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Carbon Family

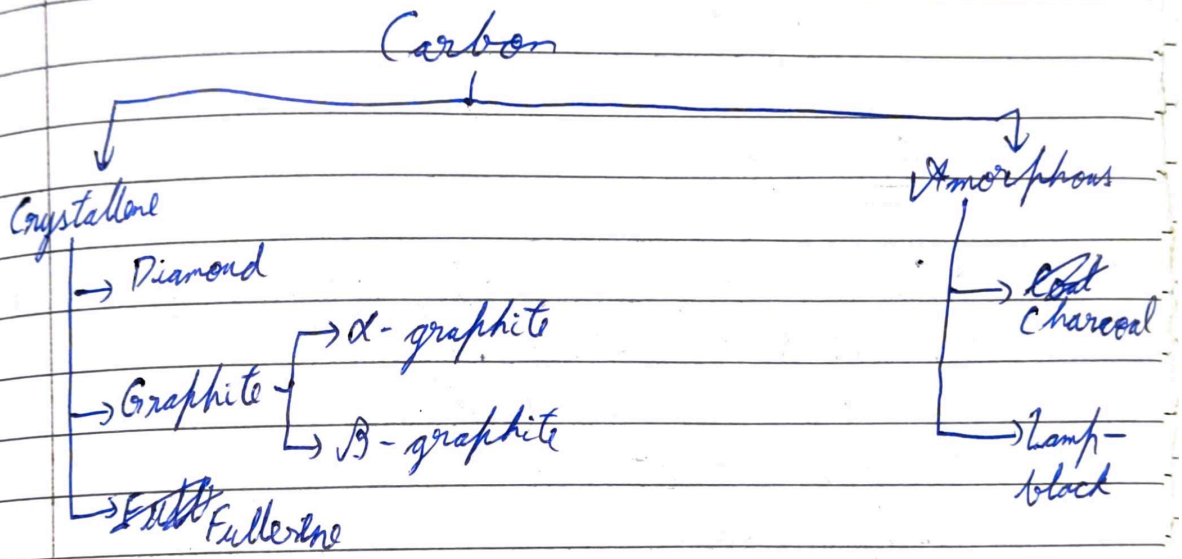
C +4

Si +2, +4

Ge

Sn

Pb +2, +4
(more stable)



Diamond

- Hybridization sp^3
- Hardest substance
- Perfect crystal
- Good conductor of heat
- Bad " " electricity
- Has FCC structure carbon is present at corners, all faces and alternate tetrahedral voids
- Bond angles 109.5°
- Bond length 1.54 A°

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Rare hexagonal form of ~~Carbon~~ Diamond is also known as (HCP)

- Blue diamond is due to presence of Al
- Black " " " " " Ni

- In diamond, strong covalent bond exist in cubic form in solid state.
- Graphite is thermodynamically more stable than diamond.
- density of diamond > graphite

Graphite

- Soft, ~~grayy~~, dark, greyish coloured crystalline solid.
- sp^2 hybridized.
- 1 free e^-.
- Layer form
- Van-der Waal Force exist b/w layers.
- Due to weak Van-der waal Force, graphite is used as a lubricant.
- Good conductor of electricity (free e^-) in ~~horizontal dimension~~ direction only along the layer (one dimensional)
- Metal carbide are super conductor (conducts electricity in all direction).

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α graphite

Layer 2
Layer 1
Layer 3
Layer 1

β-graphite

Layer 3
Layer 2
Layer 1
Layer 3

α- graphite $\underset{\text{Heating}}{\overset{\text{Grinding}}{\rightleftharpoons}}$ β graphite

Density → 2.5g/cc

C − C → 1.32 A°
Distance b/w layers → 3.4 A°

• Aromatic compound

Fullerene

• C is sp^2 hybridized
• Only covalent bond exist
• Buckminister Fullerenes have 5 & 6 member rings.
C_{60} has 12 pentagonal & 20 hexagonal face with each carbon sp^2 hybridized
C_{60} is an aromatic compound
C_{60} → 60 π bonds, 90 σ bonds
C − C distance (σ) → 1.45 A° π → 1.38 A°
Hexagonal rings are fused to both pentagonal & hexagonal rings. Pentagonal are fused only to hexagonal rings.

