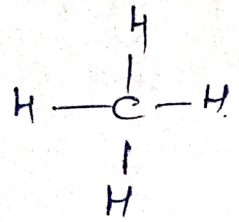
UNIT - II

[ALKANE]

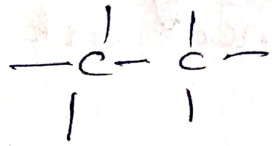
→ It is the simplest organic compound made of 'c' and hydrogen only

⇒ General formula C_nH_{2n+2}, n = 1, 2, 3, etc.

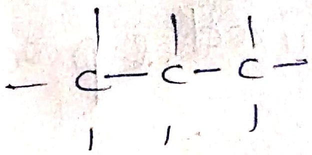
e.g.



methane



Ethane



Propane

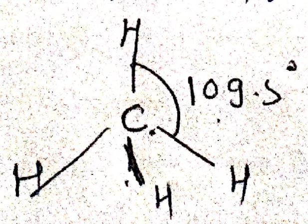
⇒ They are also called saturated hydrocarbon.

⇒ Alkane contain strong C–C or C–H bonds so this class is chemically inert hence sometime called Paraffins.

⇒ all C–H bonds are σ-bonds.

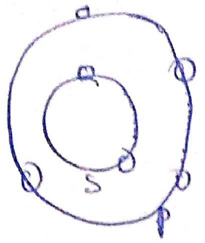
STRUCTURE

- All C–C, & C–H bonds are σ bond.
- Each 'c' atom is sp^3 hybridized.
- Alkane forms Tetrahedral structure



(Methane)

Hybridization

C = 

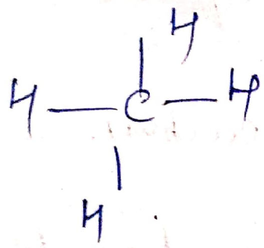
= [↑↓] [↑ | ↑ | ↑]

s

Rule

1) Atomic orbital of nearly same energy get mixed & produce new orbital of same energy.

e.g. CH_4



$C = 1s^2 2s^2 2p^2$

[↑↓] [↑ | ↑ |]

2s

jump

first excited state ⇒ [↑↓] [↑ | ↑ |]

[↑] [↑ | ↑ | ↑]

2s 2p

⇓

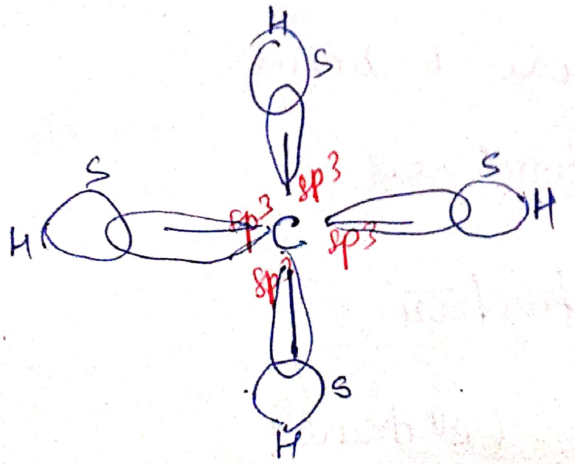
* bond is formed by unpaired electron.

Hybrid

[↑ | ↑ | ↑ | ↑]

sp^3 sp^3 sp^3 sp^3

{same energy new orbital}



Def: Intermixing of atomic orbital of same or nearly same energy to give new orbital of exactly same energy.

⇒ Hybridization is possible for following.
a) Half filled orbital
b) Empty orbital
c) filled orbital (l.p.)

⇒ No. of hybrid orbital = No. of intermixing orbital.

⇒ Hybridization is only for σ bond or l.p. not for π bond.

⇒ Hybrid orbital named after parent orbitals.

