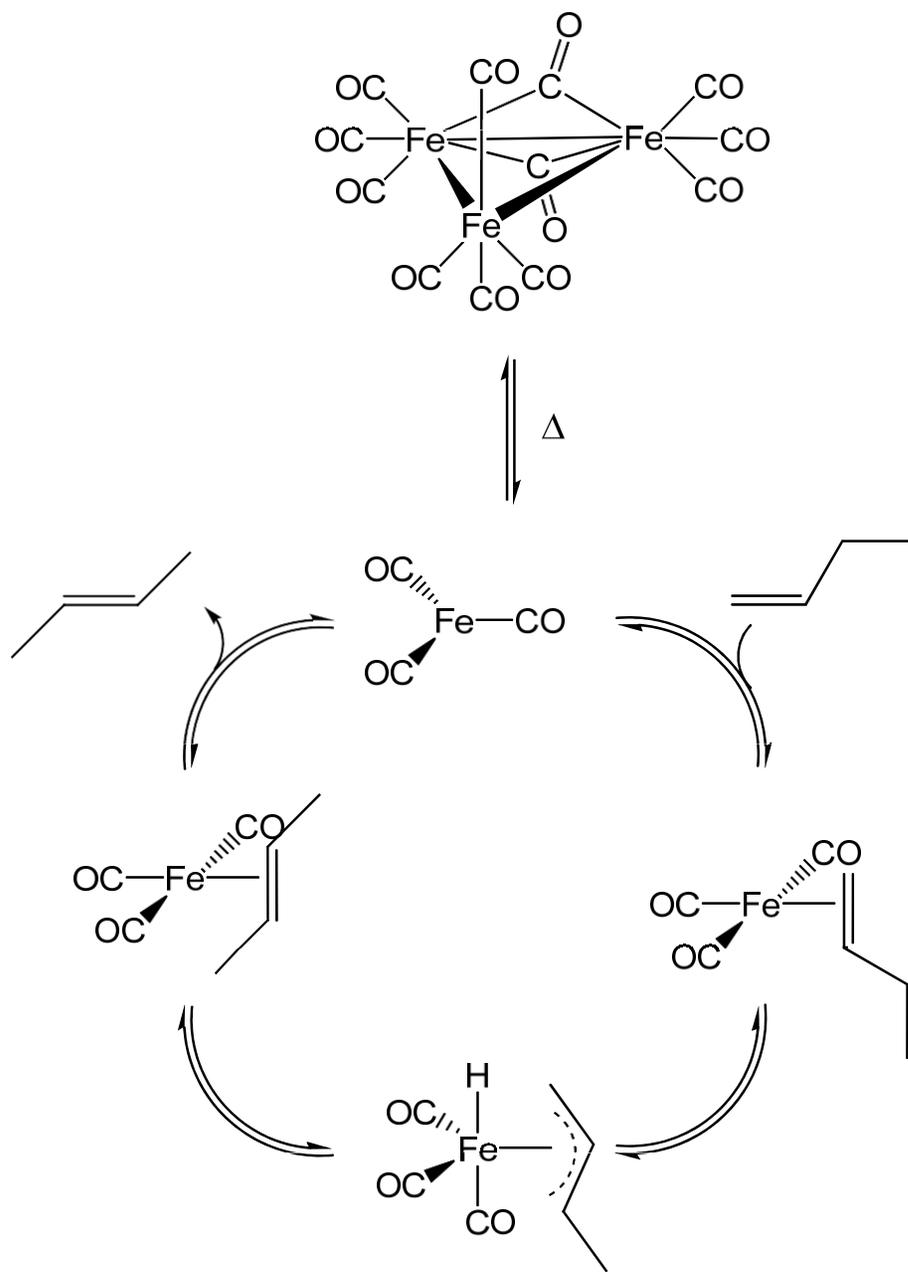
Alkyl mechanism

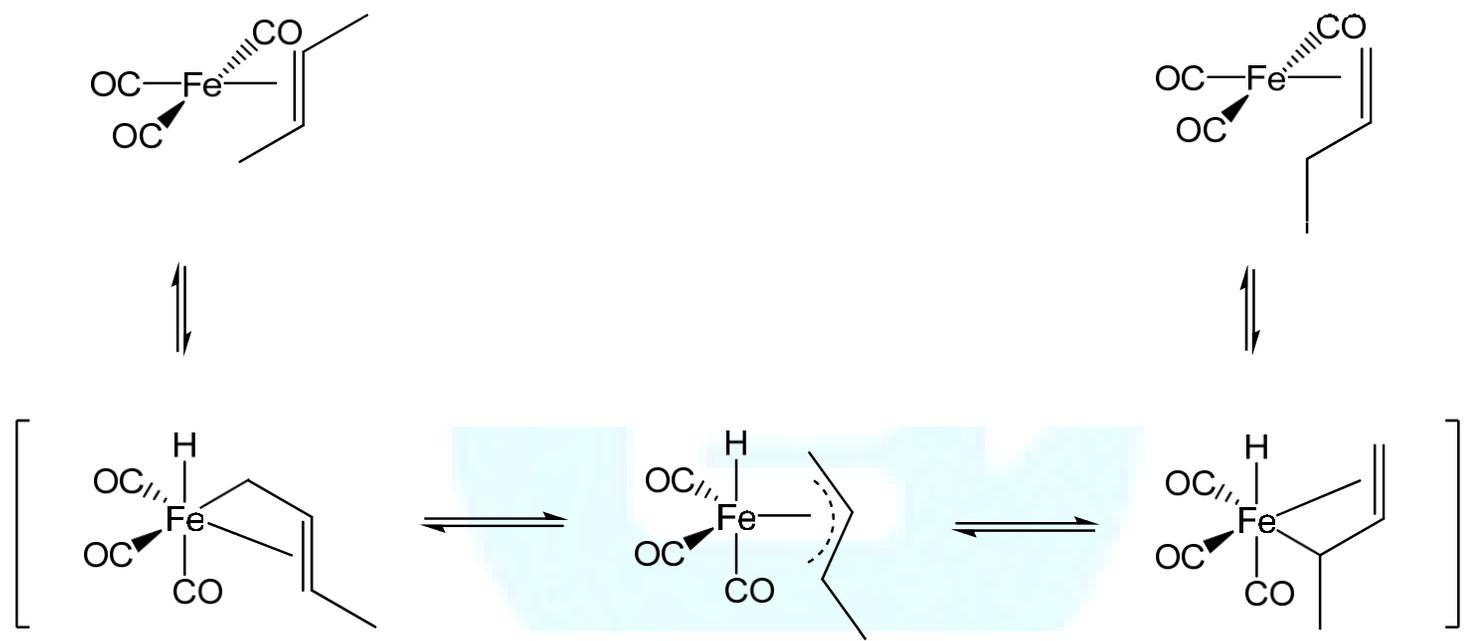
- The alkyl route *requires an M–H bond and a vacant site*.
- The alkene binds and undergoes 1,2-insertion to give the alkyl.
- For 1-butene, the alkyl might be the 1' or the 2' one, according to the regiochemistry of the insertion.
- If the 1' alkyl is formed, β *elimination* can give back only 1-butene, but β *elimination* in the 2' alkyl, often faster, can give both 1- and *cis*- and *trans*-2-butene.
- Since insertion to give the 1' alkyl is favored for many catalysts, nonproductive cycling of the 1-butene back to 1-butene is common, and productive isomerization may be slower.
- The initial *cis/trans* ratio in the 2-butenes formed depends on the catalyst; the *cis* isomer is often favored.
- The final ratio depends only on the thermodynamics, and *the trans isomer is preferred*.
- A typical isomerization catalyst is $\text{RhH}(\text{CO})(\text{PPh}_3)_3$.
- As this is a coordinatively saturated 18e species it must lose a ligand, PPh_3 in this case, to form a coordinatively unsaturated intermediate (16e), able to bind the alkene.



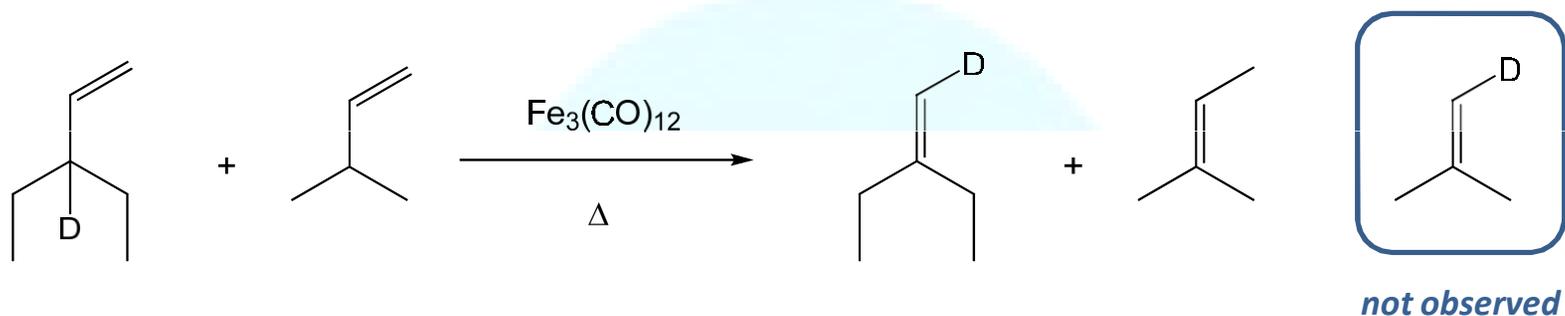
Allyl mechanism

- The second common mechanism involves allyl intermediates and is adopted by catalysts having *two 2e vacant sites but no hydrides*.
- It has been established for the case of $\text{Fe}_3(\text{CO})_{12}$ as catalyst, a system in which “ $\text{Fe}(\text{CO})_3$,” formed by fragmentation of the cluster on heating, is believed to be the active species.
- Thus the cluster itself is an example of a catalyst precursor.
- As a 14e species, $\text{Fe}(\text{CO})_3$ may not have an independent existence in solution, but may always be tied up with substrate or product (*or even solvent*).
- In this mechanism the C–H bond at the activated allylic position of the alkene undergoes an *oxidative addition* to the metal.
- The product is an η^3 -allyl hydride. Now, we only need a reductive elimination to give back the alkene.
- Again, we can have nonproductive cycling if the H returns to the same site it left, rather than to the opposite end of the allyl group.





- An experimental distinction can be made between both the alkyl and allyl routes by means of a crossover experiment using the mixture of C₅ and C₇ alkenes.
- For the allyl mechanism, we expect the D to end up only in the corresponding product having undergone an intramolecular 1,3 shift.
- **For** the hydride mechanism, the D will be transferred to the catalyst that can in turn transfer it by crossover to the C₅ product.



- Hydrogenation catalysts add molecular hydrogen to the C=C group of an alkene to give an alkane.
- Three general types have been distinguished, according to the way each type activates H₂.

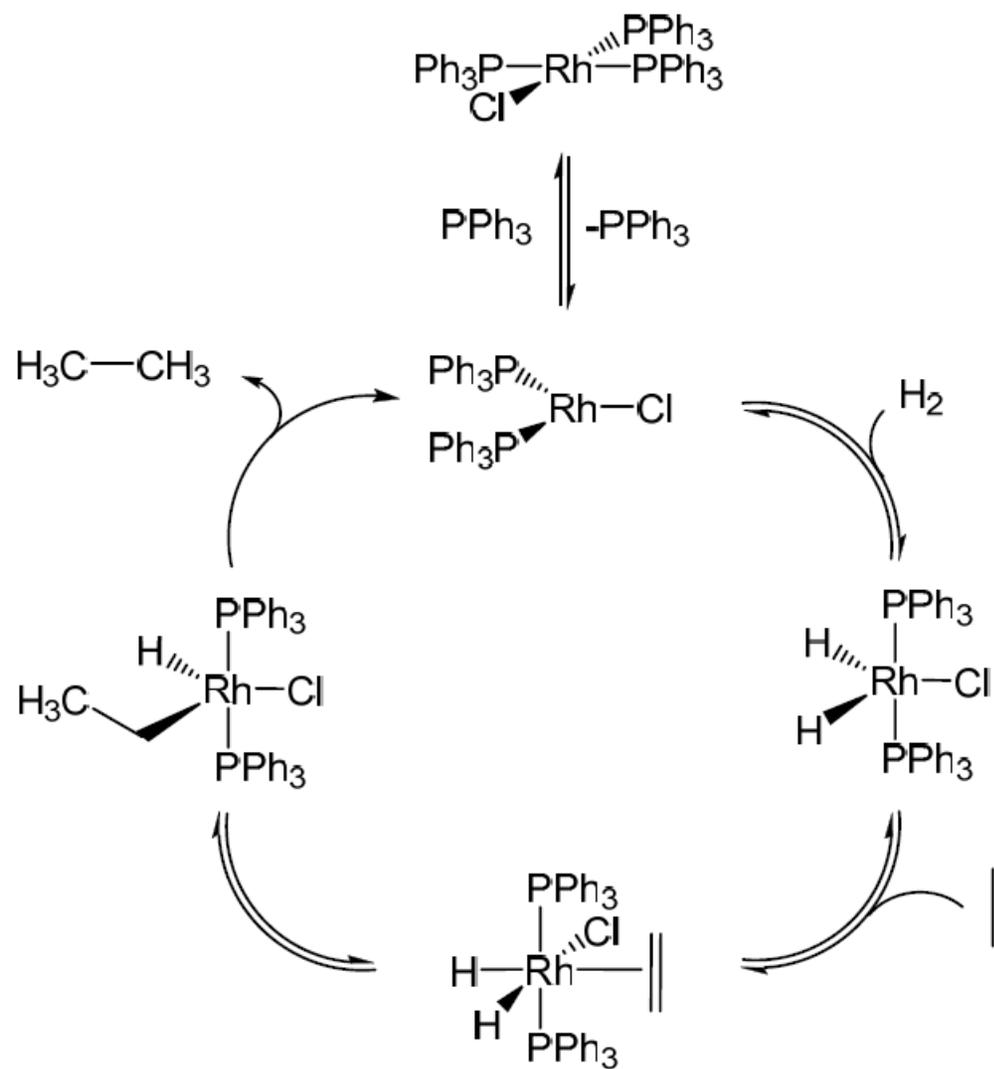
1. *oxidative addition*

2. *heterolytic activation*

3. *homolytic activation*

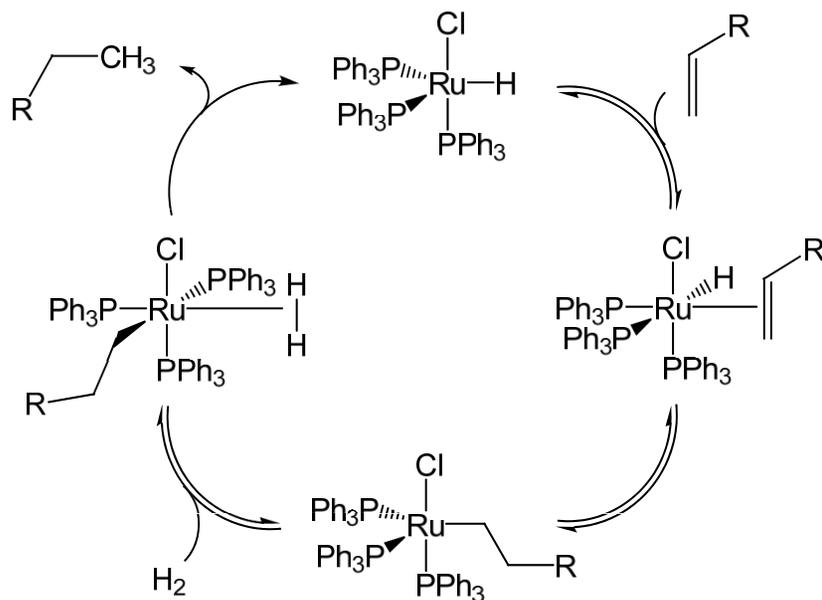
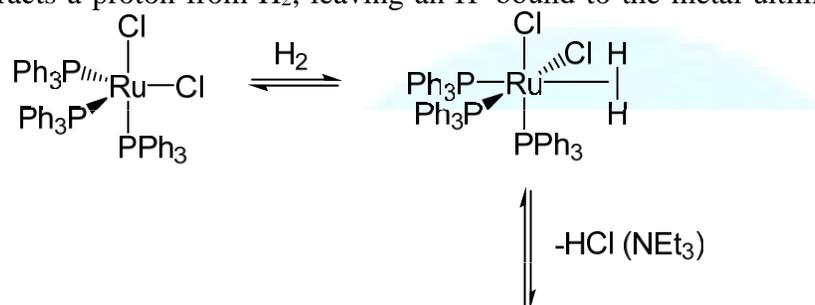
Alkene Hydrogenation via oxidative addition

- Perhaps the most important group employs oxidative addition, of which $\text{RhCl}(\text{PPh}_3)_3$ (*Wilkinson's catalyst*) is the best known.
- Hydrogen addition to give a dihydride leads to labilization of one of the PPh_3 ligands (high trans effect of H) to give a site at which the alkene binds.
- The alkene inserts, as in isomerization, but the intermediate alkyl is irreversibly trapped by reductive elimination with the second hydride to give an alkane.
- This is an idealized mechanism. In fact, $\text{RhCl}(\text{PPh}_3)_3$ can also lose PPh_3 to give $\text{RhCl}(\text{PPh}_3)_2$, and dimerize via halide bridges and each of these species have their own separate catalytic cycles that can be important under different conditions.
- Indeed, $\text{RhCl}(\text{PPh}_3)_2$ reacts so much faster with H_2 than does $\text{RhCl}(\text{PPh}_3)_3$ that the vast majority of the catalytic reaction goes through $\text{RhCl}(\text{PPh}_3)_2$ under most conditions.
- By reversibility arguments, the more rapid oxidative addition of H_2 to the 3-coordinate d^8 $\text{RhCl}(\text{PPh}_3)_2$ to give 5-coordinate d^6 $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$ relative to the corresponding 4-coordinate \rightarrow 6-coordinate conversion is consistent with the tendency for faster reductive elimination from 5-coordinate d^6 species discussed in previous lectures (*TBP Y-type intermediate*).
- The following mechanism illustrates a case where H_2 adds before the olefin. Sometimes the olefin adds first (the olefin mechanism) as is found for $[\text{Rh}(\text{dpe})(\text{MeOH})_2]\text{BF}_4$.