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- Other fullerenes are C_{50}, C_{82}, C_{96}, C_{90}, C_{84}, C_{32}

- C_{60} reacts with O_3 O_4 which adds across one of the double bonds.

Isotopes of Carbon

C_{12}, C_{13}, C_{14} (radioactive, used for carbon dating)

- Order of Covalent radius :-

~~Pb~~ $C < Si < Ge < Sn < Pb$

Order of 1st I.E :-

$C > Si > Ge > ~~Sn~~ Pb > Sn$

Order of 3rd & 4th I.E :-

~~$C > Si > Ge$~~

$C > Ge > ~~Sn~~ Si > ~~Pb~~ Pb > Sn$

M.Pt :-

$C > ~~Ge~~ > Si$ $C > Si > Ge > Pb > Sn$

B.Pt :-

$Si > Ge > Sn > Pb$

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CO (Carbon Monoxide)

- Neutral oxide, colourless, odourless, poisonous, good Reducing agent
- Toxic in nature since it forms a complex with Haemoglobin called carboxy-haemoglobin
  ↓
  Has Fe (Coordination No. 6)

Preparation

- $HCOOH + H_2SO_4 \rightarrow CO + H_2O$
  (Formic Acid) (Dehydrating agent)
- $Fe_2O_3 + 3C \xrightarrow{Temp < 710^\circ K} 2Fe + 3CO$
- ~~If~~ $ZnO + C \xrightarrow{Temp > 710K} Zn + CO$ (Temp. dependent)
  ~~If~~ Temp > 710K CO_2 is formed
- $C + H_2O \rightarrow \underbrace{CO + H_2}$
  (Hot Coke) ↓ Water gas
- $2C + O_2 + 4N_2 \rightarrow \underbrace{2CO + N_2}$
  ↓ Producer Gas

Coal gas :- $CO + CO_2 + H_2 + CH_4$

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Producer gas: 70% N_2 + 25% CO + 4% CO_2 with traces of CH_4, H_2.

$$Fe_2O_3 + 3CO \rightarrow 3CO_2 + 2Fe$$

Test for CO :-

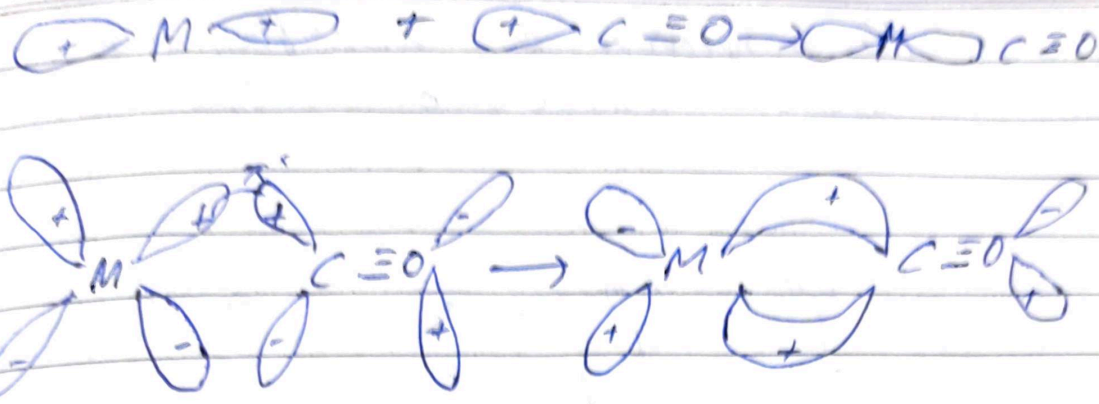
- Burn with blue flame.
- Filter paper soaked in $PdCl_2$ (Palladium chloride) turns pink, green or black due to reduction of chloride by CO.

$$CO + PdCl_2 + H_2O \rightarrow Pd\downarrow + 2HCl + CO_2$$

- Absorbed by ammonical sol^n of Cuprous Chloride.
- CO act as ligand (gives l.p in coordination compound).
  ∴ in formation of coordination complex, donates l.p & accept d - e^- in antibonding π orbitals.
  (π - a acceptor ligand / π - asset / non-classical ligand (vacant))

$$C \equiv O$$

$C \rightarrow M$
π e^- given considered σ bond.



