Alkanes [Paraffines].

"Alkanes are saturated hydrocarbon containing only carbon-carbon single bond in their molecules."

Alkanes are less reactive so called paraffins; because under normal conditions alkanes do not react with acids, bases, oxidizing agents and reducing agent.

General formula: C_nH_{2n+2}

Examples are: $\underset{\text{Methane}}{CH_4}$, $\underset{\text{Ethane}}{C_2H_6}$, $\underset{\text{Propane}}{C_3H_8}$

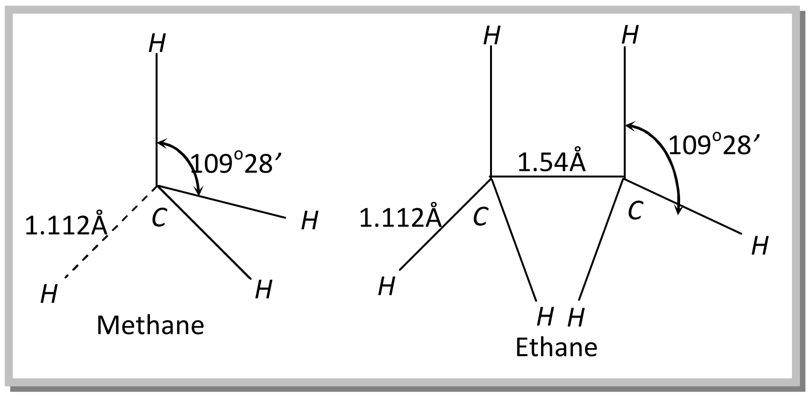
(1) **Structure**:

(i) Every carbon atom is sp^3 hybridized.

(ii) The bond length between carbon-carbon and carbon-hydrogen are $1.54\,Å$ and $1.112\,Å$ respectively.

(iii) Bond angle in alkanes are tetrahedral angles having a value of $109.5^o (109^o.28')$.

(iv) Alkaneshave $3-D$, rather than planer structure.



(v) $C-C$ bond dissociation energy is $83\,k\,cal/mol$.

(vi) $C-H$ bond dissociation energy is $99\,k\,cal/mol$.

(2)**Isomerism:**Only chain and structural Isomerism found.

No. of carbon atom in molecule $\propto$ no. of chain Isomers

Alkanes :	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}	$C_{10}H_{22}$
No. of possible Isomer :	2	3	5	9	18	75

(3) **General Methods of preparation**

(i) **By catalytic hydrogenation of alkenes and alkynes** (Sabateir and sanderen's reaction)

$$\underset{\text{Alkene}}{C_nH_{2n}} + H_2 \xrightarrow[\text{heat}]{Ni} \underset{\text{Alkane}}{C_nH_{2n+2}} \;;\qquad \underset{\text{Alkyne}}{C_nH_{2n-2}} + 2H_2 \xrightarrow[\text{heat}]{Ni} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

Note: Methane is not prepared by this method

(ii) **Birch reduction:** $R-CH=CH_2 \xrightarrow[2.\,CH_3OH]{1.\,Na/NH_3} R-CH_2-CH_3$

(iii) **From alkyl halide**

(a) By reduction: $RX + H_2 \xrightarrow{Zn/HCl} RH + HX$

(b)With hydrogen in presence of pt/pd**:** $RX + H_2 \xrightarrow{Pd\ or\ Pt.} RH + HX$

(c)With HI in presence of Red phosphorus: $RBr + 2HI \longrightarrow RH + HBr + I_2$

Purpose of Red P is to remove I

(iv) **By Zn-Cu couple:** $2CH_3CH_2OH + \underset{\text{Zn-Cu couple}}{Zn} \xrightarrow{Cu} \underset{\text{Zinc ethoxide}}{(CH_3CH_2O)_2Zn} + 2H$

$$RX + 2H \longrightarrow RH + HX$$

(v) **Wurtz reaction:** $\underset{\text{Alkyl halide}}{R\ X} + 2Na + \underset{\text{Alkyl halide}}{X\ R} \xrightarrow{Dry\ ether} \underset{\text{Alkane}}{R-R} + 2NaX$

Note: $R-Br$ or RI preferred in this reaction. The net result in this reaction is the formation of even no. of carbon atoms in molecules.

