HYDROCARBONS

ALKANE

ALKANE

Introduction

- Saturated hydrocarbons are known as alkanes or paraffins (Less reactive).
- Alkanes with carbon chains that are unbranched are called normal alkanes. Each member of the series differs from the next higher and next lower member by $>CH_2$ group.
- General formula: C_nH_{2n+2}
- All the carbon atoms in alkanes are in sp^3 state of hybridization and geometry is tetrahedral.
- All the bond angles are tetrahedral angles **i.e.,** H–C–H or H–C–C bond angle is 109º28'

Properties	C–C	C–H
(i) Overlapping	sp3 – sp3	sp3 – s
(ii) Bond length	1.54 Aº	1.112 Aº
(iii) Bond energy	80 – 85 kcal	98.6 kcal

Methods of Preparation

(i) FROM CARBOXYLIC ACIDS

(A) By de-carboxylation

$$\underset{\text{Sodium carboxylate}}{RCOONa} + \underset{\text{Soda lime}}{NaOH\ /CaO} \xrightarrow{\Delta} \underset{\substack{\text{Alkane}\\(n-1)}}{R-H} + Na_2CO_3$$

(a) The process of eliminating of Carbon-di-oxide from carboxylic acid called decarboxylation.

(b) Replacement of –COOH by hydrogen is known as decarboxylation.
The alkane formed always contains one carbon atom less than the original acid.

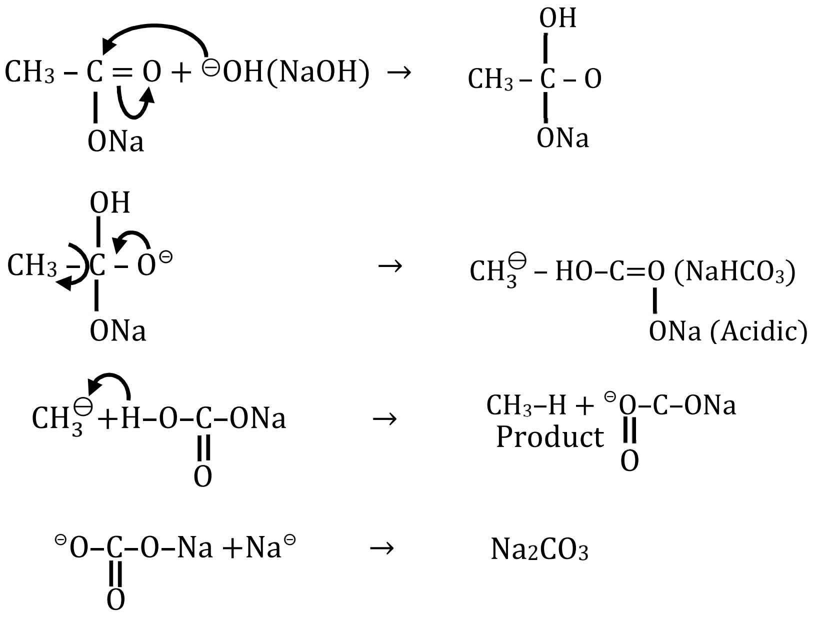
(c) This reaction is employed for stepping down a homologous series.

(d) Soda lime is prepared by soaking quick lime CaO with NaOH solution and then drying the produces.

(e) Decarboxylation of sodium format gives H_2

$$\begin{pmatrix} HCOONa + NaOH(CaO) \xrightarrow{\Delta} H_2 + Na_2CO_3 \\ CH_3COONa + NaOH + CaO \xrightarrow{\Delta} CH_4 + Na_2CO_3 \end{pmatrix}$$

Mechanism: Decarboxylation proceeds via. the formation of carbanion intermediate as follows.