Synergetic effect:- When metal make coordinate bond b/w, ~~a~~ d-e⁻ of metals go in antibonding orbitals of CO, ~~the~~ bond order decreases, increases bond length b/w C & O & decreases bond length of Metal & C bond.

∴ If C-O bond is strong, M-C bond is weak,
if C-O bond is weak, M-C bond is strong

Carbon dioxide

$$O=C=O \longleftrightarrow \overset{\ominus}{O}-C\equiv O^{\oplus}$$

sp

Preparation

$$CO + H_2O \longrightarrow CO_2 + H_2$$

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- CO_2 is recovered by absorbing it in either aqueous Na_2CO_3 or ethanol amine

$$CH_2(OH)-CH_2(NH_2) + CO_2 + H_2O \underset{}{\overset{30\text{-}60^\circ C}{\rightleftharpoons}} HO-CH_2-CH_2-NH_4HCO_3$$

$$Na_2CO_3 + CO_2 + H_2O \underset{\Delta}{\overset{Cool}{\rightleftharpoons}} 2NaHCO_3$$

$$C_6H_{12}O_6 \xrightarrow{Yeast} 2C_2H_5OH + 2CO_2$$

- CO_2 gas can be liquified below $-57^\circ C$ & $31^\circ C$)

Solid CO_2 is known as dry ice or ~~cold~~ cardice.

- CO_2 behaves like oxidizing ~~a~~ agent.
CO_2 does not react with $KMnO_4$.

Carbides

Compounds of carbon & ~~less~~ less electronegative elements are called carbide.

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Types of Carbide :-

1) Ionic or Salt Like Carbide
2) Interstitial Carbide
3) Covalent "

Ionic Carbide

Contains ~~C^-, C_2^{2-}, C^{5-} anions~~
C^-, C_2^{2-}, C_3^{4-} anions

eg :- Be_2C, Al_4C_3

Known as methanaride as they react with water to give methane.

CaC_2 → Acetalide (on reac^n with H_2O gives acetaline)

$CaO + 3C \rightarrow CaC_2 + CO$ $\quad \Delta H = +ve$

$CaC_2 + H_2O \rightarrow Ca(OH)_2 + C_2H_2$ $\quad \Delta H = -ve$

$CaC_2 + N_2 \xrightarrow{1100°C} Ca(NCN) + C$

Calcium Cyanamide

$Mg_2C_3 \xrightarrow{4H_2O} 2Mg(OH)_2 + CH_3-C\equiv CH$

Allylided (C_3^{4-}) $\quad$ Propyle / Allylene

Methanamides :- $[C^{4-}]$

$Al_4C_3 \xrightarrow{12H_2O} 4Al(OH)_3 + 3CH_4$

$Be_2C \xrightarrow{4H_2O} 2Be(OH)_2 + CH_4 + H_2$

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$Mn_3C \xrightarrow{6H_2O} 3Mn(OH)_2 + CH_4$

Acetylides (C_2^{2-} :- $[C \equiv C]^{2-}$)

$CaC_2 \xrightarrow{H_2O} Ca(OH)_2 + HC \equiv CH$

$BaC_2 \xrightarrow{H_2O} C_2H_2 + Ba(OH)_2$

$SrC_2 \longrightarrow C_2H_2 + Sr(OH)_2$

Covalent Carbide :-

B_4C : Boron Carbide
SiC : Silicon Carbide or Carborundum

$\xrightarrow{H_2O}$ No reac^n

B_4C is harder than SiC

Interstitial / Metallic Carbide (eg:- WC, TaC)