Heterolytic alkene hydrogenation (H₂ activation)

- We now look at the second mechanistic class of hydrogenation catalyst.
- RuCl₂(PPh₃)₃ is believed to activate H₂ *heterolytically*, a reaction accelerated by bases, such as NEt₃.
- The base abstracts a proton from H₂, leaving an H-bound to the metal ultimately giving RuHL₄, the true catalyst.

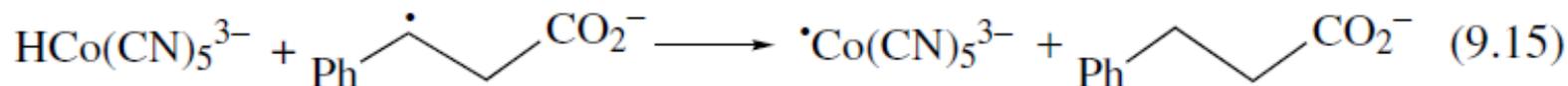
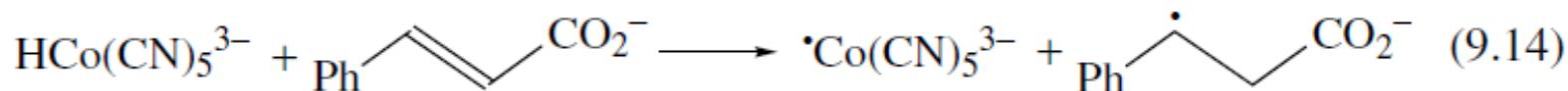
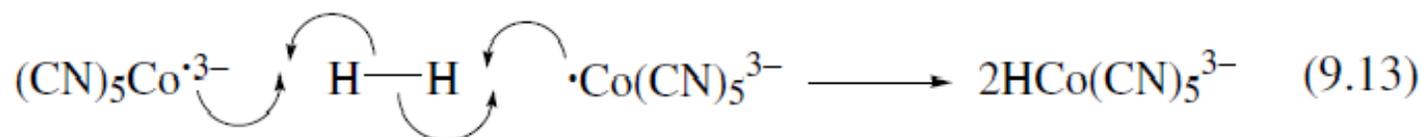


- It is likely that the intermediate in the heterolytic activation of H_2 is a dihydrogen complex.
- The protons of a dihydrogen ligand are known to be more acidic than those of free H_2 , and many H_2 complexes can be deprotonated by NEt_3 .
- In this way the metal gives the same products that would have been obtained by an oxidative addition–reductive elimination pathway, but by avoiding the oxidative addition, the metal avoids becoming $Ru(IV)$, not a very stable state for Ru .
- Other than in their method of activating H_2 , these catalysts act very similarly to the oxidative addition group.
- As a 16e hydride complex, $RuCl_2(PPh_3)_3$ can coordinate the alkene, undergo insertion to give the alkyl, then liberate the alkyl by a heterolytic activation of H_2 , in which the alkyl group takes the proton and the H^- goes to the metal to regenerate the catalyst.

Homolytic H_2 activation

- Iguchi's paramagnetic $d Co(CN)_5^-$ system was a very early (1942) example of a homogeneous hydrogenation catalyst.
- It is an example of the third and rarest group of catalysts, which activate hydrogen homolytically.
- Another way of looking at this is to say the cobalt system activates H_2 by a binuclear oxidative addition.
- This is not unreasonable for this $Co(II)$ complex ion, a metal-centered radical that has a very stable oxidation state, $Co(III)$, one unit more positive.
- Once $CoH(CN)_5^{3-}$ has been formed, a H^\bullet atom is transferred to the substrate in the second step, a reaction that does not require a vacant site at the metal, but does require the resulting organic radical to be moderately stable—hence the fact that the Iguchi catalyst will reduce only activated alkenes, such as cinnamate ion, in which the radical is benzylic and therefore stabilized by resonance.
- Finally, the organic radical abstracts H^\bullet from a second molecule of the cobalt hydride to give the final product.

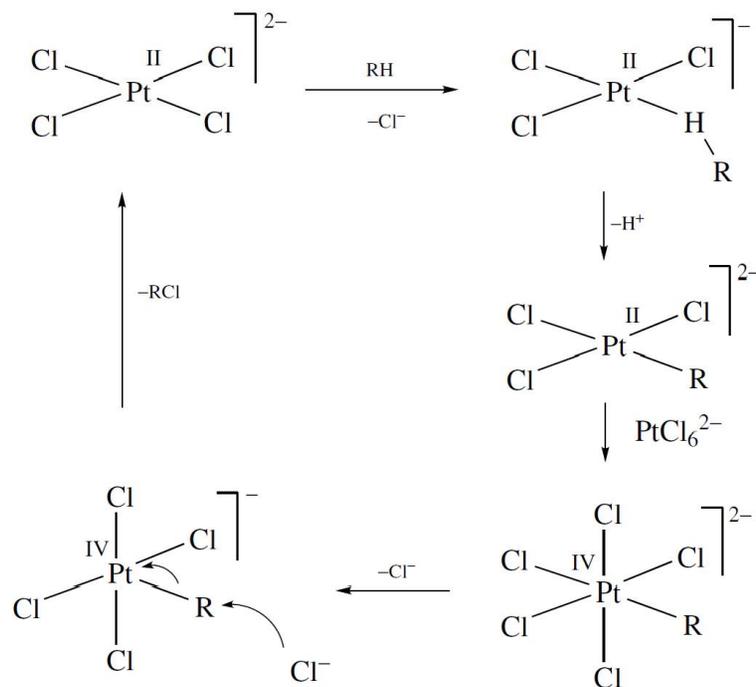
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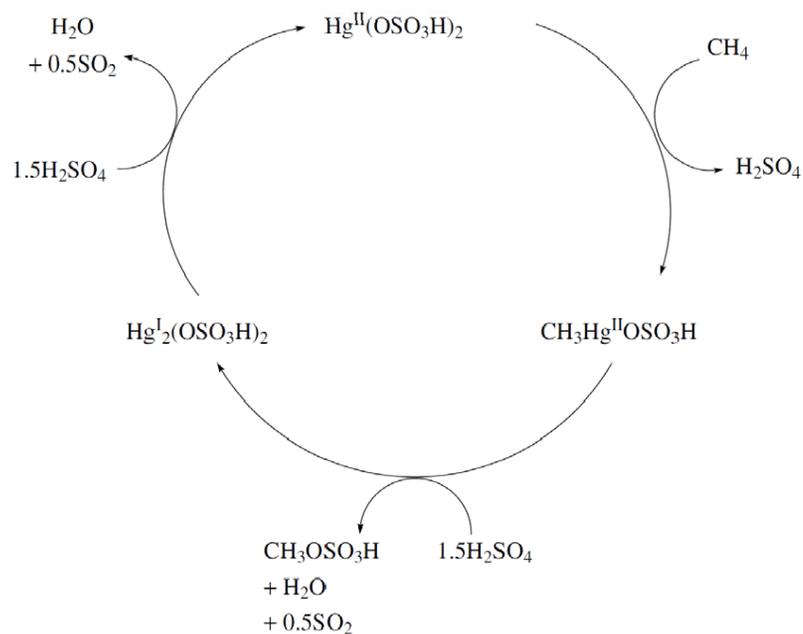
C-H activation

- The goal is *the conversion of an alkane RH into the more valuable species RX*, where X is any of a variety of useful groups.
- Classical organic procedures tend to give branched products, such as *i*-PrX from propane, but linear products are very desirable, hence the potential of transition metal complexes, where formation of *n*-PrX is favored.
- For the moment no system has proved economically viable, but steady progress is being made.
- The term CH activation emphasizes the selectivity difference between low-valent metal complexes and classical organic reagents. In a classical electrophilic or radical route, radicals such as OH[•] abstract an H[•] atom from alkanes, PrH, but always to give the branched radical *i*-Pr[•].
- Superacids, abstract H⁺ ion from PrH, but always to give the branched ion *i*-Pr⁺.
- By such classical routes, the ultimate functionalization product, *i*-PrX, is branched.
- An alkane CH bond can oxidatively add to a variety of low-valent transition metals preferentially to give the linear product, *n*-Pr-M-H, however, and in any subsequent functionalization, the linear product, *n*-PrX, is often obtained.
- In addition, *methane activation holds promise as methane seems likely to become a more important feedstock for the chemical industry.*

- During the 1970s, Shilov saw preferential activation of primary CH bonds in H/D exchange in alkanes catalyzed by Pt(II) in D₂O/DOAc.
- This was the first indication of the special reactivity pattern associated with oxidative addition.
- Moving to [Pt(IV)Cl₆]²⁻ as oxidant, alkanes were oxidized to ROH and RCl with the same Pt(II) catalyst with linear product still preferred, so the Pt(IV) clearly intercepts the same intermediate alkyl that led to RD in the deuteration experiments.
- With methane as substrate, a methylplatinum intermediate was seen.
- Labinger and Bercaw revisited the system in the 1990's using a series of mechanistic probes that confirmed Shilov's main points as well as extending the picture.



- With Hg(II) salts in H₂SO₄ at 180, the acid is both solvent and mild reoxidant .
- Methane was converted to the methanol ester, methyl bisulfate, MeOSO₃H, in which the –OSO₃H provides a powerful deactivating group to prevent overoxidation.
- At a methane conversion of 50%, 85% selectivity to methyl bisulfate (ca. 43% yield) was achieved with the major side product being CO₂.
- The expected intermediate MeHg⁺ cation was seen by NMR spectroscopy, and a Shilov-like mechanism proposed.
- Since Hg(II) is not expected to give oxidative addition, Hg(IV) being unknown, the initial activation step must occur via deprotonation of a σ complex.
- Similar selectivity is seen as for Pt(II) and indeed deprotonation of a Pt(II) σ complex still cannot be excluded for this case.



Polymers containing boron

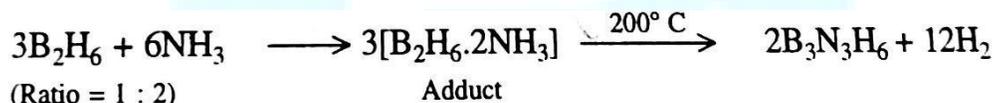
Borazine, substituted borazines and boron nitride are polymeric compounds of boron. Borazine is of special interest, because it is isoelectronic with benzene and some of its physical properties resemble those of benzene.

A. Borazine or borazole, (BH)₃(NH)₃ or B₃N₃H₆

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

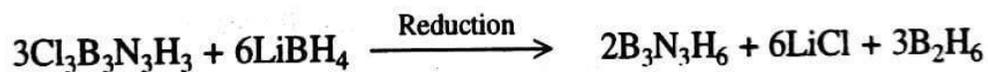
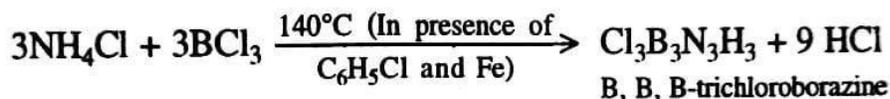
Preparation. Borazine can be prepared by the following methods :

- (i) By Stock and Pohland's method (1926): Borazine was originally prepared by Stock and Pohland, in 1926, by the action of NH₃ on diborane (B₂H₆). The adduct, B₂H₆.2NH₃, is first formed which then gets decomposed by heating in a closed tube at 200°C.



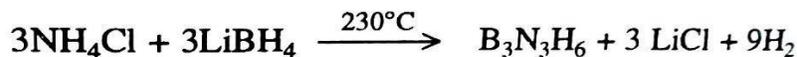
This method gives low yield of B₃N₃H₆ because of simultaneous formation of solid polymeric by-products.

- (ii) By heating BCl₃ with NH₄Cl: When BCl₃ is heated with NH₄Cl in chlorobenzene (C₆H₅Cl) 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 B₃N₃H₃) is formed. This derivative, on being reduced by LiBH₄, in polyether, gives borazine, B₃N₃H₆.



- (ii) By heating a mixture of LiBH₄, and NH₄Cl (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 $230^\circ C$.



This method gives 30% borazine.

Physical properties. (i) Borazine is a colourless mobile volatile liquid. It freezes at $-58^\circ C$. Its b.p. and m.p. are $64.5^\circ C$ and $-58^\circ C$ respectively.

(ii) Decomposition: Borazine decomposes slowly on storage even at $-80^\circ C$ 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.

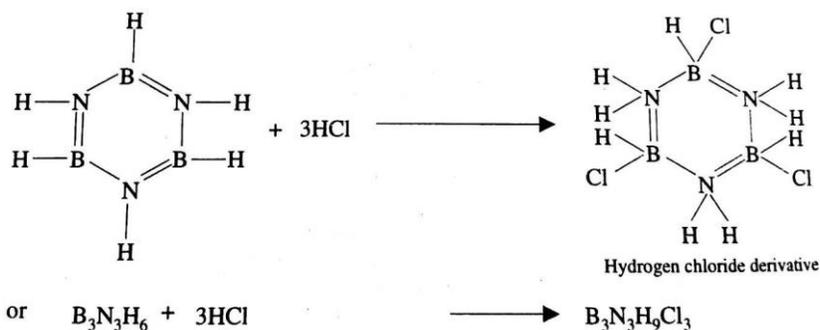
(iii) Similarities with benzene: Since borazine is isoelectronic with benzene, some of its physical properties are similar to those of benzene. This is shown below:

	<i>Mol wt.</i>	<i>M.pt.</i> ($^\circ C$)	<i>B.pt.</i> ($^\circ C$)	ΔH_{vap} ($kJ\ mole^{-1}$)	<i>Trouton's constant</i>
<i>Borazine ($B_3N_3H_6$)</i> :	80.6	-58	64.5	39.3	21.4
<i>Benzene (C_6H_6)</i> :	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.

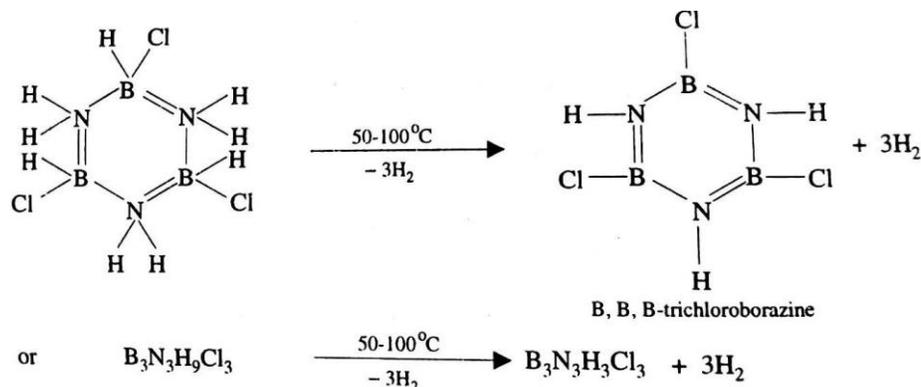
(i) Addition reactions: (a) One molecule of $B_3N_3H_6$, adds three molecules of HCl or HBr in the



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

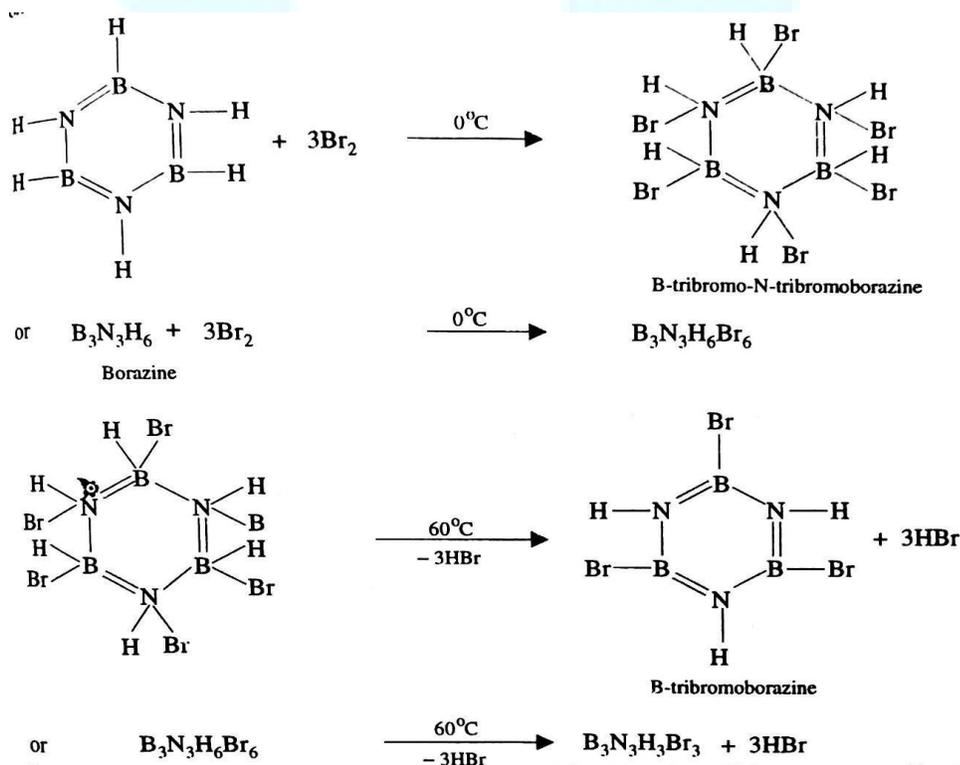
chloride derivative ($B_3N_3H_3Cl_3$) is obtained. This addition reaction is not shown by benzene.