(vi) **Frankland's reaction:** $2RX + Zn \longrightarrow R-R + ZnX_2$

(vii) **Corey-house synthesis**

$$CH_3-CH_2-Cl \xrightarrow[2.\,CuI]{1.\,Li} (CH_3-CH_2)_2LiCu \xrightarrow{CH_3-CH_2-Cl} CH_3-CH_2-CH_2-CH_3$$

Note: Reaction is suitable for odd number of Alkanes.

(viii) **From Grignard reagent**

(a) By action of acidic 'H': $\underset{\text{Alkyl magnesium halide}}{RMgX} + \underset{\text{Water}}{HOH} \longrightarrow \underset{\text{Alkane}}{RH} + Mg(OH)X$

(b) By reaction with alkyl halide: $R-X + R'MgX \longrightarrow R-R' + MgX_2$

(ix) **From carboxylic acids**

(a) Laboratory method [Decarboxylation reaction or Duma reaction]

$$R\ COONa + NaOH \xrightarrow[CaO]{heat} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

Note: NaOH and CaO is in the ratio of 3: 1.

(b) Kolbe's synthesis: $R-\underset{\underset{O}{||}}{C}-O^-Na^+ \xrightleftharpoons[\text{Ionization}]{\text{Electrolysis}} R-\overset{\overset{O}{||}}{C}-O^- + Na^+$

At anode [Oxidation]: $2R-\underset{\underset{O}{||}}{C}-O^- + 2e^- \longrightarrow 2R-\underset{\underset{O}{||}}{C}-\dot{O} \longrightarrow 2\dot{R} + 2CO_2$

$$2\dot{R} \longrightarrow R-R \text{ (alkane)}$$

At cathode [Reduction]: $2Na^+ + 2e^- \longrightarrow 2Na \xrightarrow{2H_2O} 2NaOH + H_2\ (\uparrow)$

Note: Both ionic and free radical mechanism are involved in this reaction.

(c) Reduction of carboxylic acid: $\underset{\text{Acetic acid}}{CH_3COOH} + 6HI \xrightarrow[p]{\text{Reduction}} \underset{\text{Ethane}}{CH_3CH_3} + 2H_2O + 3I_2$

(x) **By reduction of alcohols, aldehyde, ketones or acid derivatives**

$$\underset{\substack{\text{Methanol}\\ \text{(Methyl alcohol)}}}{CH_3OH} + 2HI \xrightarrow[150^oC]{\text{Red } P} \underset{\text{Methane}}{CH_4} + H_2O + I_2;\quad \underset{\substack{\text{Acetaldehyde}\\ \text{(Ethanal)}}}{CH_3CHO} + 4HI \xrightarrow[150^oC]{\text{Red } P} \underset{\text{Ethane}}{C_2H_6} + H_2O + 2I_2$$

$$\underset{\substack{\text{Acetone}\\ \text{(Propanone)}}}{CH_3COCH_3} + 4HI \xrightarrow[150^oC]{\text{Red } P} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O + 2I_2;$$

$$\underset{\substack{\text{Acetyl chloride}\\ \text{(Ethanoyl chloride)}}}{CH_3-\overset{\overset{O}{||}}{C}-Cl} + 6HI \xrightarrow[200^oC]{\text{Red } P} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O + HCl + 3I_2$$

$$\underset{\substack{\text{Acetamide}\\ \text{(Ethanamide)}}}{CH_3-\overset{\overset{O}{||}}{C}-NH_2} + 6HI \xrightarrow[200^oC]{\text{Red } P} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O + NH_3 + 3I_2$$

Note: Aldehyde and ketones when reduced with amalgamated zinc and conc. HCl also yield alkanes.