- Mostly Formed by transition elements and some lanthanides & actinides. They retain many properties of metals.
- Conduct electricity by metallic conduction

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- Lustrous
- Carbon atom occupy octahedral in closed pack structure
- Do not react with H_2O like ionic carbides
- React with conc. HF or HNO_3.
- These metal carbides in which lattice structure is not distorted are stable
- Some metals including Cr, Mn, Fe, Co, Ni having radius below 1.35 Å has distorted metal lattice.
- Structure are more complicated for V_2C, Mn_5C_2, Fe_3C, V_4C_3

- Fe_3C is known as cementite and is an imp. constituent of steel. These carbides (Complicated structure) are more reactive and are hydrolysed by dil. acid and some cases water.

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Covalent Carbide

Eg: SiC, B_4C, $B_{13}C_2$

SiC → • Hard & chemically inert

• $SiO_2 + 2C \rightarrow Si + 2CO$

$Si + C \rightarrow SiC$

• Unaffected by acid except H_3PO_4 but it react with $NaOH$ & air & Cl_2 at 100°C,

$SiC + 2NaOH + 2O_2 \rightarrow Na_2SiO_3 + CO_2 + H_2O$

$SiC + 2Cl_2 \rightarrow SiCl_4$

• SiC are dark purple, black, dark green due to traces of iron or other impurities. Pure samples are pale yellow or colourless

~~• 3-D structure of silicon~~

• Silicon carbide have Si 3-D structure of Si & C atoms & each atom is tetrahedrally surrounded by 4 of other kind. This forms a large nucleus of different crystals based on either diamond or wurtzite

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Compounds of Silicon

- SiO & SiO_2 (oxides of silicon)
- SiO_2 + Si $\longrightarrow$ $2SiO$
  - known as silica (sand & quartz)

SiO_2 :- Has $p\pi - d\pi$ bonds

- Silicon cannot form double bonds using $p\pi - p\pi$ orbitals.

Substantial no. of Si compounds are known to contain $p\pi - d\pi$ bonds in which Si atom appears to use 'd' orbitals for bonding.

- SiO_2 form an infinite 3-D structure
  High melting solid.
  Exist in atleast 12 diff. forms

Main forms of SiO_2

- quartz
- tridymite
- cristobalite

Prop
- SiO_2 is colourless.

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- Silica in any form is unreactive.
- SiO_2 is an acidic oxide & does not react with acid but react with HF

$$H_2SO_4 + CaF_2 \longrightarrow HF$$

$$HF + SiO_2 \rightarrow SiF_4 + H_2O$$

$$SiF_4 \xrightarrow{H_2O} HF + SiO_2 \cdot 2H_2O \text{ (or } Si(OH)_4\text{)}$$

- SiO_2 dissolve slowly in aqueous alkali & more rapidly in fused alkali or fused carbonate forming silicates.

$$SiO_2 + NaOH \rightarrow (Na_2SiO_3)_n + Na_4SiO_4$$

This ~~reacts~~ This accounts for

$$SiO_2 + F_2 \rightarrow SiF_4 + O_2$$

Quartz is important as a piezo electric material for crystal in the gramophone, radios & computers.

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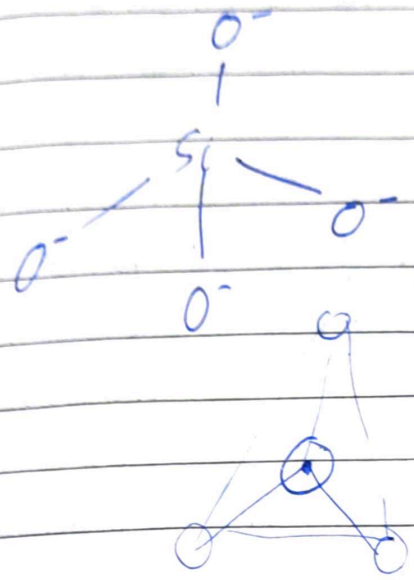
Silicates

$(SiO_4)^{-4}$



• → Silicon
○ → Oxygen

Tetrahedral units

Sodium silicate is most common silicate & can be prepared by melting powdered quartz or pure white sand with Na_2CO_3