When this derivative is heated to $50-100^\circ C$, it loses three H_2 molecules,

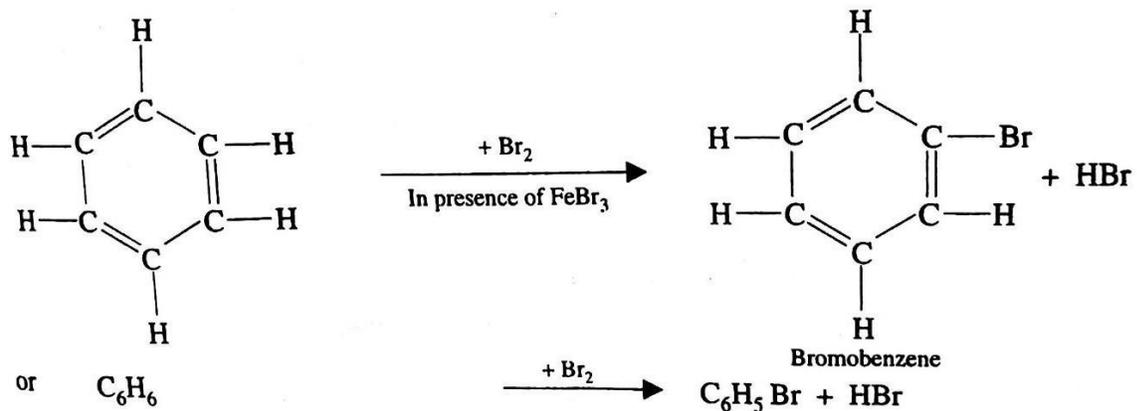


to give B,B,B-trichloroborazine, $B_3N_3H_3Cl_3$

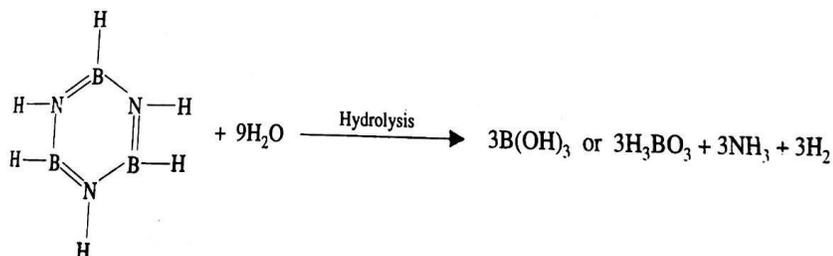
(b) One molecule of borazine also adds three molecules of Br_2 at $0^\circ C$ and gives B-tribromo-N-tribromoborazine which on being heated to $60^\circ C$, loses three molecules of HBr and forms B-tribromoborazine.



Benzene shows substitution reaction and give monobromobenzene, C_6H_5Br .

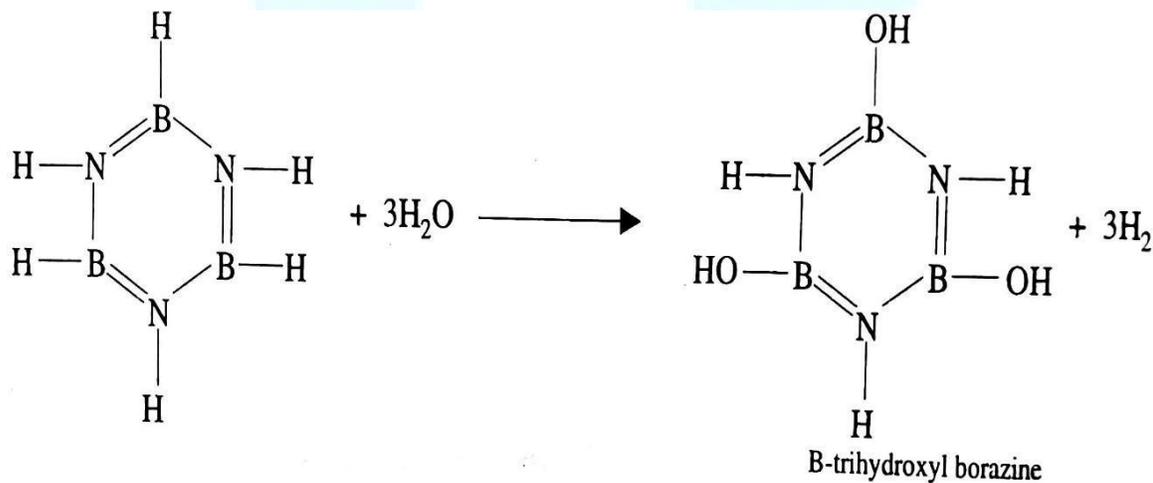


(ii) Hydrolysis. (a) Borazine gets slowly hydrolysed by water to produce boric acid [B(OH)₃ or H₃BO₃], NH₃ and H₂. Hydrolysis is favoured by the increase in temperature.



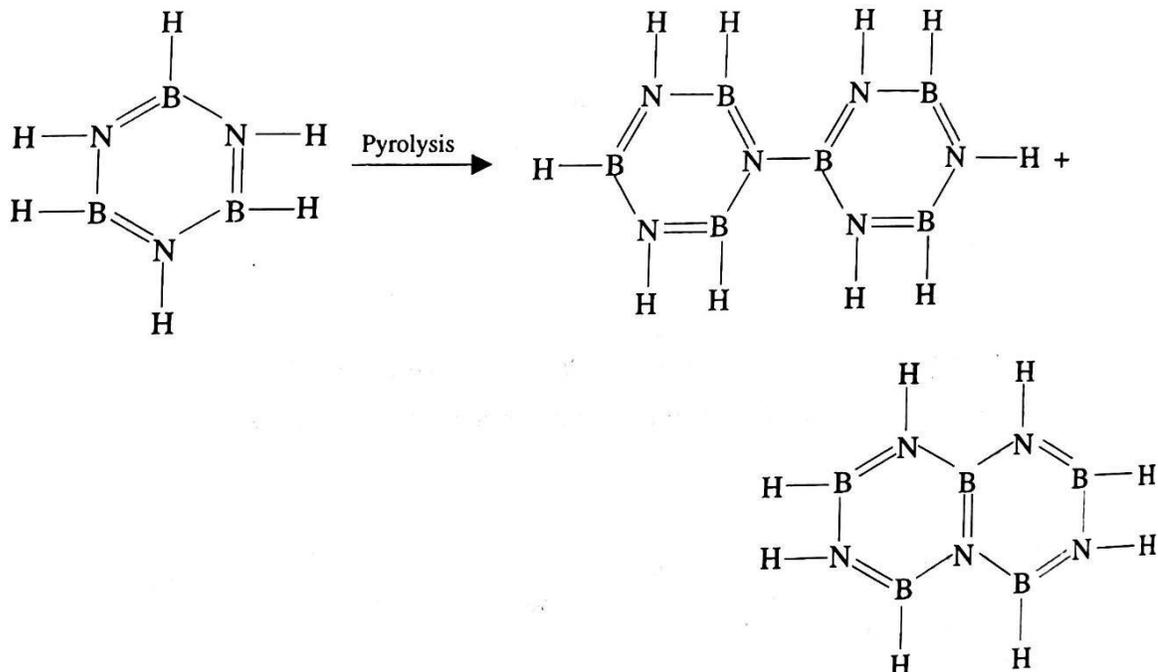
C₆H₆ does not show this type of reaction.

(b) It is reported that under proper conditions, borazine reacts with three molecules of water and gives B-trihydroxyl borazine, B₃N₃H₃(OH)₃ (substitution reaction).

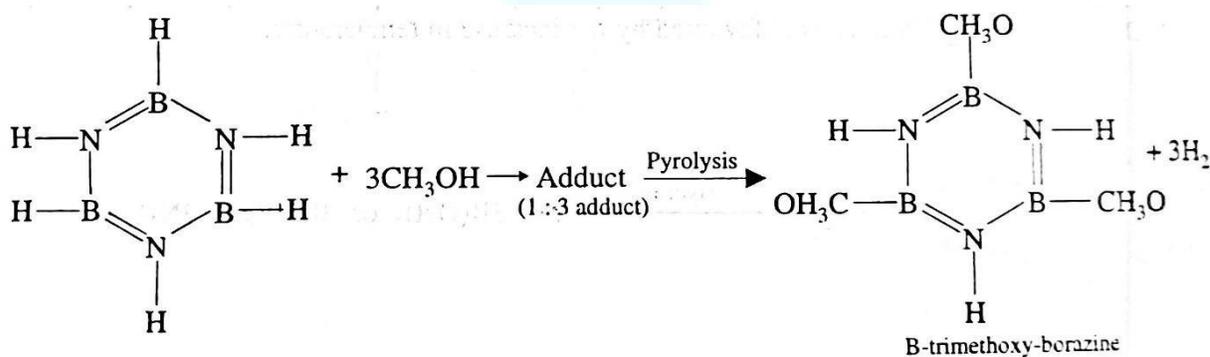


- (iii) Pyrolysis: When borazine is pyrolysed above 340°C , $\text{B}_6\text{N}_6\text{H}_{10}$ and $\text{B}_5\text{N}_5\text{H}_8$ are produced. These products are boron-nitrogen analogues of diphenyl and naphthalene respectively.

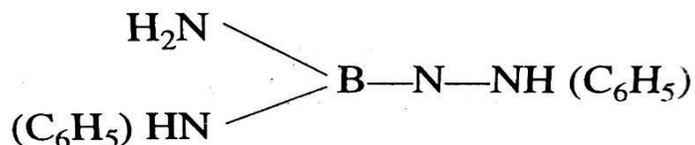




- (iv) Hydrogenation: Hydrogenation of borazine produces polymeric materials of indefinite composition.
- (v) Formation of adduct: Borazine forms an adduct with CH_3OH . This adduct undergoes pyrolysis with the elimination of H_2 and gives B-trimethoxy-borazine.



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

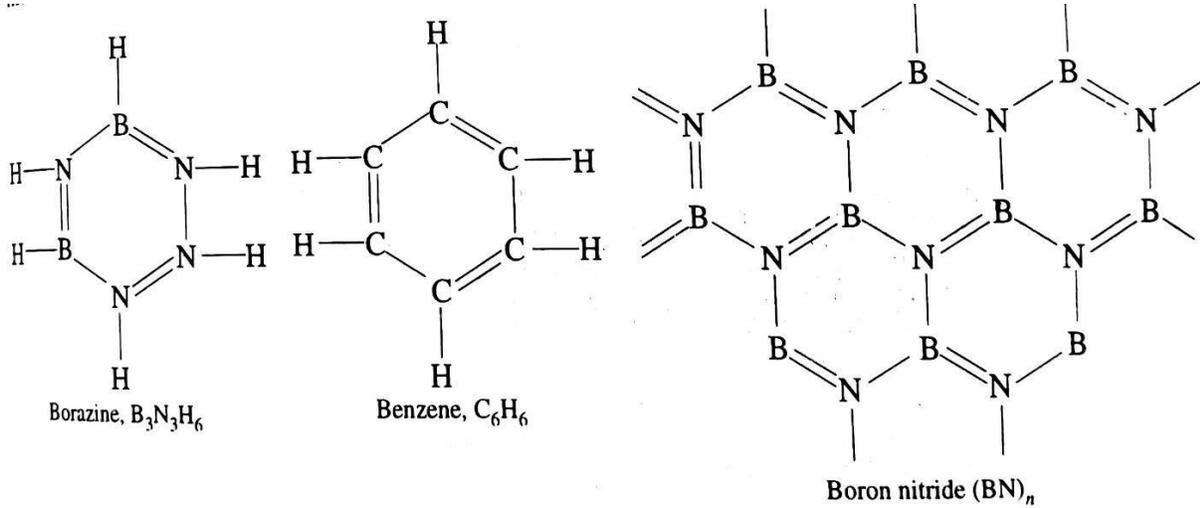


Structure borazine molecule. Various chemical reactions and electron diffraction study of borazine molecule have shown, that this molecule is isoelectronic with benzene and hence its structure is the same as that of benzene. Thus, like benzene, borazine has a planar hexagonal structure containing six-membered 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 pair 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 B₃N₃ 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 B₃N₃ 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 C₆H₆ molecule, C = C bonds are nonpolar, while in case of B₃N₃H₆ 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.



It is due to the partial delocalization of the π -electron cloud that π -bonding in B₃N₃ 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 C₆H₆, readily undergoes addition reactions.

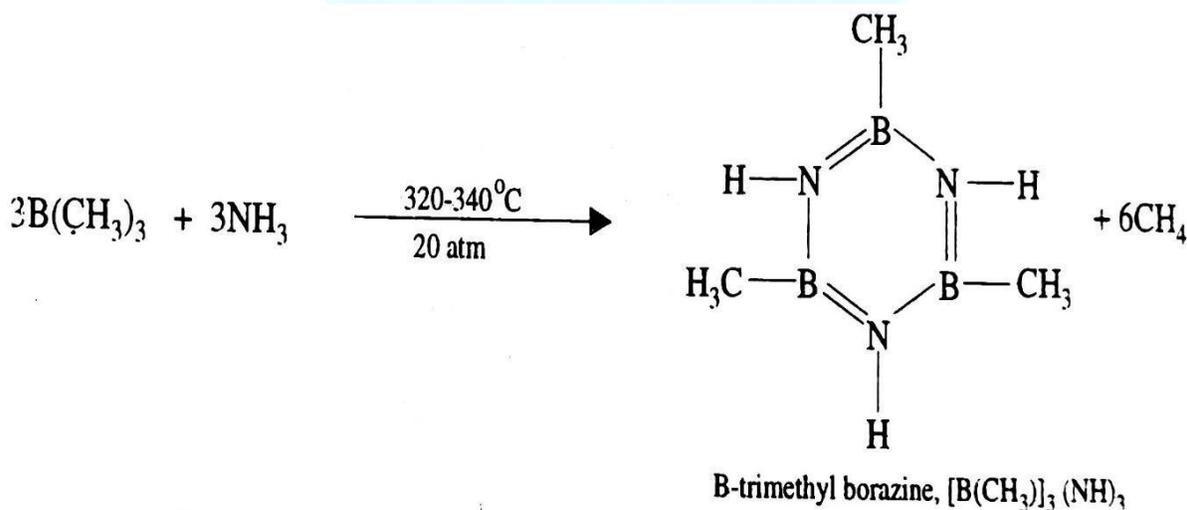
In these reactions, more electronegative atom (e.g., Cl in HCl molecule) is generally attached with B-atom, which is less electronegative than N in B-N bond.

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

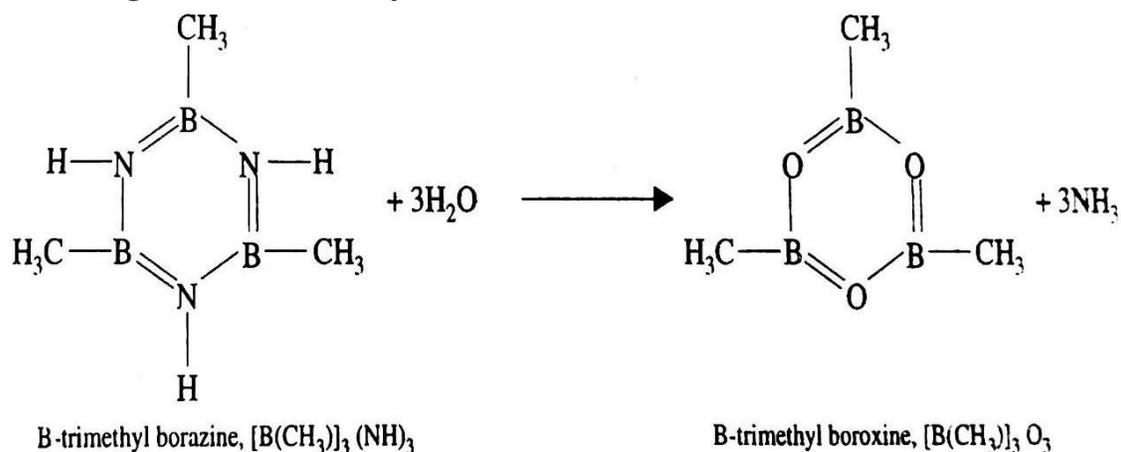
Here, we shall discuss the following substituted borazines.

1. **B-trimethyl borazine, [B(CH₃)₃](NH)₃.** It is prepared by heating B(CH₃)₂ with NH₃ at 320-340° at 20 atm. for 2 hours.



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, $[\text{B}(\text{CH}_3)]_3\text{O}_3$.

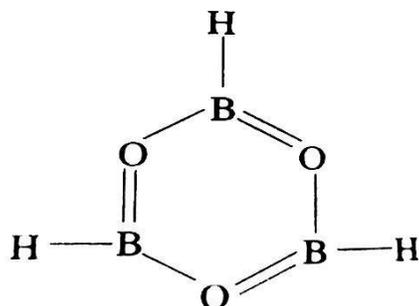


2. **Boroxine, $(\text{BH})_3\text{O}_3$.** This compound is isoelectronic with borazine, $\text{B}_3\text{N}_3\text{H}_6$ ($\text{B}_3\text{O}_3\text{H}_3$) = $3 \times 3 + 3 \times 6 + 3 \times 1 = 30$, $\text{B}_3\text{N}_3\text{H}_6 = 3 \times 3 + 5 \times 3 + 6 \times 1 = 30$). It is produced by 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).