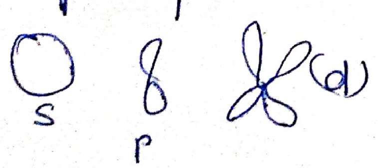
e.g. 1S + 1P = sp sp

1S + 2P = sp^2 sp^2 sp^2

1S + 3P = sp^3 sp^3 sp^3 sp^3

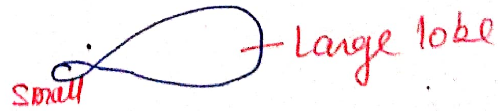
1S + 3P + 1d = sp^3d sp^3d sp^3d sp^3d sp^3d

⇒ Shape of orbital



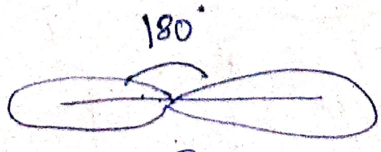
⟹

Hybridized



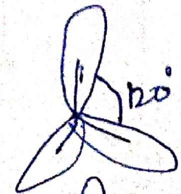
Types & Geometry

[S] + [P] = sp sp



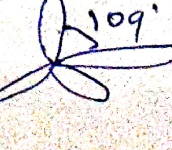
Linear

[S] + [P][P] = sp^2 sp^2 sp^2



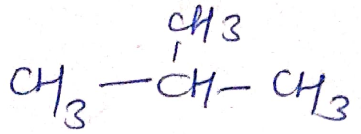
Triangular Planar

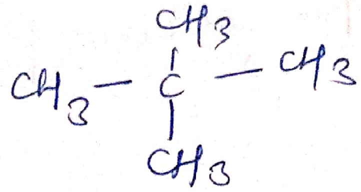
[S] + [P][P][P] = sp^3 sp^3 sp^3 sp^3



Tetrahedron.

e.g. $CH_3-CH_2-CH_2-CH_3$ - n- butane


→ Isobutane


→ neo pentane.

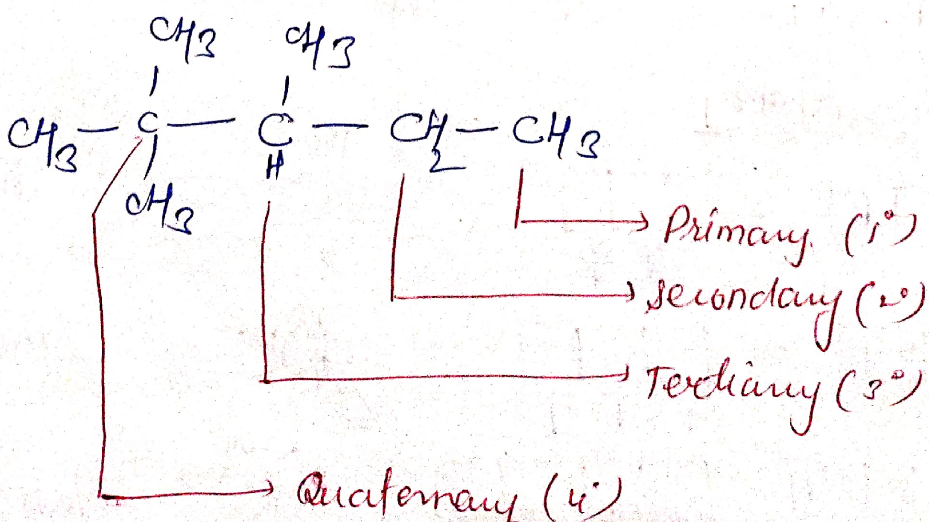
⇒ Primary, secondary and tertiary 'C' atom.

① Primary (or $1°C$) : If one 'C' attached to one another C.

② Secondary ($2°$) = one- C- attached to two other carbon.

③ Tertiary ($3°$) = C- attached to 3 other C- .

④ Quaternary ($4°$) = one 'C' attached to 4 other C'



IUPAC & Isomerism of alkane → see unit 1

METHOD OF PREPARATION OF ALKANE

① Hydrogenation of alkenes or alkynes
② Reduction of alkyl hallide
③ Decarboxylation of Carboxylic acid
④ Hydrolysis of grignard reagent.
⑤ Wurtz synthesis
⑥ Kolbe's Synthesis

① Hydrogenation

⇒ Alkenes or alkyne react c̄ -H in presence of 'Ni' catalyst at 200-300°c to form alkanes:

$$R-CH=CH_2 + H_2 \xrightarrow[\Delta]{Ni/Pt} R-CH_2-CH_3$$

$$CH_2=CH_2 + H_2 \xrightarrow[\Delta]{Ni/Pt} CH_3-CH_3$$

(Ethylene) (ethane)

$$CH_3-CH=CH_2 + H_2 \xrightarrow[\Delta]{Ni/Pt} CH_3-CH_2-CH_3$$

(Propene)