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$

$$SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2$$

Basic unit in all silicate materials is $(SiO_4)^{4-}$ (tetrahedral)

(i) Orthosilicates also known as Nesosilicates

(i) M_2SiO_4 M has +2 O.S

M → Be, Mg, Fe, Zn, Mn

(ii) M_4SiO_4 M has +1 O.S

∴ Asbestos has double chain structures, has $(Si_4O_{11})_n^{6n-}$

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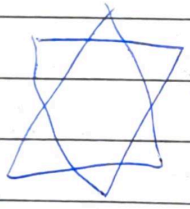
(Zircon) $ZrSiO_4$ is softer than diamond but looks like diamond. It is a gem.

eg:- Mg_2SiO_4 $\xrightarrow{fo}$ Forsterite
Mg has coordination No. 6

(ii) Pyrosilicate is known as Sorosilicate or disilicate or island structure
$(Si_2O_7)^{6-}$

(iii) Cyclic Silicate $\rightarrow (SiO_3)_n^{2n-}$ $n = 3, 4, 6, 8$
eg:- $BaTi(Si_3O_9)$ $\rightarrow$ Benitoite

$(Si_3O_9)^{6-}$



$\rightarrow (Si_6O_{18})^{12-}$

$Be_3Al_2(Si_6O_{18})$ $\rightarrow$ Beryl

(iv) Chain Silicate

$(SiO_3)_n^{2n-}$ eg:- $Mg_2(SiO_3)_2$ $\rightarrow$ Enstatite

- $CaMg(SiO_3)_2$ $\rightarrow$ Diopsite
- $Ca_3(SiO_3)_3$ $\rightarrow$ Wollastonite (Also in cyclic)

Has repeated units of 3 tetrahedral & other are known with repeat units of 4, 5, 6, 7, 12

$(SiO_3)_n^{2n-}$:- This is called Pyroxenes

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(v) Sheet Silicate

Known as ~~Eg.~~ phyllosilicate

$(Si_2O_5)_n^{2n-}$

- $SnCl_2$ more stable than $SnCl_4$
- Decomposition of oxalic acid in the presence of conc. H_2SO_4 :-

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{H_2SO_4} CO + CO_2 + H_2O$$

- C_3O_2 is not toxic
- CaO, Al_2O_3 not reduced by CO
- Coal gas :-
  - Burns with non-smoky flame
  - Good fuel
- CO is useful in preparing metal carbonyls.
  CO is not highly soluble in water.
- Fire extinguishers contain H_2SO_4 & $NaHCO_3$
- When CO_2 dissolved in water, species in water present are :-

$$CO_2,\ H_2CO_3,\ HCO_3^-,\ CO_3^{2-}$$

- Carborundum → SiC

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- In manufacture of glass, addition of MnO_2 gives Pink colour
- Solder :- 33% Pb, 67% Sn
- $\therefore$ $PbO_2 + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O + \frac{1}{2}O_2 \uparrow$
- Lead dissolves most readily in Nitric Acid
- Softening of Lead → Removal of impurities (metallic) from lead
- Carbogen : • Mixture of Oxygen with 5-10% CO_2
  • Given pneumonia patients & victims of CO poisoning
- Lead salts are slow poisons
  Lead metal is used in accumulators
  Lead is a soft metal
- C_3O_2 :- • Colourless gas
  • By dehydration of Malonic acid with P_4O_{10} only
- Lead salt heated with Na_2CO_3 in charcoal cavity → gives yellow incrustation.
- Plague or tin pest or tin disease → Conversion of white tin to grey tin

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- $SiCl_4$: Used as a smoke screen in warfare
- Lead sol^n titrated with EDTA at pH=6 using Methyl Thymol Blue indicator.
- Fusible alloys of Pb with Bi, Sn with low melting pt: • Wood's metal
  • Lipowitz alloy
  • Roso's metal