Boroxine exhibits aromatic properties of benzene. $\text{B}_3\text{O}_3\text{H}_3$ 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 \AA . 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

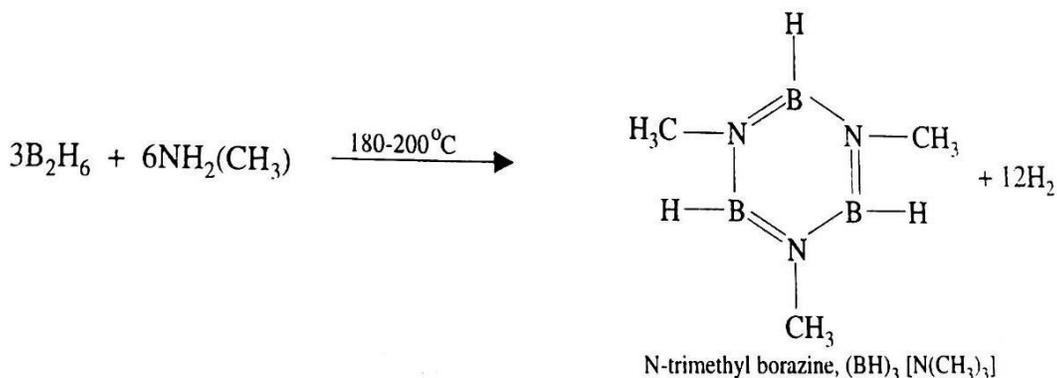


development of a formal negative charge on B- atom and equal formal positive charge on O-atom. These charges have not been shown in the Fig.

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



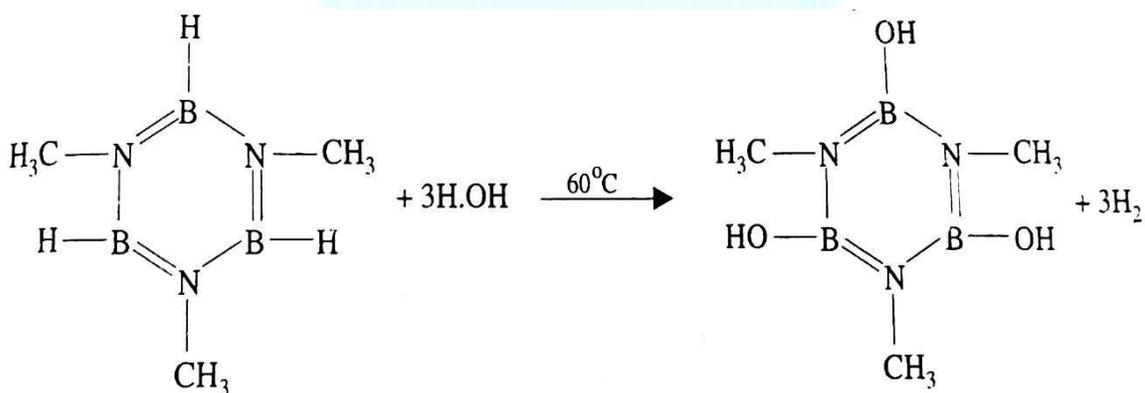
3. **N-trimethyl borazine, (BH)₃ [N(CH₃)₃]** It is obtained in 90% yield by heating mixture of B₂H₆ and NH₂(CH₃) in the correct proportions at 180-200°C for 2 hours.



This compound can also be prepared by reducing monomethyl ammonium chloride, (CH₃)NH₃ Cl with lithium borohydride, LiBH₄



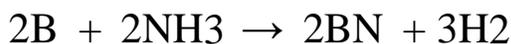
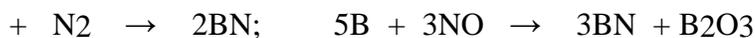
It is a colourless mobile liquid having m.pt. = -9 °C and b.p. = 132 °C. It is stable upto 500°C. At 60 °C, H-atom attached with B-atom is replaced by OH group.



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 NH₃. 2B



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



(iii) when perfectly anhydrous borax ($\text{Na}_2\text{B}_4\text{O}_7$) is heated with dry NH_4Cl to a red heat in a Platinum crucible.



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, $\text{B}(\text{NH}_2)_3$ or boron imide, $\text{B}_2(\text{NH})_3$ or by the action of NH_3 on BCl_3 .



(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.



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



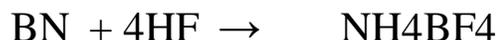
Properties:

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

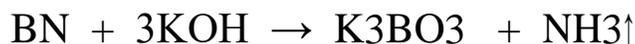
(ii) Decomposition: (a) It gets decomposed when heated in steam, evolving NH_3 .



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



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



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



Uses: BN possesses same hardness as diamond and can withstand temperature of more than 300°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 adjacent layer. The (B-N) distances are equal to 1.45 \AA and the distance between the two layers is 8.33 \AA . 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 adjacent C-atoms in graphite ($\text{BN}=3+5=8$, $\text{C}_2=4+4=8$) and hence the structure of $(\text{BN})_n$ 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°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.

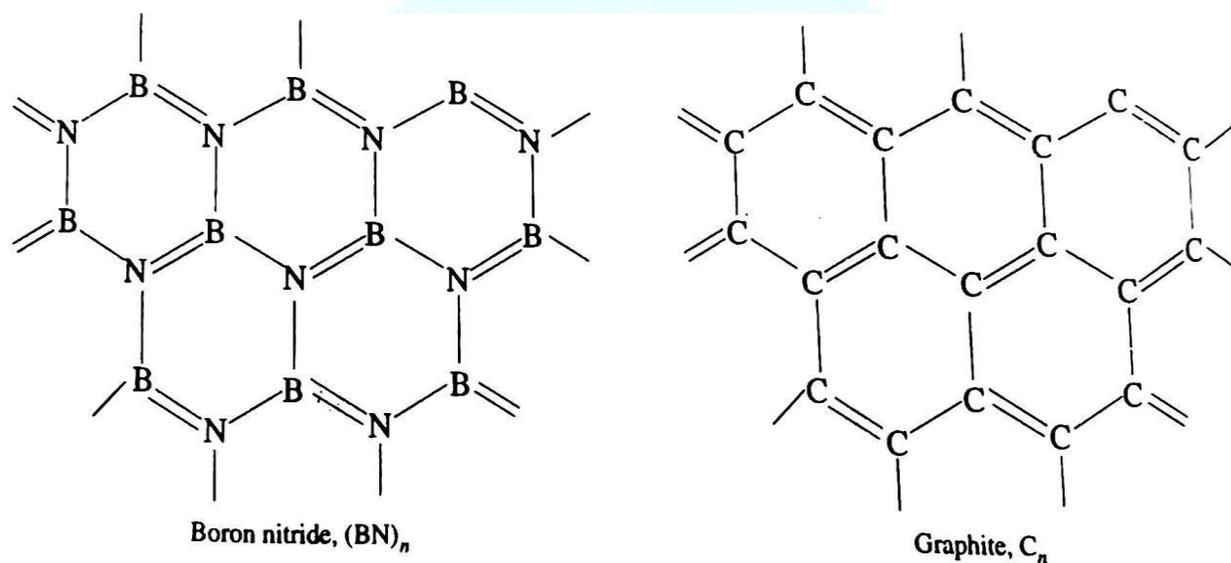


Fig.: Similarity between the structures of boron nitride and graphite.

Silicones: Polymers containing silicon

What are silicones?

Silicones are organo-silicon polymers containing ---O---Si---O--- linkages.

These may be linear silicones cyclic silicones and cross-linked silicones.

Preparation of silicones

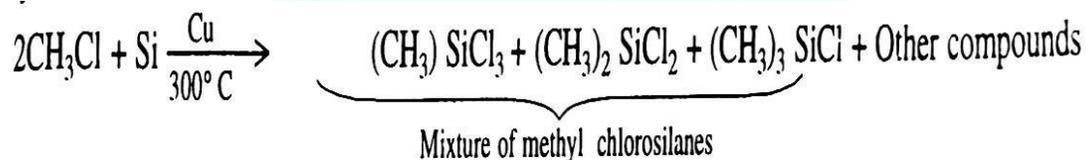
These are prepared by the hydrolysis of alkyl or aryl derivatives of SiCl_4 like RSiCl_3 , R_2SiCl_2 and R_3SiCl and polymerisation of alkyl or aryl hydroxy-derivatives obtained by hydrolysis. Thus, this method consists of the following steps:

(i) To prepare alkyl or aryl derivatives of silicon tetrachloride:

Examples of such derivatives are RSiCl_3 , R_2SiCl_2 and R_3SiCl where R is an alkyl (e.g., CH_3 , C_2H_5 etc.) or aryl (e.g., C_6H_5) group.

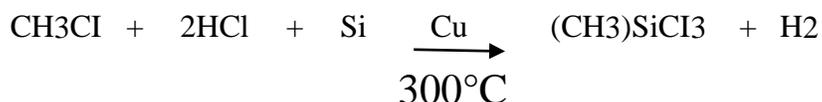
These derivatives are prepared by the following methods:

(a) Methyl chlorosilanes like $(\text{CH}_3)\text{SiCl}_3$, $(\text{CH}_3)_2\text{SiCl}_2$ and $(\text{CH}_3)_3\text{SiCl}$ are prepared by heating methyl chloride, $(\text{CH}_3)\text{Cl}$ with Si, catalyzed by Cu, at 300°C . This reaction gives a mixture of methyl chlorosilanes.

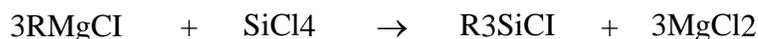
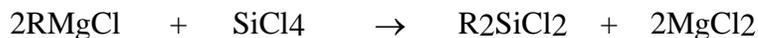
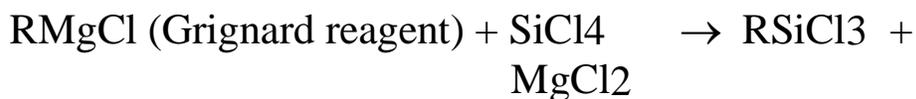


The yield of $(\text{CH}_3)_2\text{SiCl}_2$ (b.p. = 69.6°C) is over 50%. Careful fractionation is used to separate $(\text{CH}_3)_2\text{SiCl}_2$, from $(\text{CH}_3)\text{SiCl}_3$ (b.p. = 66.9°C) and $(\text{CH}_3)_3\text{SiCl}$ (b.p. = 87.7°C).

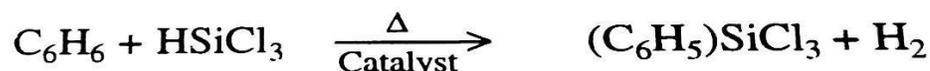
If a mixture of CH_3Cl and HCl is heated with Si, catalysed by Cu, at 300°C , then $(\text{CH}_3)\text{SiCl}_3$ is obtained as the main product.



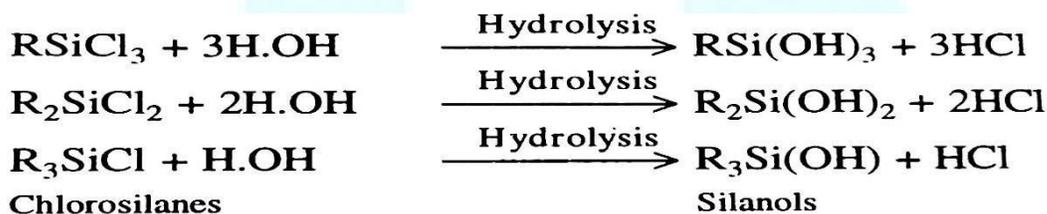
(b) Alkyl chlorosilanes can also be obtained by the action of Grignard reagent on SiCl_4 .



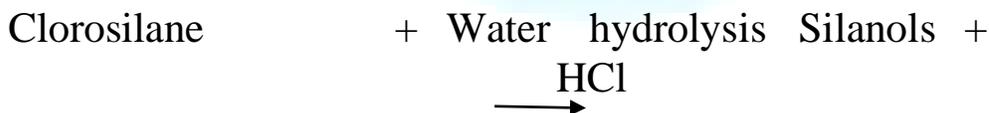
(c) Phenyl chlorosilane, $(\text{C}_6\text{H}_5)\text{SiCl}_3$ is obtained by heating C_6H_6 with HSiCl_3 at 230-300°C in presence of a catalyst like BF_3 , BCl_3 or AlCl_3 .



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

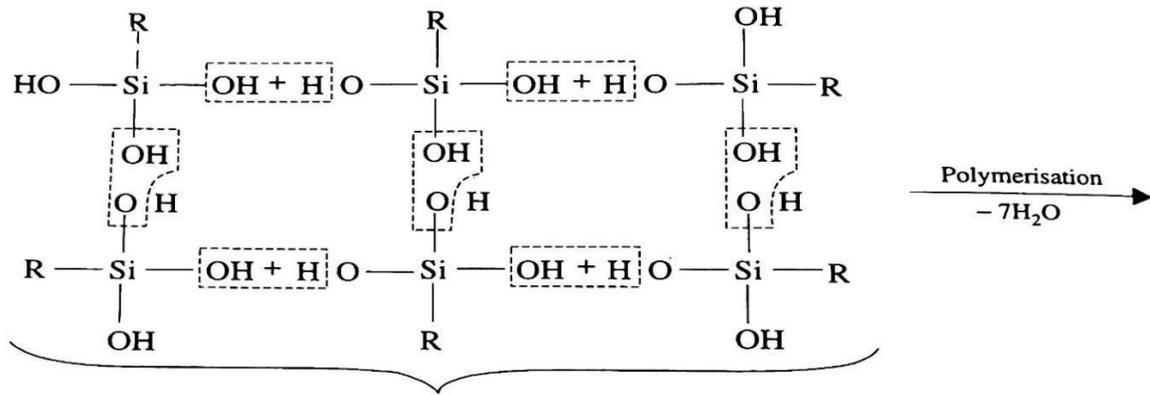


The general equation representing the hydrolysis reaction can be written as:

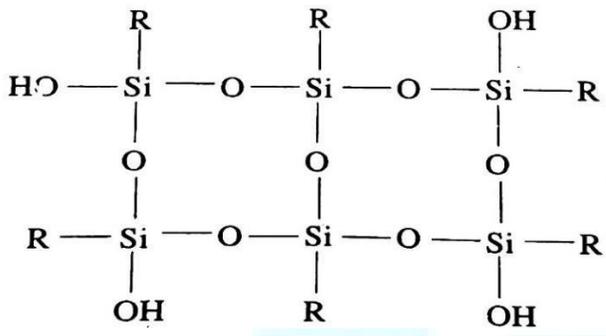


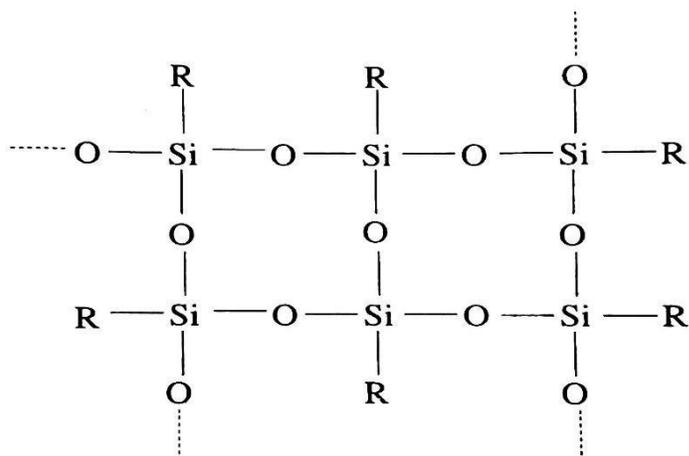
(iii) To allow the alkyl or aryl hydroxy derivatives to undergo polymerization: Polymerisation process involves removal of some H_2O molecules and leads to the formation of different types of silicones. The type of silicone obtained depends on the nature of alkyl or aryl hydroxyderivative and the way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



Polymerisation
 $\xrightarrow{-7\text{H}_2\text{O}}$

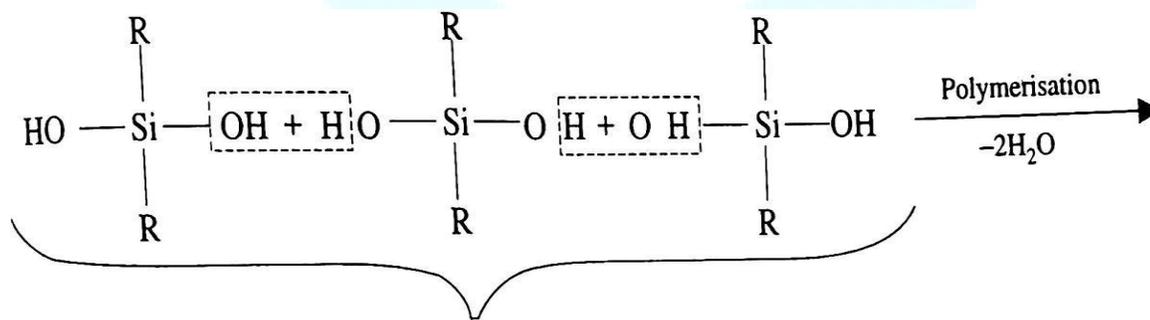




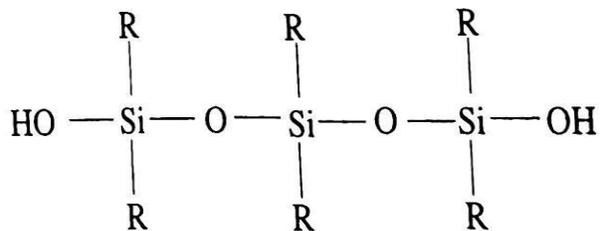
Two dimensional cross-linked silicone

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, $\text{R}_2\text{Si}(\text{OH})_2$ undergo polymerisation, a straight chain (linear) or cyclic (ring) silicone is obtained.