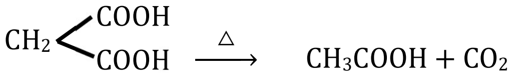
$$CH_3-\underset{\displaystyle ONa}{\underset{|}{C}}=O+{}^{\ominus}OH(NaOH)\rightarrow CH_3-\underset{\displaystyle ONa}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-O$$

$$CH_3-\underset{\displaystyle ONa}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-O^{\ominus}\rightarrow CH_3^{\ominus}-HO-\underset{\displaystyle ONa\ (Acidic)}{\underset{|}{C}}=O\ (NaHCO_3)$$

$$CH_3^{\ominus}+H-O-\underset{\displaystyle O}{\underset{\|}{C}}-ONa\rightarrow \underset{\text{Product}}{CH_3-H}+{}^{\ominus}O-\underset{\displaystyle O}{\underset{\|}{C}}-ONa$$

$${}^{\ominus}O-\underset{\displaystyle O}{\underset{\|}{C}}-O-Na+Na^{\ominus}\rightarrow Na_2CO_3$$

(a) If in a compound two carboxylic groups are present and they are attached to same carbon atom then also decarboxylation of one of the carboxylic groups takes place simply on heating.



$$CH_2\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix}\xrightarrow{\triangle}CH_3COOH+CO_2$$

(b) CH_4 can be prepared by CH_3COOH.

(c) C_2H_6 can be prepared by CH_3CH_2COOH.

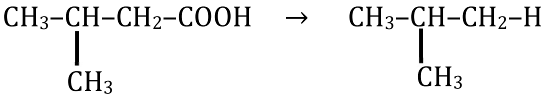
(d) $CH_3-CH_2-CH_3$ can be prepared by Butanoic acid and 2-Methyl propanoic acid.

Ex. How many acids can be taken to obtain isobutane from decarboxylation?

(A) 4 **(B)** 3 **(C)** 2 **(D)** 5

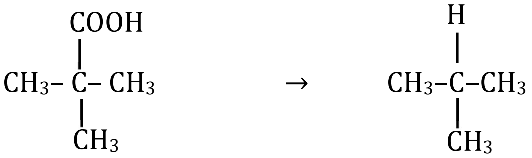
Sol. **(C)** To obtain isobutane the acids are

(i)



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-COOH\rightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-H$$

(ii)

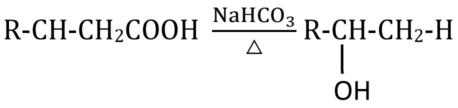


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle COOH}{\overset{|}{C}}}}-CH_3\rightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-CH_3$$

So, two acids can be taken.

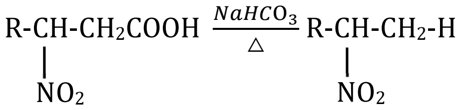
Reactivity of acid ∝ stability of carbanion Presence of electron attracting group (–I) in the hydrocarbon part of the fatty acid increases the decarboxylation.
If – I is more effective group then weak base may be taken.

(i)



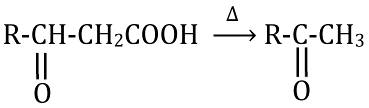
$$\text{R-CH-CH}_2\text{COOH} \xrightarrow[\triangle]{\text{NaHCO}_3} \text{R-}\underset{\text{OH}}{\text{CH}}\text{-CH}_2\text{-H}$$

(ii)



$$\text{R-}\underset{\text{NO}_2}{\text{CH}}\text{-CH}_2\text{COOH} \xrightarrow[\triangle]{NaHCO_3} \text{R-}\underset{\text{NO}_2}{\text{CH}}\text{-CH}_2\text{-H}$$

(iii) β–Keto acids are decarboxylated readily simply on heating (soda lime is not required)



$$\text{R-}\underset{\|\atop \text{O}}{\text{CH}}\text{-CH}_2\text{COOH} \xrightarrow{\Delta} \text{R-}\underset{\|\atop \text{O}}{\text{C}}\text{-CH}_3$$

(B) Kolbe's electrolytic synthesis

$$2RCOONa+2H_2O \xrightarrow{\text{Electrolysis}} R\text{-}R+2CO_2+H_2+2NaOH$$

* Methane cannot be prepared by this method.

$$2CH_3COONa+2H_2O \rightarrow CH_3-\underbrace{CH_3+2CO_2+2NaOH+}_{\text{Anode}}\underbrace{H_2}_{\text{Cathode}}$$