⇒ [s] + [p | p | p] + [d]

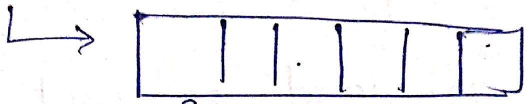
⇒ 

sp^3d

e.g. PCl_5

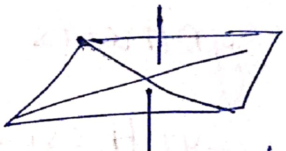
Trigonal bipyramid

⇒ [s] + [p | p | p] + [d | d]



sp^3d^2

e.g. SF_6



(octahedron)

(2) Reduction of alkyl hallide

Alkyl halides undergo reduction $\bar{c}$ nescent 'H' to form alkanes.

catalyst
Zn-HCl
Zn+CH_3COOH
$LiAlH_4$
Zn-Cu
Ni/Pt

$$R-X + 2[H] \longrightarrow R-H + HX$$

$$CH_3-Cl + 2[H] \longrightarrow CH_4 + HCl$$

$$C_2H_5I + 2[H] \longrightarrow C_2H_6 + HI$$

(3) Dehydration of Carboxylic Acid

sodium salt + soda lime

$$CH_3\text{-}COONa + NaOH + CaO \xrightarrow[\text{(decarboxylation)}]{\Delta} CH_4 + Na_2CO_3$$

(Methane)

(4) Hydrolysis of Grignard Reagent

alkyl magnisium halide = Grignard reagent

$$RX + Mg \xrightarrow{\text{ether}} RMgX$$

$$\downarrow + HOH$$

$$RH + MgX(OH)$$

e.g. $CH_3MgI + HOH \longrightarrow CH_4 + MgI(OH)$

Methane

Wurtz Synthesis

Two alkyl halide are heated $\bar{c}$ sodium metal in presence of ether.

$$R-X + 2Na + X-R \xrightarrow{ether} R-R + 2NaX$$

⇒ $CH_3-Br + 2Na + Br-CH_3 \rightarrow CH_3-CH_3 + 2NaBr.$

⇒ $CH_3-CH_2-Cl + 2Na + Cl-CH_3 \xrightarrow{ether} CH_3-CH_2-CH_3 + 2NaCl$

Propane

⇒ $CH_3-Cl + 2Na + Cl-CH_3 \xrightarrow{ether} CH_3-CH_3$ (Ethane)

* This method is only for symmetrical alkanes.

(7) Kolbe's Synthesis

When a concⁿ solution of sodium salt of carboxylic acid is electrolysed → Alkane is formed.

$$2\,CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}Na^+ + 2H_2O$$

$$\downarrow$$

$$\underset{\text{at anode}}{\underline{CH_3-CH_3}} + 2CO_2 + \underset{\text{cathod}}{\underline{2NaOH + H_2}}$$

Physical Property of alkanes

1) first four alkane methane, ethane, propane and butane are gases while next 13 members (C_5 to C_{17}) are colourless liquid.

2) Alkanes are non-polar compound, hence their solubility in non-polar solvent only i.e. CCl_4, Benzene

3) Specific gravity ∝ M.wt.

4) IR spectra of alkane shows C–H stretching at 2850–3000/cm.

Chemical Property / chemical reaction of Alkanes

→ C–H & C–C bonds are strong bonds.

– C–C – (non polar & very strong)　　C–H (non polar & strong)

→ But on high temperatur it's shows some reactions
(a) Substitution reaction
(b) Thermal and catalytic reactions.

→ Some reaction shown by Alkanes are
1. Halogination
2. Nitration
3. Sulphonation
4. Oxidation
5. Isomerism
6. Pyrolysis
7. Aromatization

(1) Halogination

→ This involve the substitution reaction (of H_2 $\bar{c}$ halogen)

(a) Chlorination

$$CH_4 + Cl_2 \xrightarrow[300-400^\circ C,\ \Delta]{UV\ light} CH_3Cl + HCl$$

This reaction continues and 3-Hydrogen of CH_3 is step by step replaced by halogen atom.

1) $CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$ — (1)
(dichloromethane)

2) $CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$
(trichloromethane)

3) $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$.
(carbon tetrachloride)

(2) Bromination

→ React c̄ similar manner but less vigorously.