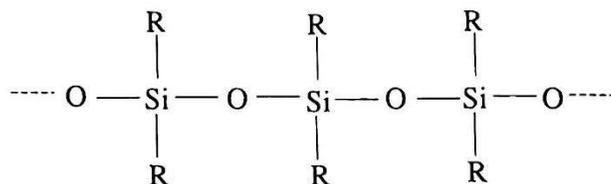


Three molecules of $\text{R}_2\text{Si}(\text{OH})_2$

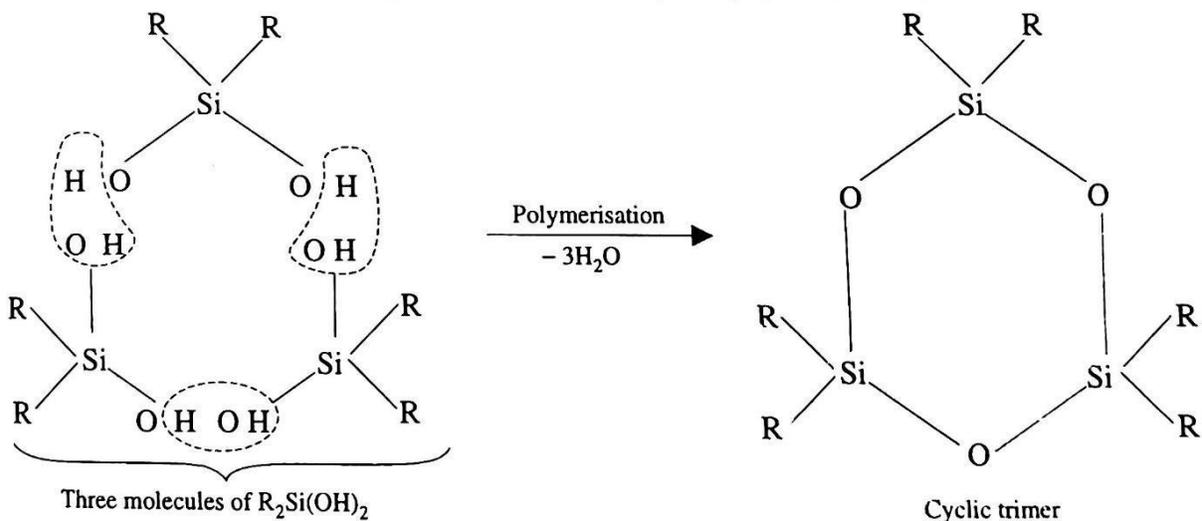


Since an active OH group is present at each end of the chain, polymerisation continues and hence the length of the chain increases and gives rise to the formation of long chains silicon, as shown below:

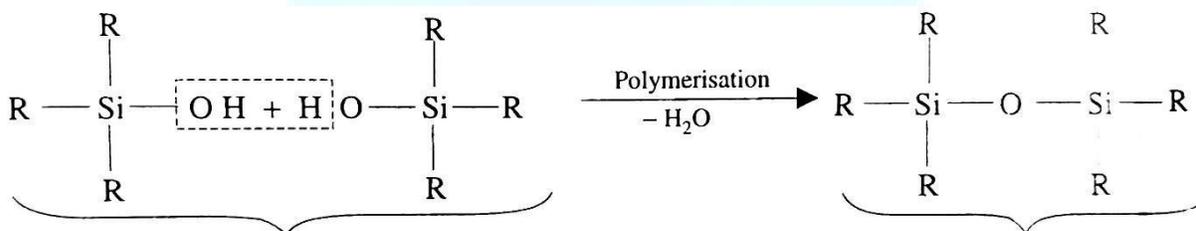




Linear or straight chain silicone (Thermoplastic polymer) (siloxane)



(c) When two molecules of trialkyl monohydroxy-silane, $\text{R}_3\text{Si}(\text{OH})$ undergo polymerisation, a straight chain silicone (dimer) is obtained.



((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 $250-300^\circ\text{C}$.
- (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 .

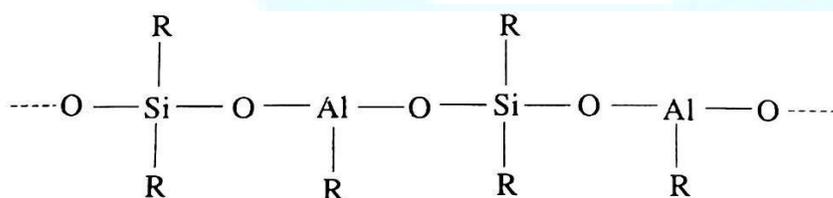


- (iv) They do not become too viscous on cooling and are, therefore, used for low-temperature, lubrication.
- (v) They are water repellent, i.e., they are not wetted by water and are, therefore used in making waterproof cloth and paper by exposing cloth or paper to the silicone vapours.
- (vi) All silicones 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.

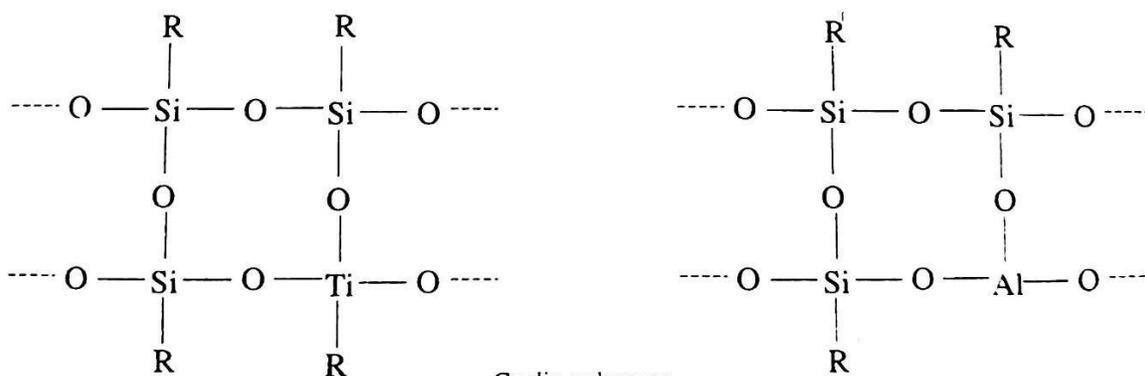
Types of silicones: Their preparation, properties and uses

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.



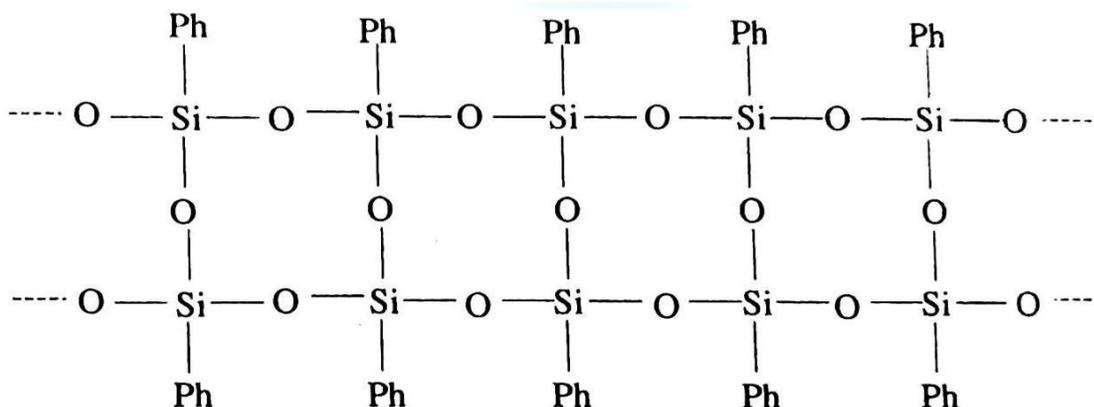
Linear polymer



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 as acrylic ester. If the hydrolysis of $(\text{CH}_3)_2\text{SiCl}_2$ is carried out in the presence of $(\text{CH}_3)_3\text{SiCl}$ and then polymerisation is allowed, a rigid silicone is obtained. This silicone is called silicone resin. There are 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 the best properties in them, baking or heat treatment is given to them. These can withstand temperatures as high as 250°C and coatings made up of silicone resin plus organic resins and Al can withstand temperatures up to 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

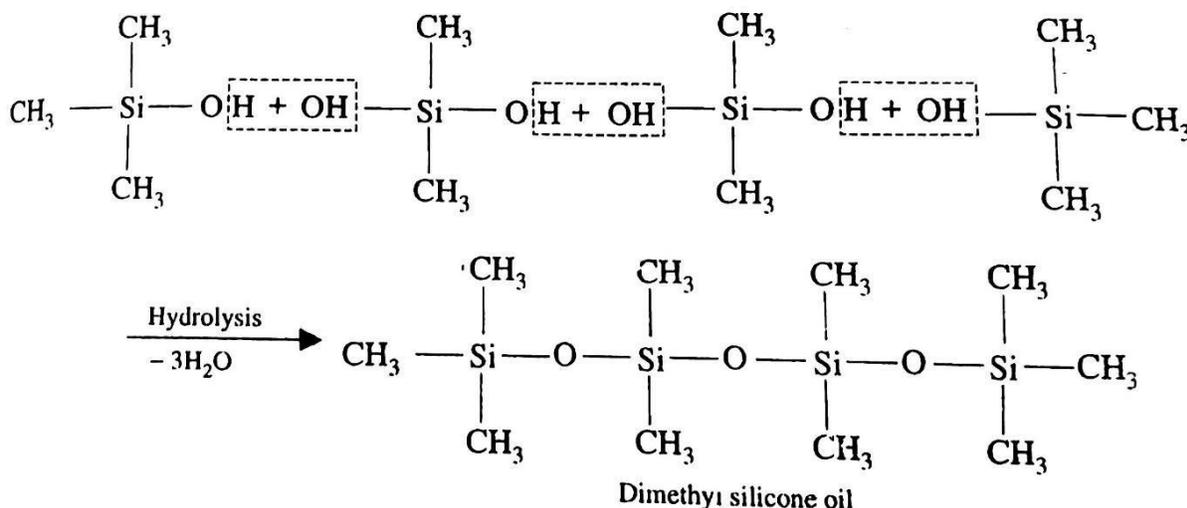
weathering. These silicone resins are not affected by soap and fruit juices.

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.



Preparation of dimethyl silicone oil: If a mixture containing $(\text{CH}_3)_3\text{SiCl}$ and $(\text{CH}_3)_2\text{SiCl}_2$, 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 $(\text{CH}_3)_2\text{SiCl}_2$ or $[(\text{CH}_3)_2\text{SiO}]_4$ followed by polymerisation. $(\text{CH}_3)_3\text{Si-O-Si}(\text{CH}_3)_3$ 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 SiO₂ 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, [NPR₂]_n in which R = Cl, OCH₃ or OC₂H₅. Polyphosphazines may be of three types namely (a) polyphosphonitrilic chlorides, [NPCI₂]_n (b) polydimethoxy-phosphazines, [NP(OCH₃)₂]_n (c) poly diethoxy-phosphazines, [NP(OC₂H₅)₂]_n (ii) polyphosphoryl chlorides, P_nO_{2n-1}Cl_{n+2} (iii) vitreous polyphosphates (phosphate glasses) (iv) crystalline polymetaphosphates. Examples are Maddrell's and Kuroll's salts (v) plasticised and flexible phosphates (vi) polyphosphoric acids.

2. Network polymers: These polymers include (i) polymeric phosphorus pentoxide (ii) polymeric boron orthophosphates, [BPO₄]_n (iii) polymeric aluminium orthophosphates [AlPO₄]_n (iv) polymeric silver orthophosphate, [Ag₃PO₄]_n, (v) polymeric ferrous orthophosphate, [Fe₃(PO₄)₂.8H₂O]_n (vi) sulphur-phosphorus polymers (vii) ultraphosphate glasses (viii) boron phosphate glasses.

Polyphosphonitrilic chlorides, [PNCI₂]_n (n = 3 to 7) :

These polymers are also called **inorganic rubbers**. These compounds

can be represented by the general structure,

$$\left[\begin{array}{c} \text{Cl} \\ | \\ \text{--- P = N ---} \\ | \\ \text{Cl} \end{array} \right]_n$$

Thus, these compounds contain $\begin{array}{c} \text{Cl} \\ | \\ \text{—P} = \text{N—} \\ | \\ \text{Cl} \end{array}$ as a repeating unit.

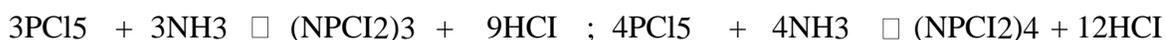


Examples of polyphosphonitrilic chlorides are triphosphonitrilic chloride, $[\text{PNCl}_2]_3$;

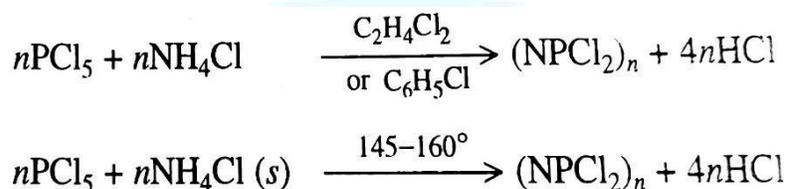
tetraphosphonitrilic chloride, $[\text{PNCl}_2]_4$ etc.

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

(i) $(\text{NPCl}_2)_3$ and $(\text{NPCl}_2)_4$ can be prepared by the ammonolysis of PCl_5 .



(ii) These compounds can be prepared by the reaction between PCl_5 and NH_4Cl in presence of $\text{C}_2\text{H}_4\text{Cl}_2$ or $\text{C}_6\text{H}_5\text{Cl}$ or by heating PCl_5 with solid NH_4Cl at $145\text{--}160^\circ\text{C}$.



Both the above reactions produce a mixture of various phosphonitrilic chlorides, but under controlled conditions, high yields of $(\text{NPCl}_2)_3$ and $(\text{NPCl}_2)_4$ can be obtained. These two compounds can be separated from each other by using the fact that $(\text{NPCl}_2)_3$ sublimes in vacuum at 50°C as a white crystalline solid whereas $(\text{NPCl}_2)_4$ does not do so under these conditions.

The formation of $(\text{NPCl}_2)_n$ takes place through the following steps :

(a) $\text{NH}_4\text{Cl} + \text{PCl}_5 \longrightarrow \text{NH}_4\text{PCl}_6$ (*Ammonium hexachlorophosphate—an unstable compound*)

(b) $\text{NH}_4\text{PCl}_6 \xrightarrow{\text{Decomposition}} \text{HN} \cdot \text{PCl}_3 + 3\text{HCl}$

(c) $n\text{HN} \cdot \text{PCl}_3 \xrightarrow[(-n\text{HCl})]{\text{Condensation}} (\text{NPCl}_2)_n + n\text{HCl}$

(iii) S_4N_4 reacts with SOCl_2 in PCl_3 to give $(\text{NPCl}_2)_3$.

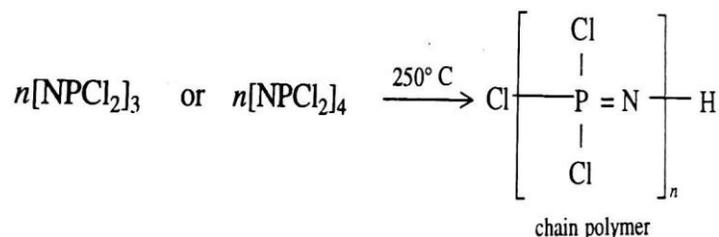


Properties. (1) $(\text{NPCl}_2)_3$; melts at 114°C , boils at 256°C at 1 atm

pressure and is readily soluble in benzene, ether and carbon tetrachloride. $(\text{NPCl}_2)_4$ melts at 123.5°C , boils at 328.5°C and has a lower solubility in benzene, ether and carbon tetrachloride than $(\text{NPCl}_2)_3$.

(2) $(\text{NPCl}_2)_3$ and $(\text{NPCl}_2)_4$ are irritating and somewhat toxic also.

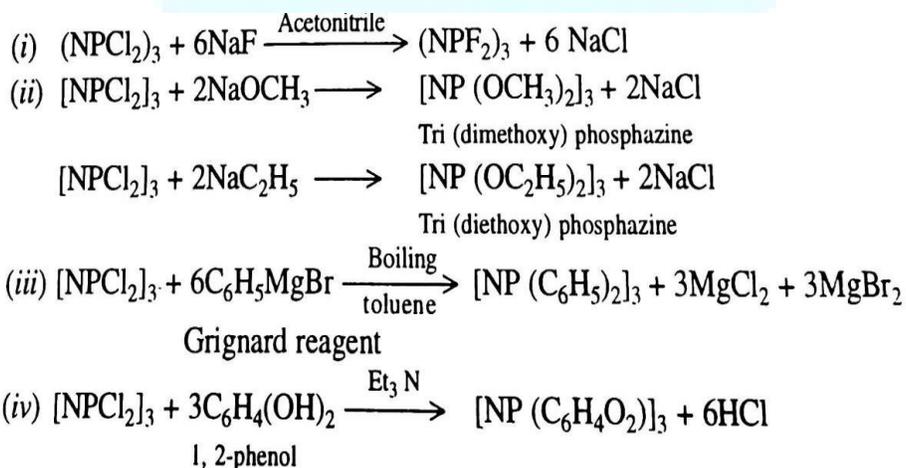
(3) Cyclic trimer. $[\text{NPCl}_2]_3$ or tetramer, $[\text{NPCl}_2]_4$, when heated in vacuum at 250°C gives a chain polymer.