Mechanism

Ionic free radical

$2CH_3COONa \rightarrow 2CH_3COO^- + 2Na^+$

At anode

$2CH_3COO^- \rightarrow 2CH_3COO^\bullet + 2e^-$

$2CH_3COO^\bullet \rightarrow 2C\mathit{H}_3+2CO_2\uparrow$

$CH_3^\bullet + CH_3^\bullet \rightarrow C_2H_6$

At cathode

$2Na^+ + 2e^- \rightarrow 2Na$

$2Na + 2H_2O \rightarrow 2NaOH+H_2\uparrow$

- Methane cannot be prepared by this method.
- Electrolysis of an acid salt gives symmetrical alkane, however in case of a mixture of Carboxylic acid salts, all probable alkanes are formed.

$$R'COOK + R'OOK \xrightarrow{\text{Electrolysis}} (R' - R' + R' - R' + R'' - R'') + 2CO_2 + H_2 + 2NaOH$$

(C) Presence of alkyl groups in α-position decreases the yield of alkanes.

(D) True aromatic acids do not undergo Kolbe's electrolytic reaction.

(E) Free radical mechanism has been suggested for Kolbe reaction.

(F) At anode alkane (major) and CO_2 gas is formed while at cathode NaOH and H_2 gas is formed.

(G) The concentration of NaOH in solution is increased with time so pH solution is also increased.

(ii) REDUCTION OF ALKYL HALIDES

$$\underset{\text{Alkyl halide}}{R - X} \xrightarrow{\text{Reductant}} \underset{\text{Alkane}}{R - H + HX}$$

Mechanism:

$$Zn \rightarrow Zn^{+2} + 2e^{\Theta} \qquad \overset{\delta'}{R} - \overset{\delta^-}{X} \xrightarrow{2e^{\ominus}} R^{\ominus} +$$

$$R^- + H^+Cl^- \rightarrow R\text{-}H + Cl^{\Theta} \qquad Zn^{+2} + 2Cl^- \rightarrow ZnCl_2$$

$$R^- + H^+Cl^- \rightarrow R\text{-}H + Cl^{\Theta} \qquad Zn^{+2} + 2Cl^- + 2Cl^- \rightarrow ZnCl_2$$

Reductants: Zn–Cu couple/EtOH, Na–EtOH, Zn–HCl, Pt or Pd or Ni/H_2Al-Hg/EtOH, $LiAlH_4$ etc.

(iii) WURTZ REACTION

$$R - Br + 2Na + Br - R \xrightarrow[\text{DryEther}]{\Delta} \underset{\text{Alkane}}{R} - R + 2NaBr$$

- Methane cannot be prepared by this method.
- The alkane produced is higher and symmetrical **i.e.,** it contains double in the number of carbon atoms present in the alkyl halide taken.
- When the two reacting alkyl halides are different, a mixture of three different alkanes is obtained. So, the Wurtz reaction is not useful for preparing alkanes containing odd no. of C atoms.
  $C_2H_5I + CH_3IC_2H_6 + C_3H_8 + C_4H_{10}$

Mechanism: Wurtz reaction may proceed via the formation of organometallic compound or alkyl free radicals.
[**i.e.,** Both ionic and free radical mechanisms are proposed]

$$2C_2H_5Br + 2Na \xrightarrow{\text{Dry ether}} C_2H_5 - C_2H_5 + 2NaBr$$

Ionic Reaction Mechanism

$$C_2H_5Br + 2Na \rightarrow C_2H_5^-Na^+ + NaBr$$

Ethyl sodium
(Oregano metallic)

$$C_2H_5^- Na^+ + C_2H_5Br \rightarrow C_2H_5\text{-}C_2H_5 + NaBr$$

Free radical Reaction Mechanism

$$C_2H_5Br + Na \rightarrow \underset{\text{Ethyl free radical}}{C_2\dot{H_5}} + NaBr$$

$$C_2\dot{H_5} + C_2\dot{H_5} \xrightarrow{\text{Dim erisation}} C_2H_5\text{-}C_2H_5$$

(iv) FROM GRIGNARD REAGENT

$$RMgX \xrightarrow{Z-H} RH + Mg(Z)X$$

Z–H [compound containing active hydrogen]

HOH, NH_3, RC ≡ CH, C_6H_5OH, CH_3COOH, RNH_2, R_2NH, Pyrrole, C_2H5OH etc.