Silicate	No. of O atoms shared in each tetrahedral	Unit Formula
• Orthosilicate	0	SiO_4^{4-}
• Pyrosilicate	1	$Si_2O_7^{6-}$
• Single Chain Silicate	2	$(SiO_3)_n^{-2n}$
• Double Chain	2.5	$(Si_4O_{11})_n^{-6n}$
• Sheet Silicate (2-D silicate)	3	$(Si_2O_5)_n^{-2n}$
• 3-D Silicate (Polymeric Giant Molecule)	4	$(SiO_2)_n$

→

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Organo Silicon Compound

① Grignard's Reagent

$RMgX$

$R-X \xrightarrow{Mg,\ Dry\ ether} RMgX$

Source of R^- which behaves like a base or nucleophile

$SiCl_4 \xrightarrow{RMgX} RSiCl_3 \xrightarrow{RMgX} R_2SiCl_2 \xrightarrow{RMgX} R_3SiCl \xrightarrow{RMgX} R_4Si$

Sources of R^- :-

① $RMgX$
② LiR
③ R_2CuLi (Gilman Reagent)
④ R_2Cd

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② $4LiR + SiCl_4 \rightarrow R_4Si + 4LiCl$

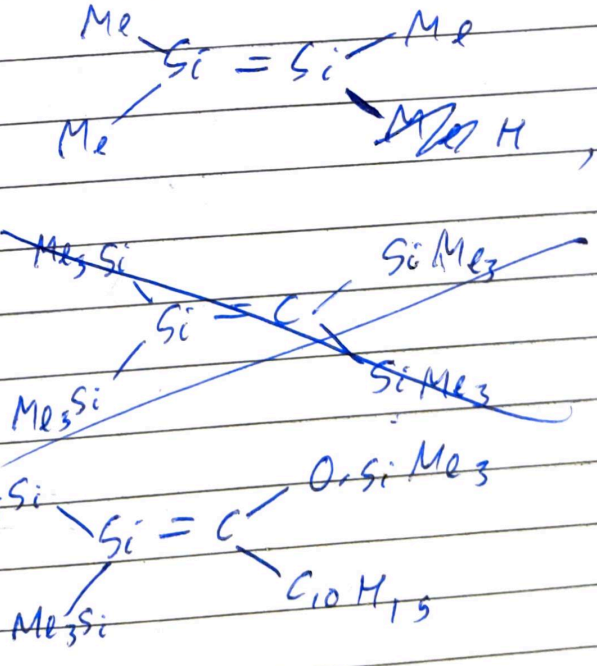
③ $Si + 2CH_3-Cl \xrightarrow[280-300^\circ C]{Cu} (CH_3)_2SiCl_2$

Organo Silicon

Si-C > C-C
stronger

- Silicon carbide is extremely hard & stable
- Many organic compounds are not replicated by Silicon because:-
  (i) Si has little tendency to bond to itself (catenation)
  (ii) Largest chain of silicone are contained in $Si_{16}F_{34}$, Si_8H_{18} but they are exceptions.
  (iii) Si does not form $p\pi-p\pi$ double bond while carbon form $p\pi-p\pi$ " "

Exceptions:- Disilene



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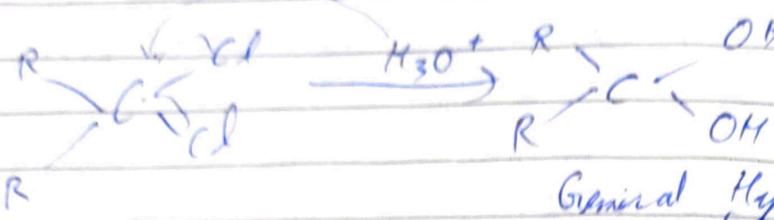
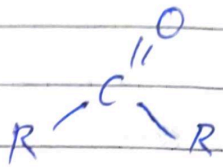
Silicones :- Group of organo silicon polymers