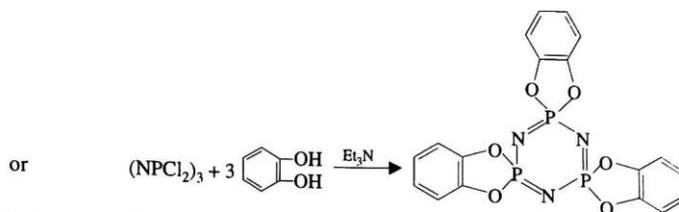


Chain polymer obtained in this way is somewhat cross-linked and hence has low solubility in organic solvents.

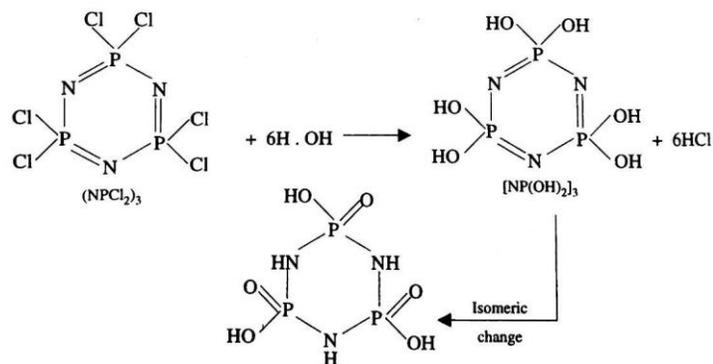
(4) *Reactions involving replacement of Cl-atom of P-Cl bond:* Cl-atom in P-Cl bond is fairly reactive and can be replaced by many nucleophiles. The mechanism of this replacement is not well understood. However, it appears to involve $\text{S}_{\text{N}}2$ attack on

P-atom. The following reactions illustrate the replacement of Cl-atom.



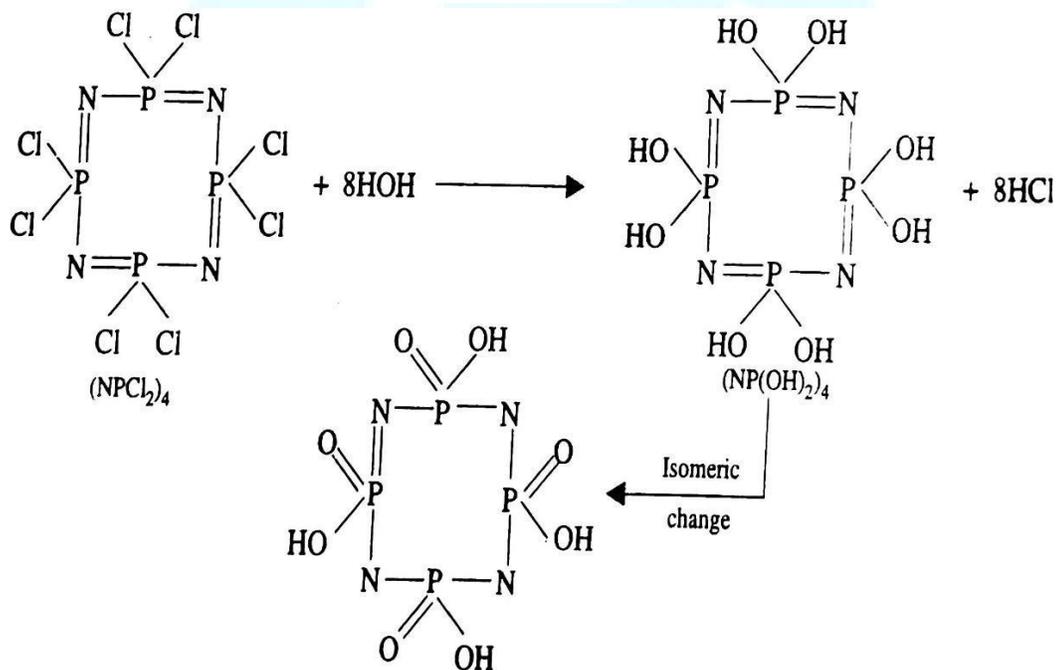


(v) *Hydrolysis.* (a) When $(\text{NPCl}_2)_3$ reacts with H_2O (aqueous ether), all Cl-atoms are replaced by OH groups.

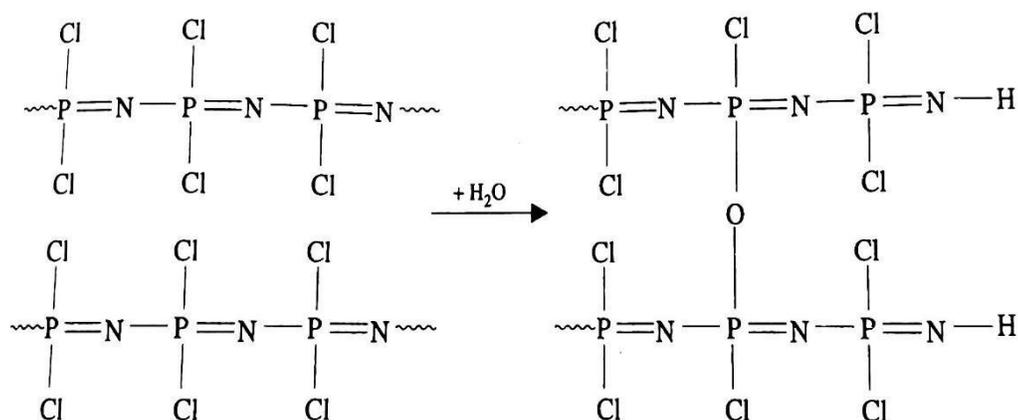


$(\text{NPCl}_2)_3$ in acid solution is hydrolysed to H_3PO_4 and NH_3 .

(b) Hydrolysis of $(\text{NPCl}_2)_4$ in boiling water is rapid and a stable product is obtained.

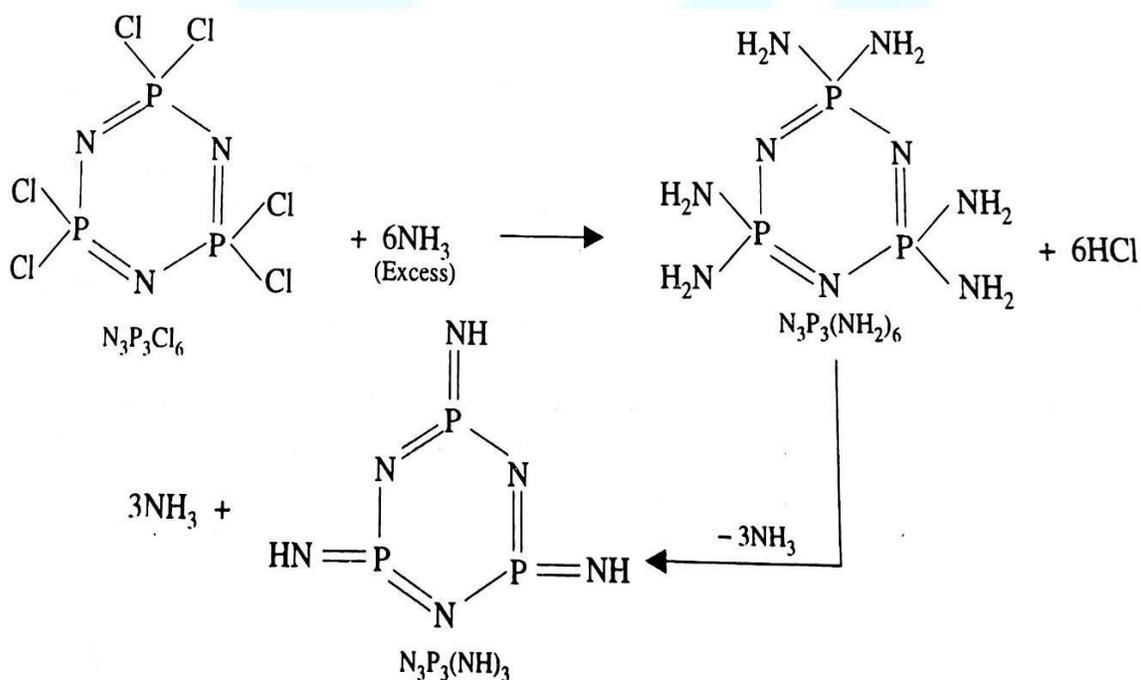


(c) When $[\text{NPCl}_2]_n$ polymers are stored in air, they become brittle. This is due to the reaction of H_2O which forms O-bridges between P-atoms.

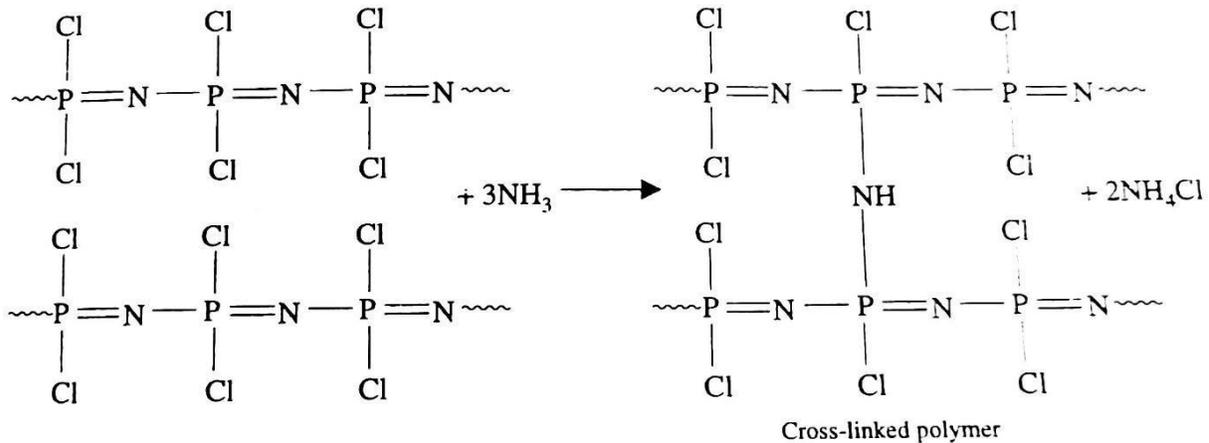


(vi) Reaction with NH_3 :

(a) When $[\text{NPCl}_2]_3$ reacts with excess of NH_3 all the six Cl-atoms are replaced by NH_2 groups and $\text{N}_3\text{P}_3(\text{NH}_2)_6$ is produced. This compound loses 3NH_3 molecules, forming phospham, $\text{N}_3\text{P}_3(\text{NH})_3$ undergoes similar reaction with excess of NH_3 .



(b) When $[\text{PNC}_2]_n$ 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 $AlCl_3$ (Friedel-Crafts reaction) to form diphenyl derivative $N_3P_3Cl_4(C_6H_5)_2$.



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



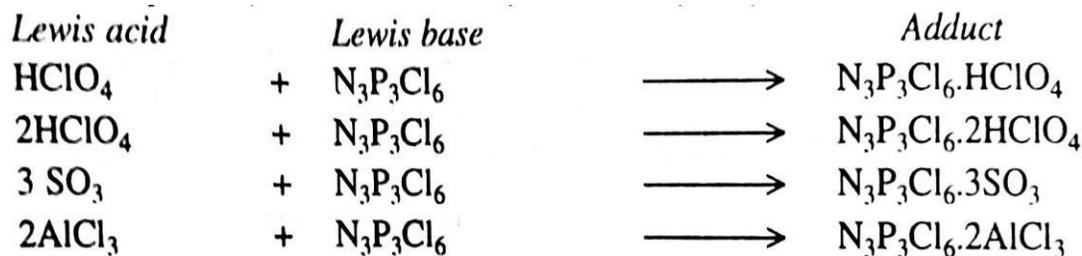
Some of the trimer ($N_3P_3Cl_3$) is also converted into the derivatives of the tetramer ($N_4P_4Cl_8$) such as $N_4P_4Cl_4F_4$ and $N_4P_4Cl_2F_6$.



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



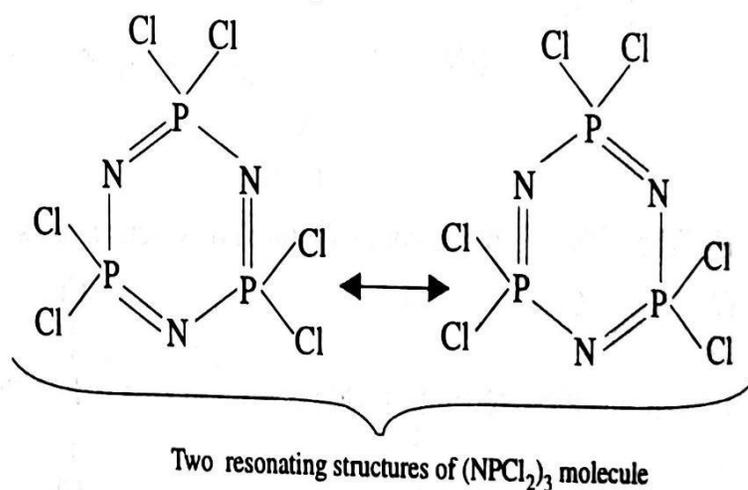
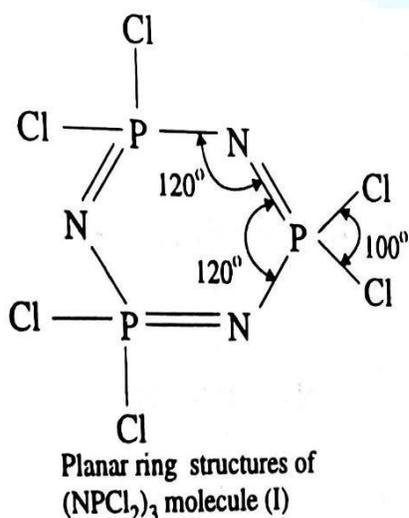
(5) Basic properties of $N_3P_3Cl_5$: Formation of addition compounds: The lone pair of electrons present on each N-atom in $N_3P_3Cl_6$ molecule makes it basic and hence this molecule forms adducts (addition compounds) with Lewis acids, like $HClO_4$, SO_3 , $AlCl_3$, etc.



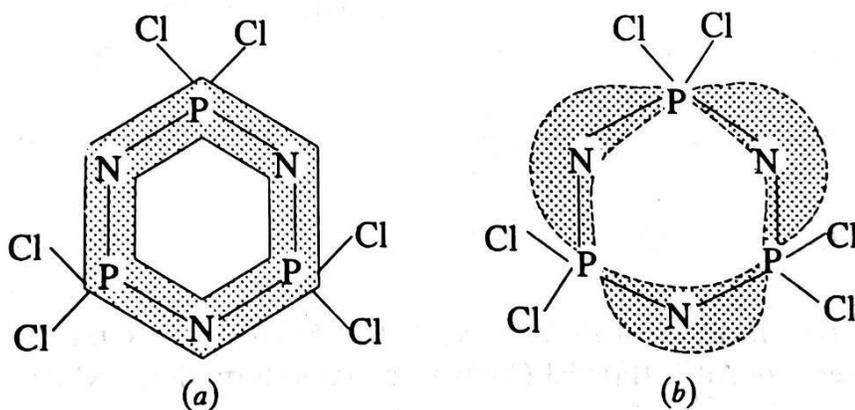
(6) Freshly-prepared $(\text{NPCl}_2)_n$ polymers are soluble in chloroform but insoluble in petroleum ether. When their solution is allowed to stand, $(\text{NPCl}_2)_n$ get cross-linked and slowly gel.

(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 $(\text{NPCl}_2)_3$ molecule: X-ray analysis has shown that $(\text{NPCl}_2)_3$ 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 $(\text{NPCl}_2)_3$ 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.



Unlike benzene which involves extensive ($p\pi - p\pi$) bonding, $(N_3P_3Cl_6)$ molecule involves ($d\pi - p\pi$) bonding. The extent of ($d\pi - p\pi$) bonding appears to be quite appreciable as the N-P distance ($\approx 1.6 \text{ \AA}$) is considerably shorter than the N-P single bond distance ($1.75 - 1.80 \text{ \AA}$). 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

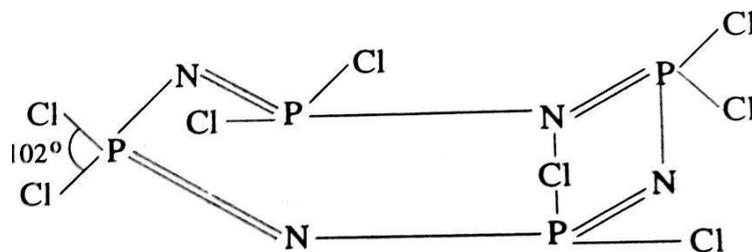
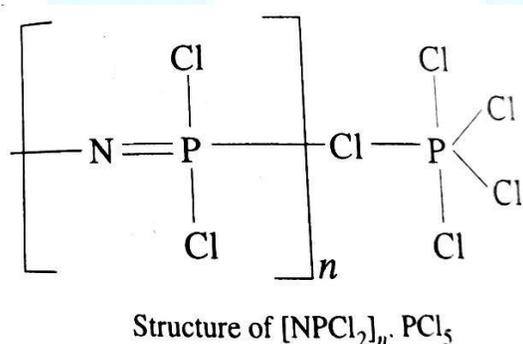


Fig.: tube-like puckered structure of $(\text{NPCl}_2)_4$ molecule

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, $[\text{NPCl}_2]_n \cdot \text{PCl}_5$, 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.