(v) FROM ALKENES AND ALKYNES (HYDROGENATION)

$$\underset{\text{Olefin}}{R-CH=CH-R'+H_2} \xrightarrow{Ni/20^\circ} \underset{\text{Alkane}}{R–CH_2–CH_2R'}$$

$$R-C\equiv C-R' + 2H_2 \xrightarrow{Ni/300^\circ} R-CH_2-CH_2-R'$$

- When the catalyst is Pt or Pd, hydrogenation proceeds smoothly at ordinary temperature and pressure.
- With Nickel catalyst, higher temperature (200º – 300ºC) and pressure are needed. (In this case the reaction is known as **Sabatier Sandreen's** reaction)
- With Raney Nickel, the reaction takes place at room temperature.

Ni / Al + NaOH → Ni in powdered form **(Raney Nickel)**

In this reaction following alkanes are not formed from unsaturated hydrocarbons

Alkene / Alkyne → Methane

Alkene / Alkyne → Neopentane

Alkyne → Isobutane

- The reaction is exothermic. The heat released in the reaction is known as heat of hydrogenation.

(vi) REDUCTION OF ALCOHOLS, ALDEHYDES, KETONES AND ACIDS BY RED P AND HI (150°C)

(a) **By the reduction of alcohols**

$$R-OH+HI \xrightarrow[150^\circ C]{\text{RedP}} RI+H_2O$$

$$R-I+HI \xrightarrow{\triangle} R-H+I2$$

- Since iodine is produced during the reaction, it may react with the resulting alkane, so it is removed by adding red phosphorus.

$$2P+3I_2 \rightarrow 2PI_3 \text{ (volatile)}$$

(b) **By reduction of acid**

$$RCOOH + 6HI \xrightarrow[150^\circ C]{RedP} RCH_3 + 3I_2 + 2H_2O$$

(viii) FROM DIALKYL ZINC: [FROM FRANKLAND REAGENT]

$$R_2Zn \xrightarrow{R'-X} R\text{-}R' + RZnX$$

(ix) COREY-HOUSE SYNTHESIS

$$R - Br + 2Li \xrightarrow{Ether} R - Li + LiBr$$

Alkyl bromide Alkyl lithium

$$2R - Li + CuI \xrightarrow{Ether} LiR_2Cu + LiI$$

Lithium diallyl cup rate

$$R_2LiCu + R' - X \rightarrow R - R' + RCu + Lix$$

Alkane

- This method is useful for preparation of alkanes containing odd no, of c-atoms.

SPECIFIC METHODS OF PREPARATION OF CH_4

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

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

(ii) $$CS_2+H_2S \xrightarrow[Cu]{Heat} CH_4$$

(iii) **Sabatier sender n's**

$$CO_2 + 4H_2 \xrightarrow{Ni,\Delta} CH_4 + 2H_2O$$

$$CO + 3H_2 \xrightarrow{Ni,\Delta} CH_4 + H_2O$$

PHYSICAL PROPERTIES

(i) Alkanes from C_1–C_4 are gases.

C_5–C_{17} are liquids, C_{18} – onwards are waxy, white solids.

Note: Neopentane is a gas.

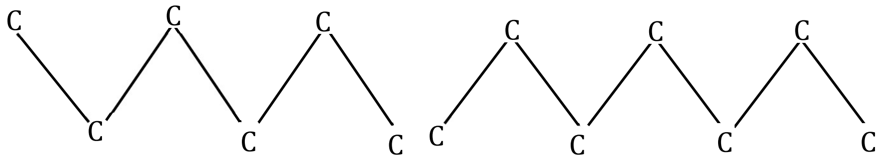
(ii) **Boiling point**

Boiling point $\propto$ molecular weight (for homologs) $\propto \frac{1}{\text{Branches}}$ (For isomers)

Ex. order of boiling point

n-pentane > isopentane > neopentane

(iii) **Melting point:** Alkanes containing even no. of carbon atoms have higher melting points than its next higher or next lower homologue having odd no. of carbon atoms. It is because of more symmetricity of alkane molecules with even no. of carbon atoms as compared to alkanes with odd no. of carbon atoms.