$CH_4 + Br_2 \longrightarrow CH_3Br + HBr$

(3) Iodination

$CH_4 + I_2 \longrightarrow CH_3I + HI$

(4) Fluorination

florin is most reactive. it react c̄ alkane explosively under most conditions.

(2) Nitration

Normally alkane do not react c̄ HNO_3 but on higher temperature $400°-500°c$, one H is replaced by NO_2.

$$R-H + HO-NO_2 \xrightarrow[\Delta]{400-500°} R-NO_2 + H_2O$$

(nitro alkane)

e.g. $CH_3-H + HO-NO_2 \xrightarrow[450°c]{} CH_3-NO_2 + H_2O$

(Nitromethane)

$C_2H_5-H + HO-NO_2 \xrightarrow[450°c]{} C_2H_5-NO_2 + H_2O$

(Nitroethane)

(3) Sulphonation

→ Substitution of one H_2 c̄ $-SO_3H$ sulphonic acid.

$$R-H + HO-SO_3H \xrightarrow{\Delta} R-SO_3H + H_2O$$

(fuming) Alkane sulphonic acid

* $R = C_6H_{13}^-$ or higher alkane
* lower alkane did not give this reaction.

(4) Oxidation; combustion

When ignited in presence of excess of O_2, alkane burnt to give CO_2 & H_2O.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat}$$

$$2CH_3CH_3 + 7O_2 \rightarrow 4CO_2 + 6H_2O + \text{heat}$$

When burnt in insufficiently O_2 it forms CO & C (carbon black)

$$2CH_4 + 3O_2 \xrightarrow{\text{flame}} 2CO + 4H_2O$$

$$CH_4 + O_2 \xrightarrow{\text{flame}} C + 2H_2O$$

(5) Isomerisation.

Normal alkane are converted to their branched chain isomers in presence of $AlCl_3$ & HCl at 25°C.

e.g.

$$\underset{\text{(n-butane)}}{CH_3-CH_2-CH_2-CH_3} \xrightarrow[\text{\& HCl}]{AlCl_3} \underset{\text{(isobutane)}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3}$$

⑥ Pyrolysis (cracking)

→ Decomposition of a compound is called Pyrolysis

→ When this process applied on alkanes are called cracking.

→ conditions
- → High temp (500-800°c)
- → absence of air.
- → Product
  - → Alkane
  - → Alkene
  - → Hydrogen.

→ In this process we use catalyst as finely divided silica-alumina, so this process is also called catalytic cracking.

$$CH_3-CH_3 \xrightarrow[\text{-nce of air}]{500\,°c} CH_2=CH_2 + CH_4 + H_2$$

mixture of Alkane, Alkene & H_2

Mechanism

(1) chain initiation

$$CH_3 : CH_3 \longrightarrow 2\,{}^{\cdot}CH_3$$

(2) chain Propogation

$$H_3C^{\cdot} + H : CH_2 - CH_3 \longrightarrow CH_4 + \boxed{{}^{\cdot}CH_2CH_3}$$

(ethyl free radical)

$${}^{\cdot}CH_2 - CH_2 : H^{\cdot} \longrightarrow CH_2 = CH_2 + \boxed{H^{\cdot}}$$

this reaction continue.

(3) Termination

$$H^{\cdot} + {}^{\cdot}CH_2 - CH_3 \longrightarrow CH_3 - CH_3$$

[Hydrogen free radical] [Ethyl free radical] (ethane)

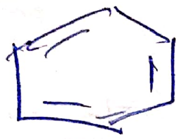
$${}^{\cdot}H + {}^{\cdot}H \longrightarrow H_2 \uparrow$$

(7) Aromatisation

Alkane containing 6 to 10 C atoms are converted into C_6H_6 & homologues at high temp.

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$
(n-hexane)

$\downarrow$ 600°/10 atm, $Cr_2O_3-Al_2O_3$

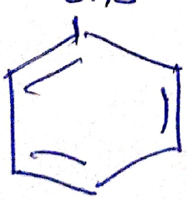
 + $4H_2\uparrow$

(C_6H_6)

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$
(n-heptan)

$\downarrow$ Pt $-Al_2O_3$, 600°C/10 ATM

CH3

 + $4H_2$

anilin

Mechanism of free radical Substitutions

① Chorination [$CH_4 + Cl_2$]

→ A seris of product is obtained in this process.