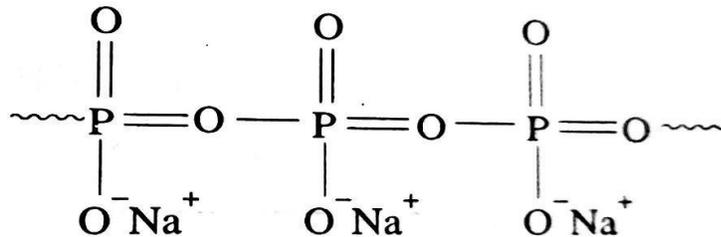
This structure has been confirmed by the fact that ^{31}P n.m.r. spectrum of this compound has two peaks.

A similar product is formed when $(\text{NPCl}_2)_3$ 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-chain 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:



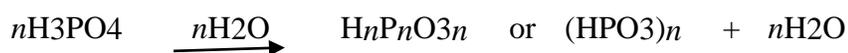
The polyphosphate anions present these polymers have long straight chains, but one P-atom out of 1000 P-atoms forms a cross-linked between the chains. These cross-links disappear within 12 hours when the polymer is dissolved in water or in a neutral aqueous salt solution.

Vitreous sodium polyphosphate can be obtained by heating $\text{Na}_4\text{P}_2\text{O}_7$, or Na_3PO_4 , with P_2O_5 .

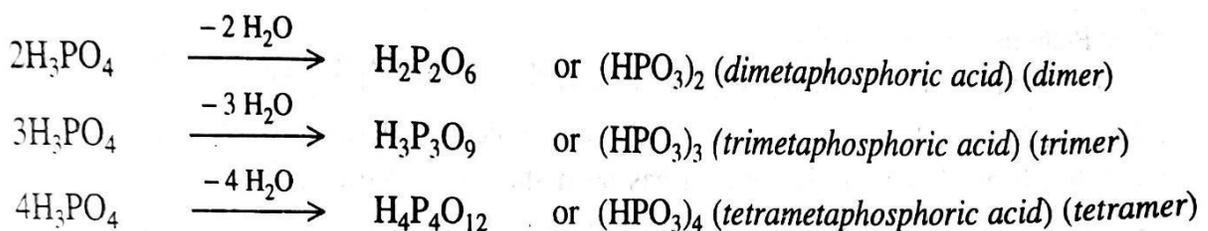
The short chain vitreous polyphosphate polymers are used for deflocculation of proteins. The long chain vitreous sodium phosphate polymers are used in food processing industry. Their use in this industry is based on the interaction of phosphates with proteins.

Crystalline polymetaphosphates:

polymetaphosphates are the salts of polymetaphosphoric acids. These acids are represented by general formula $\text{H}_n\text{P}_n\text{O}_{3n}$ or $(\text{HPO}_3)_n$ and can be regarded as having been obtained by eliminating n moles of H_2O from n moles of H_3PO_4 . Thus:

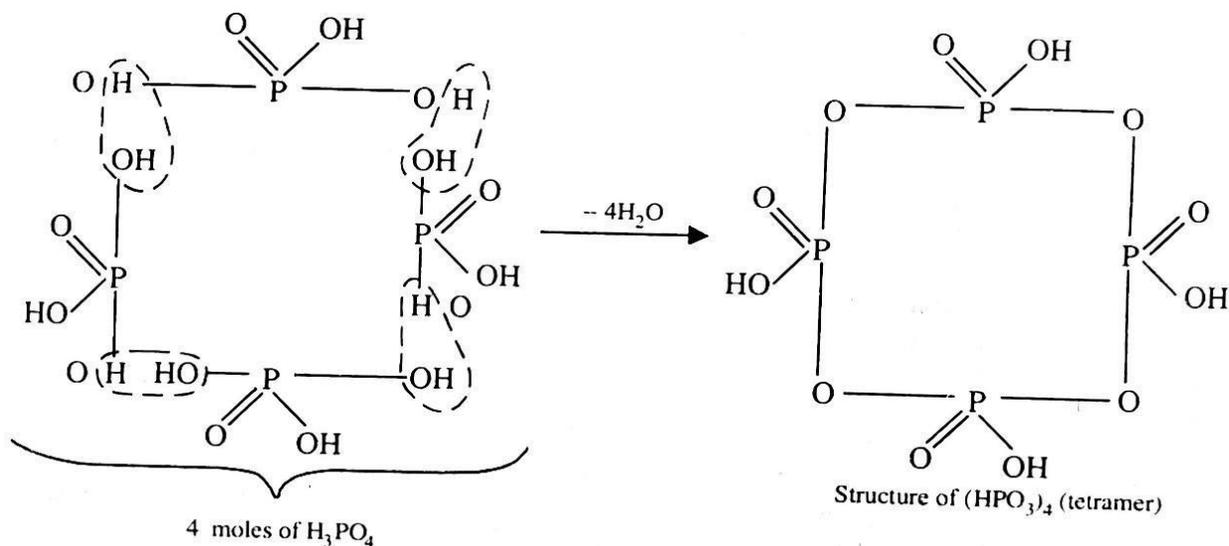


The above discussion shows that $\text{H}_2\text{P}_2\text{O}_6$ or $(\text{HPO}_3)_2$, $\text{H}_3\text{P}_3\text{O}_9$, or



$(\text{HPO}_3)_3$ and $\text{H}_4\text{P}_4\text{O}_{12}$ or $(\text{HPO}_3)_4$ can be obtained as:

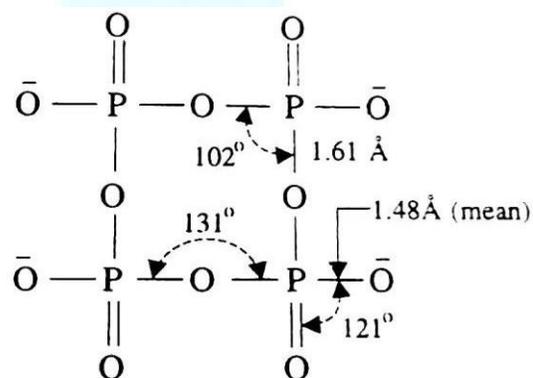
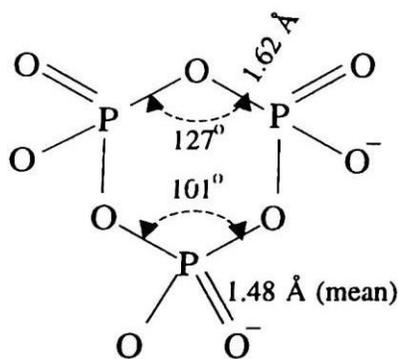
Polymetaphosphoric acids and polymetaphosphates have cyclic structure. The structures of $(\text{HPO}_3)_2$ (dimer), $(\text{HPO}_3)_3$ (trimer) and $(\text{HPO}_3)_4$ (tetramer).



The structure of trimetaphosphate ion, $[(\text{PO}_3)_3]^{3-}$ or $\text{P}_3\text{O}_9^{3-}$ has been shown below in Fig. The ring structure of $[(\text{PO}_3)_3]^{3-}$ ion has been established by the X-ray analysis and ^{31}P

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, $[(\text{PO}_3)_4]^{4-}$ or $\text{P}_4\text{O}_{12}^{4-}$ can be obtained by removing 4OH-atoms from 4OH groups present in $(\text{HPO}_3)_4$ molecule. Thus $[(\text{PO}_3)_4]^{4-}$ 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 $\text{Na}_4\text{P}_4\text{O}_{12}$ that $\text{P}_4\text{O}_{12}^{4-}$ 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. $\text{P}_4\text{O}_{12}^{4-}$ ion can exist in both boat and chair forms.



The above discussion shows that polymetaphosphate ions, $[(\text{PO}_3)_n]^{n-}$ 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 polyphosphoric acids.

Insoluble crystalline sodium or potassium polyphosphates have been prepared by the condensation of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ or $\text{K}_2\text{H}_2\text{P}_2\text{O}_7$. By using different condensation conditions, a number of polyphosphates having the same general formula, MPO_3 ($\text{M} = \text{Na}$ or K) but different properties have been obtained. Important polyphosphates 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, $[\text{Na}$ (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 Kuroll'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, $\text{NaPO}_3\text{-II}$ has shown that this polymer has long $-\text{P-O-P}-$ chains which are composed of interconnected PO_4 groups. The pattern repeats itself after every three units and the chains do not spiral.

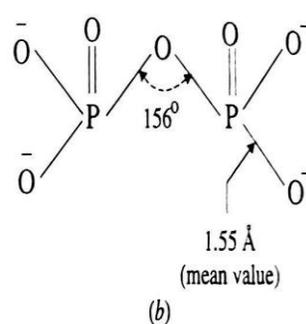
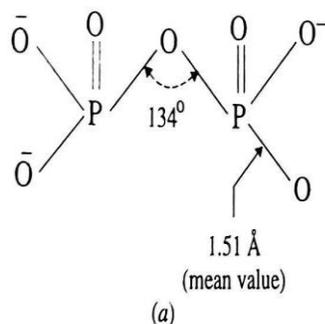
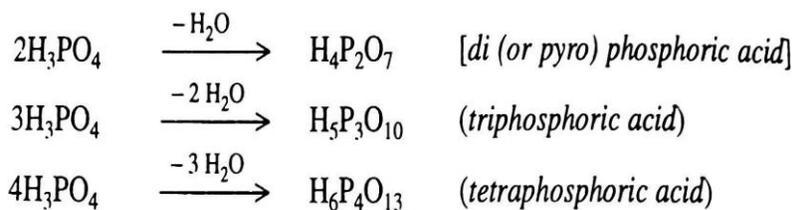
Sodium Maddrell's salt is used as a polishing agent in dental surgery while potassium Kuroll's salt is employed in the manufacture of sausages to prevent water loss.

Polyorthophosphoric 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 .



Thus, these acids can be represented by the general formula, $\text{H}_{n+2} \text{P}_n \text{O}_{3n+1}$



The above discussion shows that $\text{H}_4\text{P}_2\text{O}_7$, $\text{H}_5\text{P}_3\text{O}_{10}$, $\text{H}_6\text{P}_4\text{O}_{13}$ etc., can

be obtained as:

Bond parameters of $P_2O_7^{4-}$ ion found in $Na_4 \cdot P_2O_7 \cdot 10H_2O$ and in α - $Mg_2P_2O_7$

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 tetrahedrons. The structure of pyrophosphate ion, $P_2O_7^{2-}$ found in $Na_4 \cdot P_2O_7 \cdot 10H_2O$ and in α - $Mg_2P_2O_7$, salts are shown below in Fig.

The structures of $H_5P_3O_{10}$ and $P_3O_{10}^{5-}$ molecules and the anions derived from them are given below in Figs.

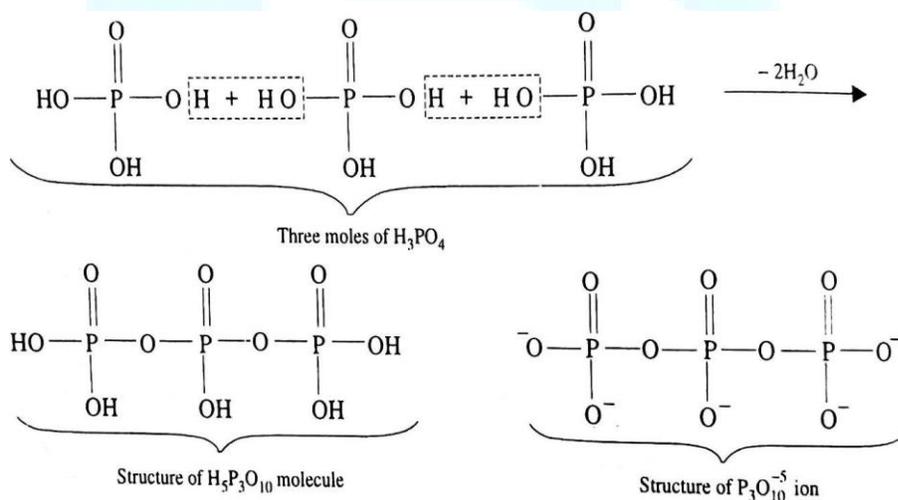


Fig.: Structure of $H_5P_3O_{10}$ molecule and $P_3O_{10}^{5-}$ ion

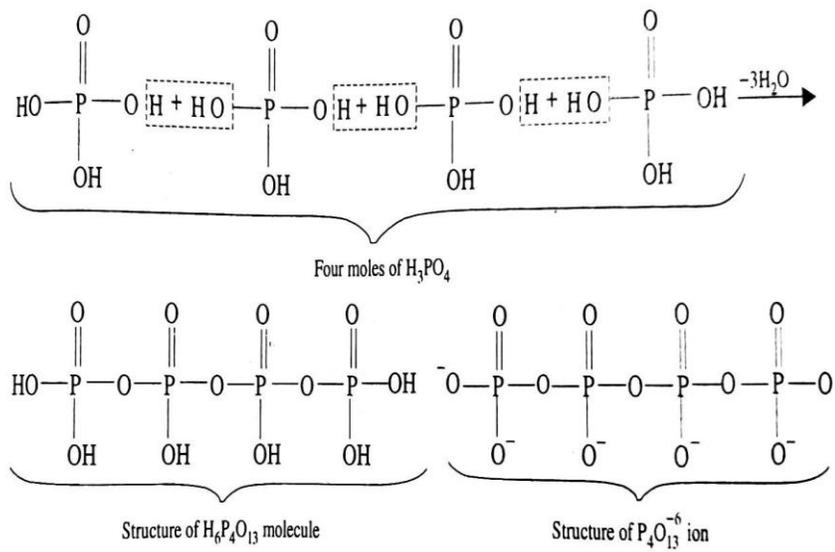
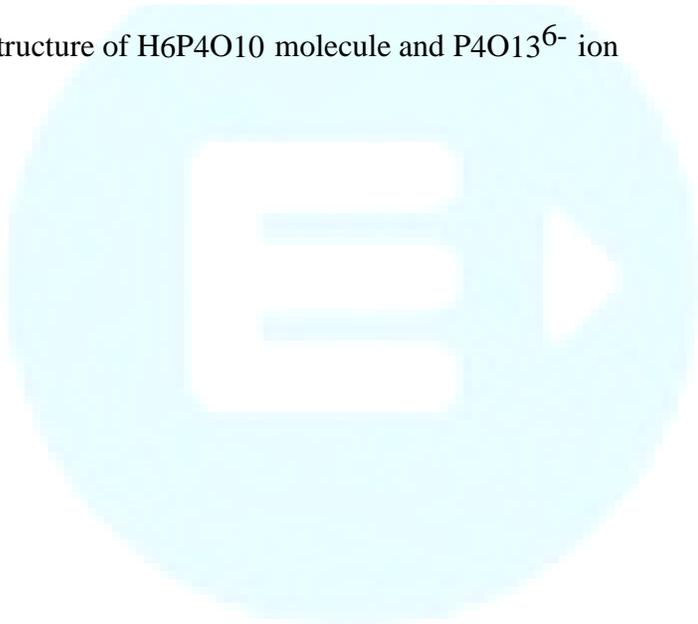
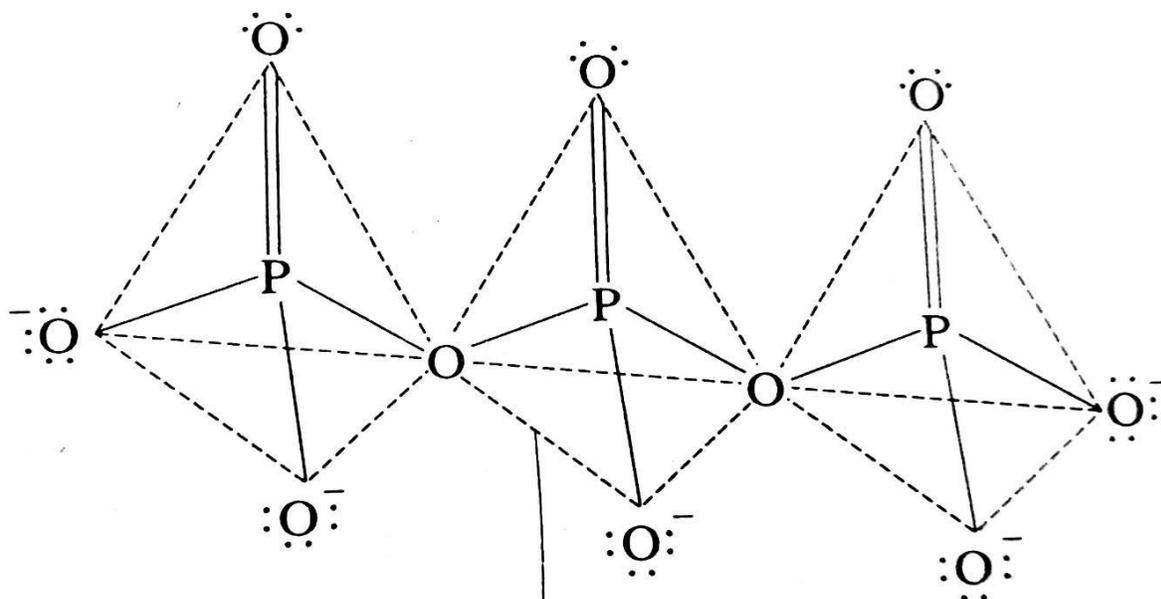


Fig.: Structure of $\text{H}_6\text{P}_4\text{O}_{13}$ molecule and $\text{P}_4\text{O}_{13}^{6-}$ ion



The linking of three PO_4 tetrahedrons through three O-atoms, to get the Structure of $\text{P}_3\text{O}_{10}^{5-}$ ion has been shown below in Fig.