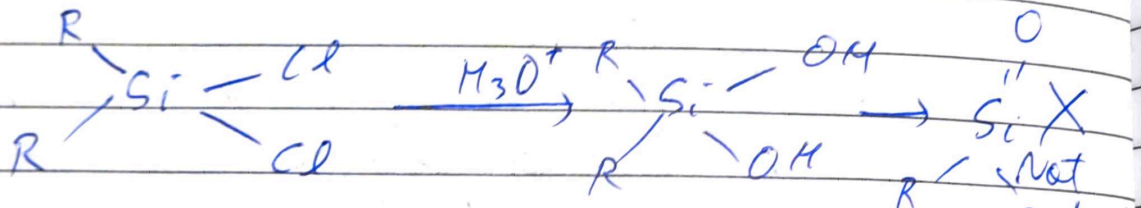


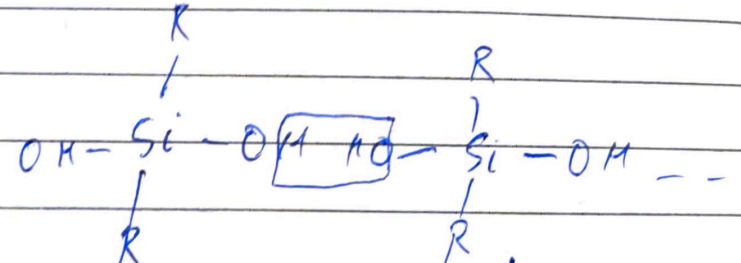
Geminal Hydroxide are unstable

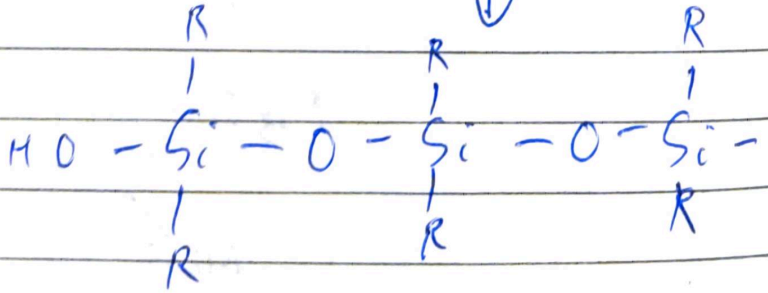
$\downarrow -H_2O$



But in case of Silicon







Silicones

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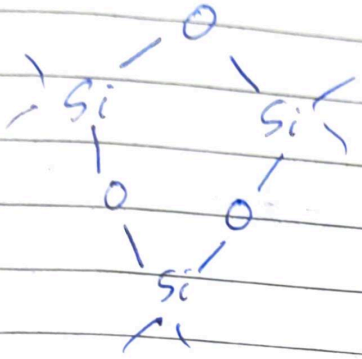
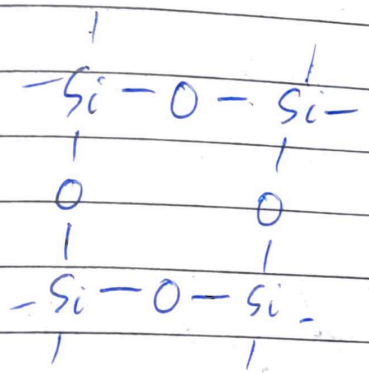
- Hydrolysis under carefully controlled situation, cyclic compound can be formed. No. of eg Si atoms in a ring can be 3, 4, 5, 6

eg:-



Tris cyclo dimethyl siloxane



Tetra kis cyclo dimethyl siloxane

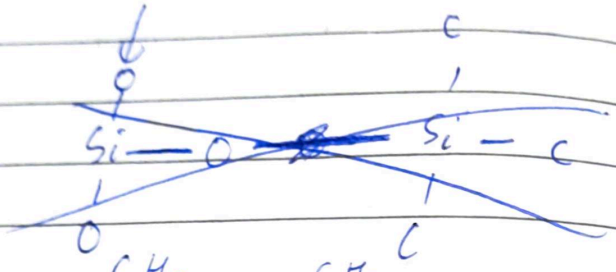
Hydrolysis of Methyl trichloro silane

$RSiCl_3$ give a complex cross-linkaged polymer

Hydrolysis of trimethyl monochloro silane gives trimethyl silanol as a volatile liquid, which can condense, giving hexamethyl ~~disiloxane~~ disiloxane