Clemmensen reduction: $\underset{\text{Acetaldehyde (Ethanal)}}{CH_3CHO} + 2H_2 \xrightarrow[HCl]{Zn-Hg} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O$

$$\underset{\text{Acetone (Propanone)}}{CH_3COCH_3} + 2H_2 \xrightarrow[HCl]{Zn-Hg} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O$$

Note: Aldehydes and ketones $(>C=O)$ can be reduced to hydrocarbon in presence of excess of hydrazine and sodium alkoxide on heating.

Wolff-kishner reduction: $\begin{matrix} R \\ R' \end{matrix}\rangle C=O \xrightarrow[-H_2O]{H_2NNH_2} \begin{matrix} R \\ R' \end{matrix}\rangle C=NNH_2 \xrightarrow[180^oC]{C_2H_5ONa} \begin{matrix} R \\ R' \end{matrix}\rangle CH_2$

(xi) **Hydroboration of alkenes**

(a) On treatment with acetic acid

$$\underset{\text{Alkene}}{R-CH=CH_2} \xrightarrow{B_2H_6} \underset{\text{Trialkyl borane}}{(R-CH_2-CH_2)_3B} \xrightarrow{CH_3COOH} \underset{\text{Alkane}}{R-CH_2-CH_3}$$

(b) Coupling of alkyl boranes by means of silver nitrate

$$6[R-CH=CH_2] \xrightarrow{2B_2H_6} [2R-CH_2-CH_2-]_3B \xrightarrow[NaOH]{AgNO_3\ 25^oC} 3[RCH_2CH_2-CH_2CH_2R]$$

(4) **Physical Properties**

(i) **Physical state:** Alkanes are colorless, odorless and tasteless.

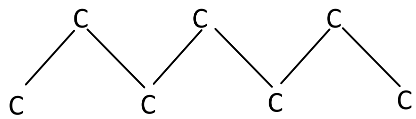
Alkanes	State
C_1-C_4	Gaseous state
C_5-C_{17}	Liquid state [Except neo pentane] [gas]
C_{18} & above	Solid like waxes

(ii) **Density:** Alkanes are lighter than water.

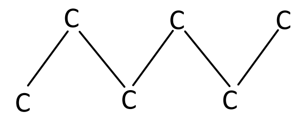
(iii) **Solubility**: Insoluble in water, soluble in organic solvents, solubility $\propto \frac{1}{\text{Molecular mass}}$

(iv) **Boiling pts and Melting pts:** Melting pt. and boiling pts. $\propto$ Molecular mass $\propto \frac{1}{\text{No. of branches}}$

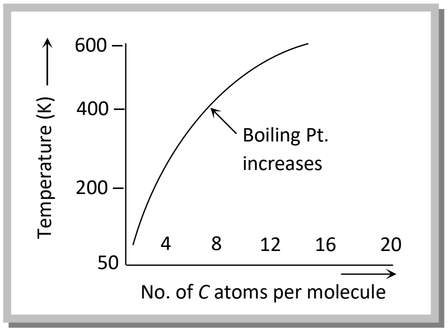
Alkane :	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}
M.P. (K) :	85.9	138	143.3	179	182.5	216.2

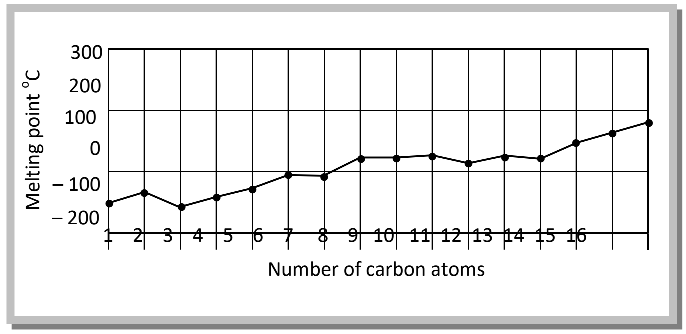


Odd no. of Carbons



Even no. of carbons





Note: Melting points of even > Odd no. of carbon atoms, this is because, the alkanes with even number of carbon atoms have more symmetrical structure and result in closer packing in the crystal structure as compared to alkanes with odd number of carbon atoms.