CH_3Cl, CH_2Cl_2, CH_3-CH_3, $CHCl_3$ & CCl_4

Steps

(1) Chain Initiation Step

On high pressure Cl_2 → convert to free radicles.

$$Cl - Cl \longrightarrow Cl^{\cdot} + Cl^{\cdot}$$

(2) Step - II (Chain-Propogation)

→ It have many reactions.

→ $Cl^{\cdot} + H - CH_3 \longrightarrow HCl + \boxed{^{\cdot}CH_3}$ methyl free radical

→ $^{\cdot}CH_3 + Cl - Cl \longrightarrow CH_3Cl + \boxed{Cl^{\cdot}}$

(chloro methane)

→ $Cl^{\cdot} + H - CH_2 - Cl \longrightarrow {}^{\cdot}CH_2Cl + HCl$

Step-III : chain termination step

finally stable molecules are produced due to combination of many free radicals.

$$Cl\cdot + \cdot Cl \longrightarrow Cl_2$$

$$CH_3^{\cdot} + {}^{\cdot}Cl \longrightarrow CH_3Cl$$

$$CH_3^{\cdot} + CH_3^{\cdot} \longrightarrow CH_3-CH_3$$

$$CH_2Cl\cdot + Cl\cdot \longrightarrow CH_2-Cl_2$$

Parafins

- It is more commonly reffered as alkanes. (saturated hydrocarbons)
- General formula C_nH_{2n+2}.
- Paraffins are major constituents of natural gas and petrolium.
- Branched chain paraffins have higher octan no. than straight chain.
- They are immiscible in H_2O.
- All paraffins are colourless.
- It is strong-smelling liquids.

Paraffin wax

→ It is a white wax obtained from petrol or coal.
→ It is used to make candle and in beuty treatment.
→ It contains more than 16 C in series of Paraffins.
→ It is in solid state at room temp.

USES OF PARAFFINS

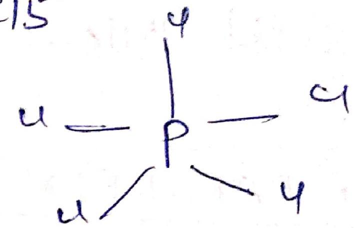
1) liquid paraffins is used in cosmetics and for medical purpose.
2) It is used for intestinal tract as it passes th it out absorbing water so used in constipation.
3) It is used as an occassional luxatives.
4) liquid paraffin is used in many preparations like. cream, lotion, lip balm, soap & ointments.
5) In burns it is used to cover the area affected to heal properly.
6) It is used to soften the skin.
7) white soft paraffin and liquid paraffin is used as a barrier cream by providing a layer of oil on surface of skin to prevent H_2O evaporation of skin surface.

Short method to know Hybridization in molecules

① Z = No. of σ bond of central atom + l.p.

Z =	Hybridization
2 →	sp
3 →	sp^2
4 →	sp^3
5 →	sp^3d
6 →	sp^3d^2

e.g. ① PCl_5

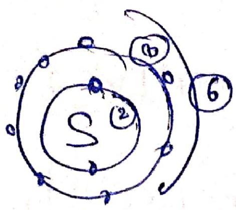


σ = 5, no. l.p.

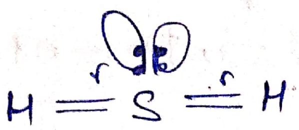
$Z = 5$

so Hybridization = sp^3d

e.g. ② H_2S



~~valence~~ e^- = 6



$Z = 2 + 2 = 4$

|| sp^3 ||

(2) 2 trick ē out drawing structure

$$Z = \frac{1}{2}\left[\text{No. of valance } e^- \text{ on Central atom} + (-ve\ charge) - [+ve\ Charge] + \text{No. of monovalent atoms}\right]$$

(Cl, F, Br, I, H)

e.g.

① NH_3

$$Z = \frac{1}{2}[5+3] = \frac{1}{2}(8) = (4) \longrightarrow sp^3$$

② CO_3^{2-}

$$Z = \frac{1}{2}[4+2+0+0] = \frac{1}{2}(6) = (3) = sp^2$$

③ SO_3^{2-}

$$Z = \frac{1}{2}(6+2+0) = \frac{1}{2}(8) = (4) = sp^3$$

④ H_2S

$$Z = \frac{1}{2}(6+0+0+2) = \frac{1}{2}(8) = (4) = sp^3$$