$$\equiv Si-Cl \xrightarrow{H_3O^+} Si-OH$$

$$CH_3-Si-OH \quad HO-Si-$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

Hexamethyldisiloxane

$(CH_3)_3SiCl$

If some trimethyl monochloro silane is mixed with $(CH_3)_2SiCl_2$ and hydrolysed, $(CH_3)_3SiCl$ will block the end of straight chain produced by $(CH_3)_2SiCl$.

$(CH_3)_3SiCl$ is a chain stopping unit and ratio of $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$ in the starting mixture will determine the average chain size.

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~~Hydrolysis~~

In a similar way addition of small amount of CH_3SiCl_3 to hydrolysis mixture produces a few cross links or provides a site of ~~attack~~ attaching other molecules

Silicon Hydrides

Silicon form a limited no. of saturated hydrides. They may exist as a straight chain or branch chain containing upto 8 Si atoms

Si_nH_{2n+2} → Silanes

SiH_4 → Monosilane

↓

Thermally Unstable

$$2Mg + Si \xrightarrow{\Delta} Mg_2Si \xrightarrow{H_2SO_4} \underset{\text{Major product}}{SiH_4\ (40\%)} + Si_2H_6\ (30\%) + Si_3H_8 \ldots$$

$$SiCl_4 + LiAlH_4 \rightarrow SiH_4 + AlCl_3 + LiCl$$

$$Si_2Cl_6 \xrightarrow{6LiH} Si_2H_6 + 6LiCl$$

$$Si_3Cl_8 \xrightarrow{8NaH} Si_3H_8 + NaCl$$

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Silanes are more reactive than alkanes, strong reducing agents, ignite in air, explode in Cl_2

Pure Silanes do not react with dilute acid or pure H_2O in silica apparatus but they hydrolyze

$$Si_2H_6 + (4+n)H_2O \xrightarrow{\text{Trace of alkali}} 2SiO_2 \cdot nH_2O + 7H_2$$

$$Si + 2HCl \longrightarrow SiH_2Cl_2$$

$$Si + 3HCl \longrightarrow SiHCl_3 + H_2$$

$$Si + 2CH_3-Cl \longrightarrow CH_3SiHCl_3 + H_2 + C$$

$$R-CH=CH_2 \xrightarrow{SiHCl_3} R-CH_2-CH_2-SiCl_3$$

$$GeCl_4 \xrightarrow{LiAlH_4} GeH_4 + LiCl + AlCl_3$$

$$GeO_2 \xrightarrow{NaBH_4} GeH_4 + NaBO_2$$

Sn_2H_6 : unstable
Distannane

$$CS_2 + 3Cl_2 \xrightarrow[30^\circ C]{FeCl_3} CCl_4 + S_2Cl_2$$

$$CS_2 + 3S_2Cl_2 \xrightarrow[60^\circ C]{FeCl_3} CCl_4 + 6S$$

$$CCl_4 + 2HF \xrightarrow{SbCl_3} CCl_2F_2 + 2HCl$$

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$CCl_4 + H_2O \xrightarrow{\Delta} COCl_2 + 2HCl$

Phosgene
(Carbonyl chloride)

$CH_4 \xrightarrow{Sr Cl_2} CH_3 - Cl$

Reac^n of Pb_3O_4

$Pb_3O_4 :- \; 2PbO . PbO_2$

PbO is basic in nature
PbO_2 is oxidizing agent as PbO_2 has Pb in +4 O.S

- $Pb_3O_4 + 8HCl \longrightarrow 4H_2O + 3PbCl_2 + Cl_2$

($\because Cl^- \rightarrow Cl_2$ oxidized by PbO_2)
(PbO is basic so acid base reac^n to form $PbCl_2$)

- $Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

As HNO_3 is an oxidizing agent itself so PbO_2 left unreacted. Acid-Base reac^n b/w PbO & HNO_3

→