(Both methyl groups are directed in opposite direction) (Both methyl groups are on the same side)

- Alkanes are colourless, odourless and tasteless.
- Alkanes are lighter than water. These are insoluble in water and soluble in organic solvents.

Ex. Alkanes are inert is nature, why?

Sol. Alkanes are quite inert substances with highly stable nature. Their inactiveness has been explained as:

(i) Alkanes have all the C – C and C – H bonds being stronger σ bonds and are not influenced by acid, oxidants under ordinary conditions.

(ii) The C – C bond is completely non polar and C – H is weaker polar. Thus, polar species **i.e.,** electrophiles or nucleophiles are unable to attack these bonds under ordinary conditions.

CHEMICAL REACTIONS

1. Stability
2. Substitution reactions:
   (a) Halogenation
   (b) Nitration
   (c) Sulphonation
   (d) Chlorosulphonation (Reed reaction)
3. Oxidation:
4. Isomerisation
5. Cracking / Pyrolysis:
6. Aromatization
7. Addition of CH_2

1. STABILITY

Although alkanes are chemically unreactive under ordinary conditions due to the presence of strong C – C and C – H sigma σ bonds, yet they give following reactions under special conditions

2. SUBSTITUTION REACTION

Halogenation

$$R - H + X_2 \xrightarrow{hv} R - X + HX$$

- Reactivity order of hydrogen atoms in alkanes is

$$3°H > 2°H > 1°H$$

$$3ºH > 2ºH > 1ºH$$

- Reactivity order of halogens is

$$F_2 >> Cl_2 > Br_2 > I_2$$

Fluorine can react in dark. Cl_2 and Br_2 require light energy. I2 does not show any reaction at room temperature, on heating it shows iodination.

Fluorination

- Direct-fluorination of alkanes is usually explosive.

$$CH_4 + F_2 \longrightarrow \text{Carbon black (explosive reaction)}$$

- It is carried out successfully by diluting fluorine with nitrogen (Inert gas).

$$CH_4 + F_2 \longrightarrow CH_3F + HF$$

Chlorination

$$CH_4 + Cl_2 \longrightarrow CH_3Cl \xrightarrow{Cl_2} CH_2Cl \xrightarrow{Cl_2} 2CHCl_3 \xrightarrow{Cl_2} CCl_4$$

The monochorea derivative of alkane is obtained as a major product by taking alkane in excess.

Ex. $\underset{\text{Methane (excess)}}{CH_4 + Cl_2} \xrightarrow{hv} \underset{\text{Methyl chloride}}{CH_3Cl + HCl}$

- When chlorine is in excess, carbon tetrachloride will be the major product.

Ex. $\underset{\text{Methane (excess)}}{CH_4 + Cl_2} \xrightarrow{hv} \underset{\text{(Main)}}{CCl_4}$

Chlorination of alkanes takes place in the following conditions.

- No reaction at room temperature in darkness.
- At 300ºC in darkness.
- At 100ºC in the presence of organic peroxides.
- At 150ºC in the presence of Tetra ethyl lead

- Chlorination of methane is based on free radical mechanism and it completes in the following three steps:

(a) Chain initiating (first) step

$$Cl_2 \xrightarrow{hv} Cl^{\bullet} + Cl^{\bullet}$$

(b) Chain propagating (second) step

$$Cl^{\bullet} + CH_4 \longrightarrow CH_3^{\bullet} + HCl$$

$$CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

(c) Chain terminating (third) step

$$CH_3^{\bullet} + {}^{\bullet}Cl \longrightarrow H_3Cl$$

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

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

Bromination: Bromination of alkanes is similar to chlorination but not so vigorous.