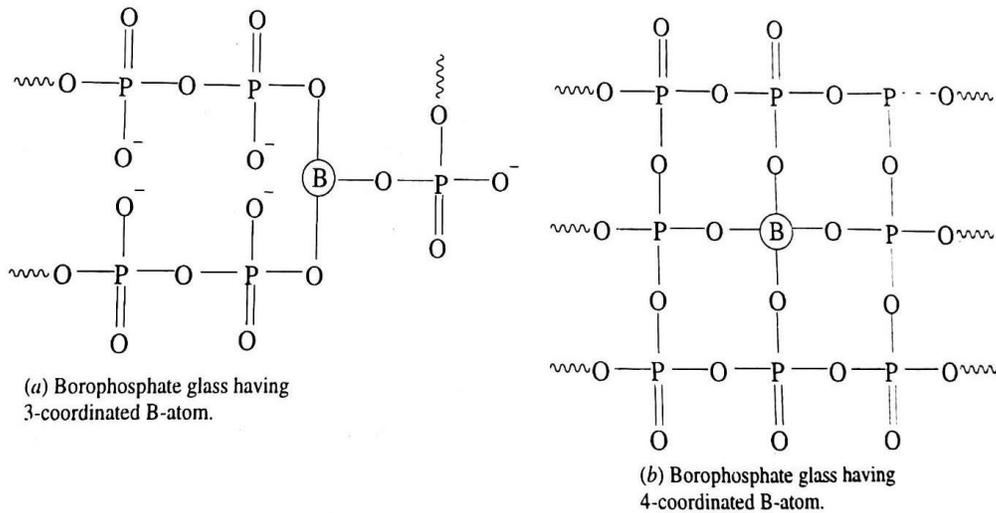
The structures of polyphosphate molecules and ions, as given above each structure is sp^3 hybridised.

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 molepercent 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.



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, S₄N₄ or (SN)₄ :

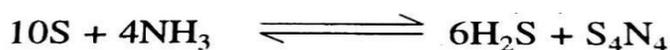
This tetramer is the starting material for the preparation of many compounds containing S-N bonds.

Preparation.

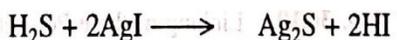
(i) When sulphur monochloride, S₂Cl₂ reacts with NH₃ (ammonolysis of S₂Cl₂) either in solution in an inert solvent or is heated over solid NH₄Cl, S₄N₄ is obtained.



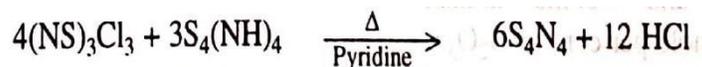
(ii) When anhydrous NH₃ reacts with sulphur, S₄N₄ is obtained.



Since the reaction is reversible, AgI is added to remove H₂S. AgI is readily soluble in anhydrous NH₃ while Ag₂S is not and hence Ag₂S is removed from the reaction.



(iii) When trithiazyl trichloride, $(\text{NS})_3\text{Cl}_3$ is heated with tetrasulphur tetraimide, $\text{S}_4(\text{NH})_4$ in presence of pyridine, $(\text{NS})_3\text{Cl}_3$ undergoes reduction and tetrasulphur tetranitride (S_4N_4) is obtained.



Pyridine used in the reaction absorbs HCl.

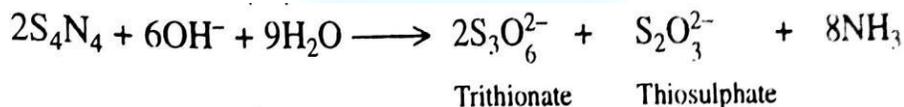
Properties. (i) It is an orange-yellow crystalline solid which melts and boils with decomposition at about 443 K. It is strongly exothermic and explodes on heating. It may explode even on impact or if submitted to friction (e.g., when removing stopper from a bottle).

(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).

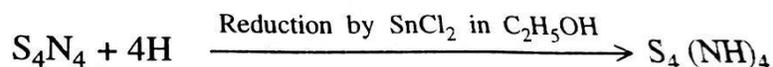
(v) Action of a boiling alkali: S_4N_4 undergoes hydrolysis readily by a boiling alkali. In the reaction all nitrogen of S_4N_4 is converted into NH_3 .



(vi) Fluorination: Fluorination of S_4N_2 by AgF_2 gives tetrathiazyl tetrafluoride, $(\text{NS})_4\text{F}_4$ or $\text{N}_4\text{S}_4\text{F}_4$.



(vii) Reduction: Reduction of S_4N_4 with SnCl_2 , in ethanol gives tetrasulphur tetraimide, $\text{S}_4(\text{NH})_4$ or $\text{S}_4\text{N}_4\text{H}_4$ which is a colourless compound.

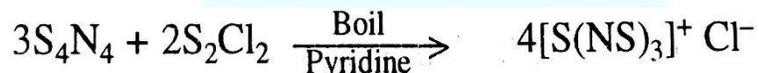


(viii) Oxidation: Oxidation of S_4N_4 with Cl_2 gives trithiazyl trichloride, $(\text{NS})_3\text{Cl}_3$.



(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.

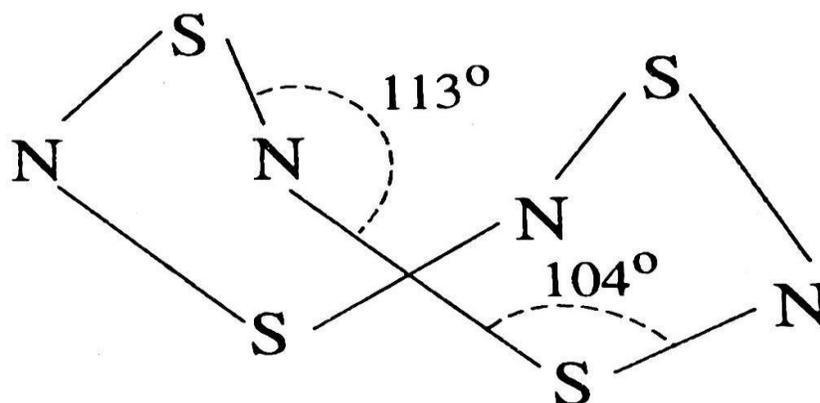
(v) Reaction with S_2Cl_2 : When S_4N_4 is boiled with S_2Cl_2 in CCl_4 solution, thiotrithiazyl chloride, $[\text{S}(\text{NS})_3]^+ \text{Cl}^-$ or $[\text{N}_3\text{S}_4]^+$ is obtained. As is evident, it is an ionic compound.



(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 $\text{S}_4\text{N}_4 \cdot \text{A}$ ($\text{A} = \text{SbCl}_5, \text{MoCl}_5, \text{BF}_3, \text{WCl}_4$) or $\text{S}_4\text{N}_4 \cdot 2\text{A}$ ($\text{A} = \text{SnCl}_4$) type.

(xii) Reaction with PCl_3 : S_4N_4 , reacts with PCl_3 and forms an ionic compound whose formula is $[\text{Cl}_3\text{P} \cdot \text{N} \cdot \text{PCl}_2 \cdot \text{N} \cdot \text{PCl}_3]^+ [\text{PCl}_6]^-$.

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, S₂N₂: As already stated, when S₄N₄ is heated to about 575 K in a high vacuum or on silver wood, S₂N₂ 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.

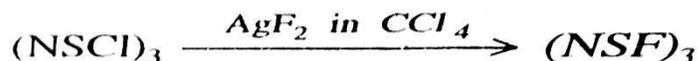
3. Pentasulphur dinitride, S₅N₂: When S₄N₄ is heated in solution, S₅N₂, is obtained. It is a somewhat less stable than S₄N₄. and is a deep red oil which freezes to a grey solid at 284 K.

II. Thiazyl halidesonide:

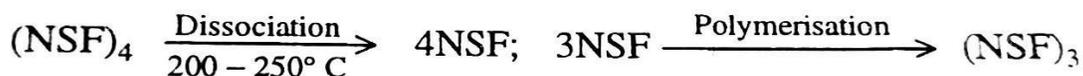
Thiazyl halides can be represented by the general formula (NS)_n X_n or (NSX)_n (X = F, Cl, Br, n = 3, 4 etc.). Examples of such compounds are trithiazyl trifluoride [(NSF)₃], tetrathiazyl tetrafluoride [(NSF)₄] and trithiazyl trichloride [(NSCl)₃].

1. Trithiazyl trifluoride, (NS)₃F₃ or (NSF)₃: It is prepared:

(i) by fluorinating trichloride, (NSCl)₃ with AgF₂ in CCl₄.

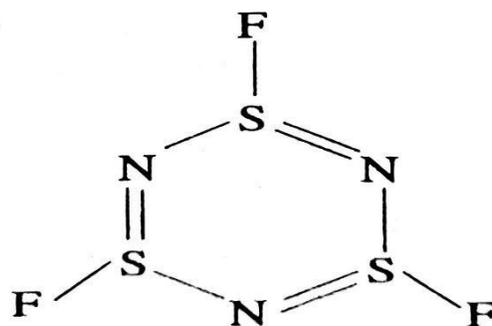


(ii) by heating tetrathiazyl tetrafluoride, (NSF)₄ at 200-250 °C which dissociates into NSF, followed by polymerization.



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



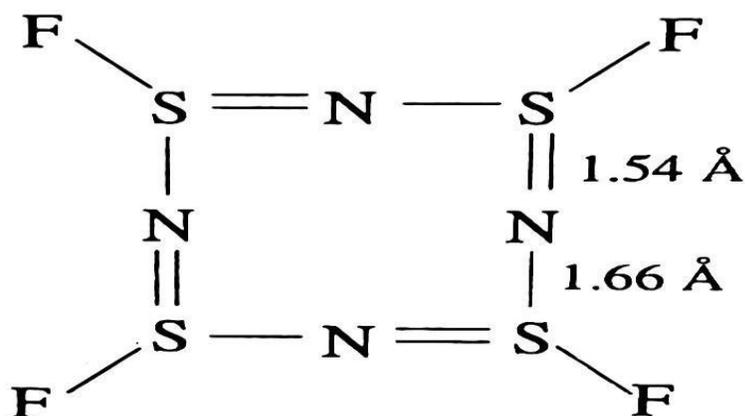
2. **Tetrathiazyl tetrafluoride, (NSF)₄**: It is prepared by fluorinating S₄N₄ with AgF₂



It is a white sensitive solid. It dissociates at 200-250 °C into NSF, which polymerises to trimer, (NSF)₃.



The ¹⁹F 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.



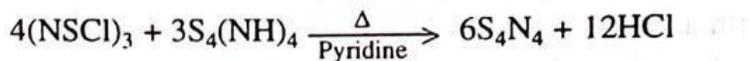
3. Trithiazyl trichloride, (NSCl)₃:

Preparation. It is prepared by oxidising tetrasulphur tetranitride (S₄N₄) by Cl₂.

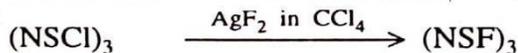


Properties. (i) When (NSCl)₃ is heated with tetrasulphur tetraimide, S₄(NH)₄ in presence of pyridine, (NSCl)₃ undergoes reduction and tetrasulphur tetranitride (S₄N₄) is obtained.

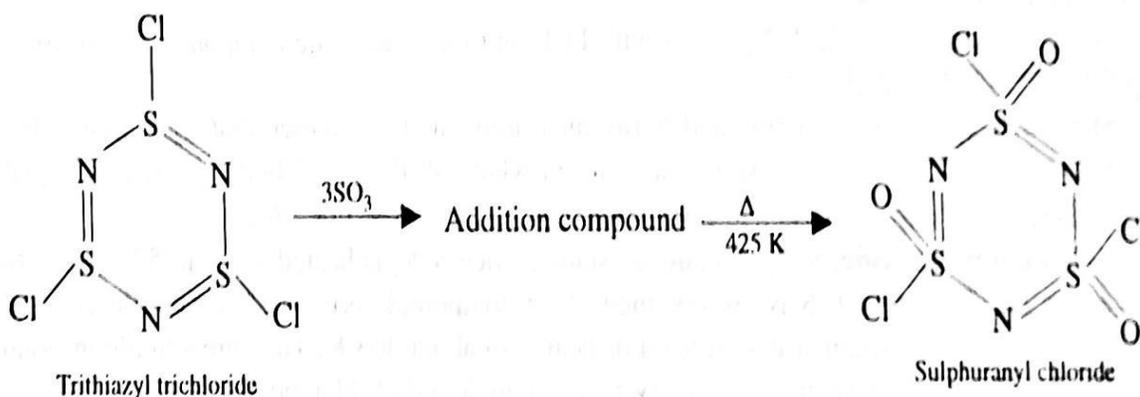
Pyridine used in the above reaction absorbs HCl.



(i) (NSCl)₃ is converted into (NSF)₃ by fluorinating it with AgF₂ in CCl₄



(iii) This compound forms an addition compound with three molecules of SO₃. The addition compound, on being heated to 425 K, gives sulphuranyl chloride.



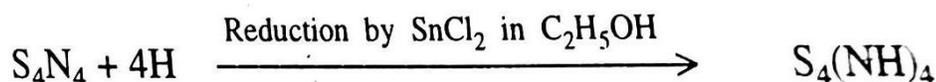
Structure: (NSCl)₃ molecule has the same structure as (NSF)₃ molecule has.

III. Imides of Sulphur:

These compounds may be regarded as having been obtained by replacing one or more S-atom in S₈ 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 S₇(NH) 1, 3-S₆ (NH)₂ ; 1, 4-S₆ (NH)₂ ; 1, 5-S₆ (NH)₂ ; 1, 3, 5-S₅ (NH)₃ ; 1, 3, 6-S₅(NH)₃ ; S₄(NH)₄ etc. The numbering system is based on S₈ ring.

Preparation: When S₂Cl₂ reacts with NH₃ (ammonolysis of S₂Cl₂) in dimethylformide, S₇(NH), 1, 3-S₆(NH)₂, 1, 4-S₆ (NH)₂, 1, 5, S₆ (NH)₂, 1, 3, 5-S₅ (NH)₃, 1, 3, 6-S₅ (NH)₃, etc., are obtained. These products are separated from each other by chromatography and fractional crystallisation.

Tetrasulphur tetraimide, S₄(NH)₄ is prepared by reducing S₄N₄ with SnCl₂ in C₂H₅OH.



Properties of S₇(NH):

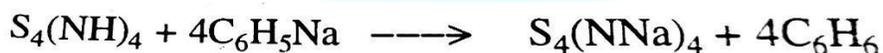
- (i) The reaction of S₇(NH) with C₆H₅Na gives S₇(NNa).



- (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.

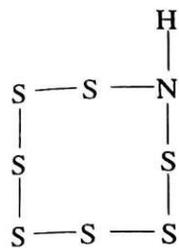
Properties of $S_4(NH)_4$:

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

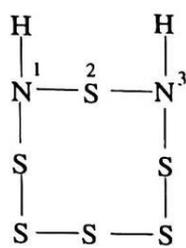


- (ii) N-H bonds in $S_4(NH)_4$ molecule can be acetylated and benzoylated.
- (iii) Air oxidation of $S_4(NH)_4$ at $100^\circ C$ gives a tetrameric thionyl imide, $(OS)_4(NH)_4$ or $(OSNH)_4$

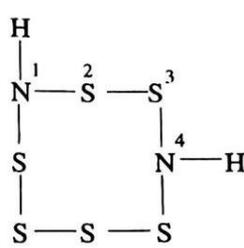
Structure of imides of Sulphur: None of the imides has N-N bonds. The structures of some imides are given below in Fig. $S_7(NH)$ does not have any isomer and hence, it is represented by the structure shown in the figure.



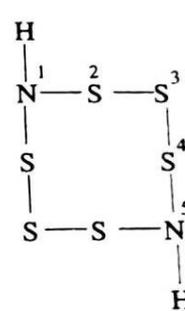
$S_7(NH)_1$



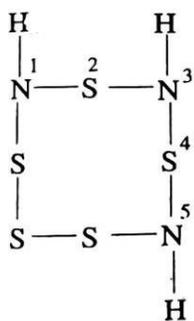
1, 3 - $S_6(NH)_2$



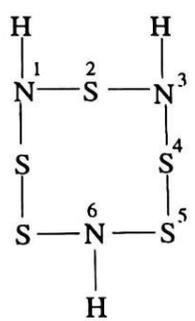
1, 4 - $S_6(NH)_2$



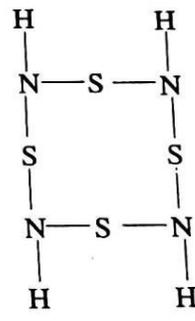
1, 5 - $S_6(NH)_2$



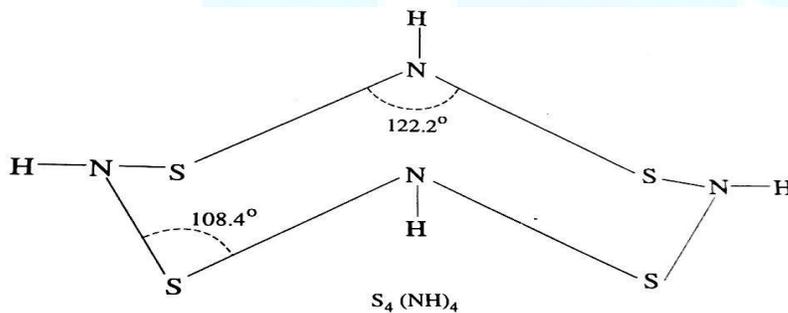
1, 3, 5 - $S_5(NH)_3$



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



$S_4(NH)_4$



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 ($= 1.67 \text{ \AA}$). $S_4(NH)_4$ 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