Iodination: Iodination of alkanes is slow and reversible.

$$CH_4 + I_2 \overset{\triangle}{\rightleftharpoons} CH_3 - I + HI$$

- Iodination may be carried out in the presence of an oxidising agent such as HIO_3, HNO_3, HgO, etc. which destroys the HI as it is formed and so drives the reaction to the right.

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Reactivity selectivity Principle

(i) **Probability factor:** The factor is based on the number of each kind of H atom in the molecule.

For example, is $CH_3–CH_2–CH_2–CH_3$ there are six equivalent 1° H's and four equivalent 2° H's.

The probability of abstracting 1° H's to 2° H's is 6 to 4. **i.e.,** 3 to 2

(ii) **Reactivity of halogen free radical:** The more reactive chlorine free radical is less selective and more influenced by the probability factor. On the other hand, the less reactive Br radical is more selective and less influenced by the probability factor (Reactivity selectivity principle).

(iii) **Reactivity of alkanes (ease of abstraction of 'H' atoms):** Since the rate determining step in halogenations is abstraction of hydrogen by a halogen atom be the formation of alkyl radical, halogenation of alkanes follows order of stability of free radical is

$$3° > 2° > 1° > CH_3.$$

Rapacity ratio of H atom for Chlorination (1° : 2° : 3° H)

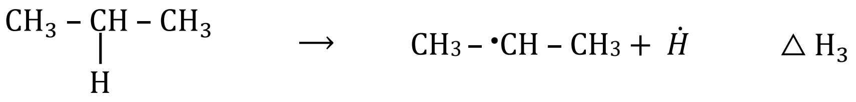
1 : 3.8 : 5

Reactivity ration of H atom for bromination (1 : 82 : 1600)

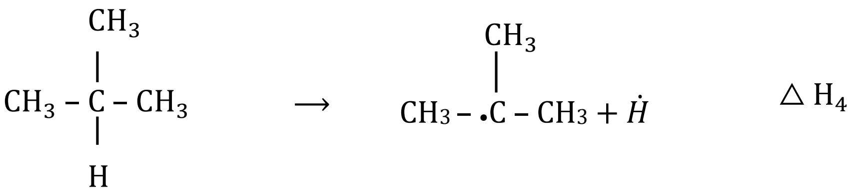
The above order of stability of radicals is due to the ease of their formation from the corresponding alkane which in turn is due to difference in the value of $\triangle$H.

$$CH_3-H \longrightarrow {}^{\bullet}CH_3 + H^{\bullet} \qquad \triangle H_1$$

$$CH_3-CH_2-H \longrightarrow {}^{\bullet}CH_3-CH_2 + H^{\bullet} \qquad \triangle H_2$$



$$CH_3-\underset{\underset{H}{|}}{CH}-CH_3 \longrightarrow CH_3-{}^{\bullet}CH-CH_3 + \dot{H} \qquad \triangle H_3$$



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_3 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{{}^{\bullet}C}-CH_3 + \dot{H} \qquad \triangle H_4$$

Reactivity of any H-atom ∝ number of H atoms of that kind × reactivity of that H.

Thus, the amount of energy required to form the various classes of radicals decreases in the order $CH_3 > 1° > 2° > 3°$ ($\triangle H_1 > \triangle H_2 > \triangle H_3 > \triangle H_4$). Therefore, it easiest to form 3° radical and it is most difficult to form CH_3. We can also interpret this in an alternative way the case of abstraction of H atoms from hydrocarbon fallows the sequence $3° > 2° > 1°$ CH_4 which should also be the case of formation of free radicals. The above order of stability is in accordance with the stability of free radicals on the basis of delocalization of odd electron. Order of stability of free radical is:

Allyl, benzyl > 3° > 2° > 1° > methyl, vinyl.

(a) **Nitration:** When a mixture of vapour of alkane nitric acid is heated at high temperature (400°C – 450°C) a mixture of all possible nitroalkanes is obtained (The reaction involves both C–C and C–H bond cleavage).

$$R-\boxed{H + HO}-NO_2 \xrightarrow{\text{high temp.}} R-NO_2 + H_2O$$

(b) **Sul phonation:** In this reaction, hydrogen atom of the C–H bond is replaced by –SO_3H group.

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

(Fluming) Alkane sulphonic acid

- Fuming H_2SO_4 = mixture of SO_3 + Conc. $H_2SO_4 = H_2S_2O_7$ **(Oleum)**
- Alkanes containing 6 or more carbon atom and lower branched alkenes (not lower unbranded) can be sulphonated).

(c) Chlor sulphuration **(Reed reaction)**: Reaction with a mixture of SO_2 and Cl_2 at ordinary temp. in the presence of UV light is called Chlor sulphuration.

$$C_3H_7SO_2Cl \xrightarrow{UV} \underset{\text{Propane sulphonyl Chloride}}{C_3H_7SO_2Cl} + HCl$$

Further hydrolysis of alkane sulphonyl chloride gives alkane sulphonic acid.

$$C_3H_7SO_2Cl \xrightarrow{H_2O} \underset{\text{Propane sulphonic acid}}{C_3H_7SO_3H} + HCl$$

$$C_3H_7SO_3H + HCl \longrightarrow C_3H_7SO_3Na + HCl$$

Sodium salt of sulphonic acid (used as detergent)

(3) OXIDATION

(a) **Complete oxidation or combustion:** All alkanes readily burn in excess of air or oxygen to form CO_2 and H_2O.

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right) O_2 \longrightarrow nCO_2 + (n+1)H_2O + \text{heat}$$

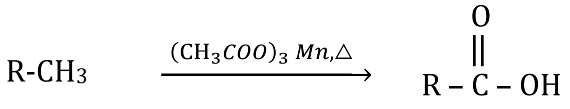
$$\frac{\text{Volume of alkane}}{\text{Volume of oxygen}} = \frac{2}{3n+1}$$

(b) Catalytic oxidation

(i) $CH_4 + \frac{1}{2} O_2 \xrightarrow[250^\circ C/100\ atm.]{\text{Red hot Cu or Fe tube}} CH_3OH$

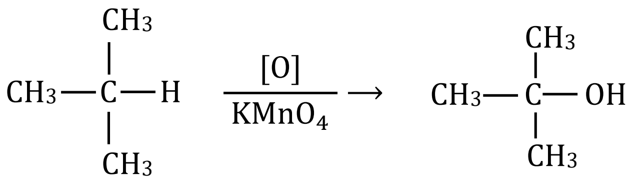
(ii) $CH_4 + O_2 \xrightarrow[250^\circ C/100\ atm.]{MO_2O_3} HCHO$

(iii)



$$R\text{-}CH_3 \xrightarrow{(CH_3COO)_3\ Mn, \triangle} R - \overset{\overset{\large O}{||}}{C} - OH$$

Tertiary alkanes are oxidized to give tertiary alcohols by $KMnO_4$.

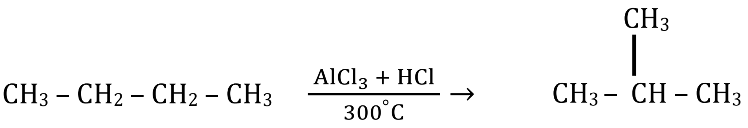


$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - H \xrightarrow[KMnO_4]{[O]} CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH$$

(4) ISOMERISATION

Straight chain alkanes are converted into their branched chain isomers when heated in the presence of $AlCl_3$ + HCl at 300°C.

Ex.

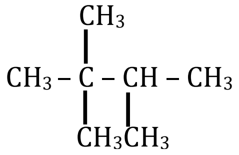


$$CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow[300^\circ C]{AlCl_3 + HCl} CH_3 - \overset{\overset{CH_3}{|}}{CH} - CH_3$$

"If we take n-heptane then it converts into highly branched alkane (triptane).

Ex. $CH_3-(CH_2)_5-CH_3 \longrightarrow$

n-heptane

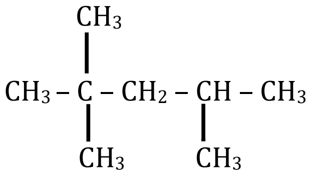


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

Triptane [2,2,3-Trimethyl butane]

If we take n-octane then it converts into most stable form iso-octane.

$CH_3-(CH_2)_6-CH_3 \longrightarrow$



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

n-Octane iso-octane [2,2,4-Trimethyl pentane]

Isomerisation of alkanes is of great importance in petroleum industry to increase the octane number of petrol (gasoline).

(5) PYROLYSIS OF CRACKING OR THERMAL DECOMPOSTION

When alkanes are heated to 500 700°C they are decomposed in to lower hydrocarbon. this decomposition is called pyrolysis. In petroleum industry it is also termed as cracking. Cracking is used for the manufacture of petrol, petrol gas/oil gas etc.

Ex. $CH_4 \xrightarrow{100\ ^\circ C} C + H_2$

$$CH_3-CH_3 \xrightarrow[absence\ of\ air]{500^\circ C} CH_2-CH_2+H_2$$

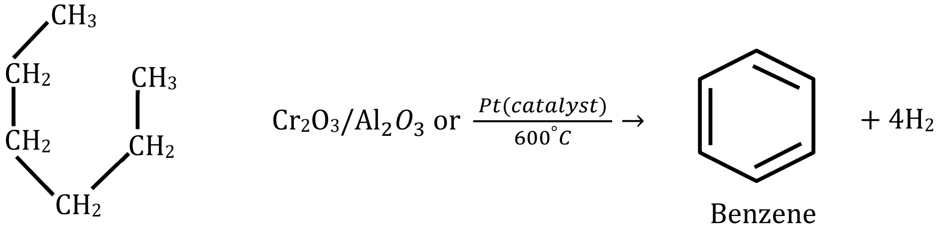
$$CH_3CH_2CH_3 \left\{\begin{array}{l} \longrightarrow CH_2=CH_2+CH_4 \\ \longrightarrow CH_3-CH_2=CH_2+H_2 \end{array}\right.$$

n-Butane $\xrightarrow{\text{Cracking}}$ 1-Butane + 2-Butene + Ethane + Ethene + Propene + CH_4 + H_2

(6) AROMATIZATION, HYDROFORMING OR CATALYSTIC REFORMING

The conversion of aliphatic compounds into aromatic compounds is referred to as aromatization. Alkanes having six or more carbon atoms are heated at 600°C in the presence of a catalyst such as Cr_2O_3 supported over alumina or Pt, an aromatic hydrocarbon result.

Ex. (i)



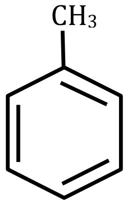
Cr_2O_3/Al_2O_3 or $\xrightarrow[600^\circ C]{Pt(catalyst)}$ + $4H_2$

n–Hexane

Benzene

(ii) $CH_3(CH_2)_5CH_3$ Cr_2O_3/Al_2O_3 or $\xrightarrow[600^\circ C]{Pt(catalyst)}$

n–Heptane



Toluene

$+ 4H_2$

Aromatization involves cyclization and dehydrogenation.

Dehydrogenation

Ex. $CH_3 - CH_2 - CH_3 \xrightarrow[600^\circ C]{Cr_2O_{3/AlO_3}} CH_3 - CH = CH_2 + H_2$

Propane Propene

(7) SPECIAL PROPERTIES OF CH_4

(i) $CH_4 + O_3 \xrightarrow{\triangle} HCHO + O_2 + H_2O$

(ii) $CH_4 + H_2O \longrightarrow CO + 3H_2$

Synthetic gas

(iii) $3CH_4 + O_2 \xrightarrow{150\ ^\circ C} C_2H_2 + 5H_2 + CO_2$

acetylene

(iv) $CH_4 + N_2 \xrightarrow{\text{Electric arch}} HCN + H_2$

(v) $CH_4 + NH_3 \xrightarrow[\text{High temp.}]{Al_2O_3} HCN + H_2$