(5) **Chemical properties**

(i) **Substitution reactions of Alkanes**

(a) Halogenation: $R-H+X-X \longrightarrow R-X+HX$

The reactivity of halogen is: $F_2 > Cl_2 > Br_2 > I_2$

Note: Fluorine can react in dark Cl_2, Br_2 require light energy. I_2 does not show any reaction at room temperature, but on heating it shows iodination.

Iodination of methane is done in presence of oxidizing agent such as $HNO_3 / HIO_3 / HgO$ which neutralizes HI.

Chlorination of methane: $CH_4 + Cl-Cl \xrightarrow[-HCl]{u.v.light} CH_2-Cl_2 \xrightarrow[-HCl]{u.v.light} CHCl_3 \xrightarrow{-HCl} CCl_4$

(ii) **Reaction based on free radical mechanism**

(a) Nitration: $\underset{\text{Alkane}}{R-H} + HONO_2 \xrightarrow[temp.]{High} \underset{\text{Nitroalkane}}{R-NO_2} + H_2O$

Nitrating mixture: (i) $(Con.HNO_3 + Con.H_2SO_4)$ at $250^o C$

(ii) (HNO_3 vapour at $400^o - 500^o C$).

(b) Sulphonation**:** Free radical mechanism $R-H+HOSO_3H \xrightarrow[\text{Prolonged heating}]{SO_3} R-SO_3H+H_2O$

Note: Lower alkanes particularly methane, ethane, do not give this reaction.

(iii) **Oxidation**

(a) Complete Oxidation or combustion: $C_nH_{2n+2}+\left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2+(n+1)H_2O+Q$

Note:This is exothermic reaction.

(b) Incomplete combustion or oxidation

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

$$CH_4+O_2 \longrightarrow C \ +2H_2O$$

(c) Catalytic Oxidation: $CH_4+[O] \xrightarrow[100\ atm\ /\ 200^o C]{Cu-tube} CH_3OH$

This is the industrial method for the manufacture of methyl alcohol.

Note: Higher alkanes are oxidized to fatty acids in presence of manganese stearate.

$$CH_3(CH_2)_nCH_3 \xrightarrow[100-160^o C]{O_2} CH_3(CH_2)_nCOOH$$

(d) Chemical oxidation: $\underset{\text{Isobutane}}{(CH_3)_3CH} \xrightarrow{KMnO_4} \underset{\text{Tertiary butyl alcohol}}{(CH_3)_3.C.OH}$

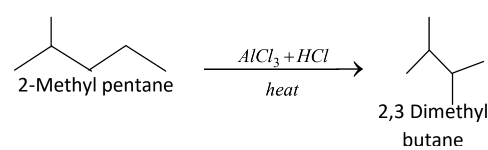
(iv) **Thermal decomposition or cracking or pyrolysis or fragmentation**

$$\underset{\text{Methane}}{CH_4} \xrightarrow{1000^o C} C+2H_2;\ \underset{\text{Ethane}}{C_2H_6} \xrightarrow[Cr_2O_3+Al_2O_3]{500^o C} \underset{\text{Ethylene}}{CH_2=CH_2}+H_2$$

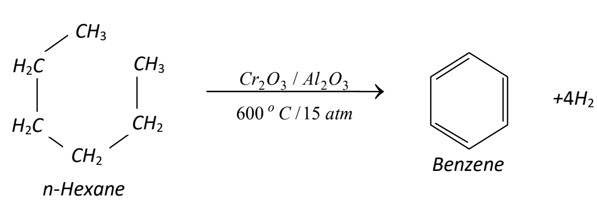
$C_3H_8 \longrightarrow C_2H_4+CH_4$ or $C_3H_6+H_2$

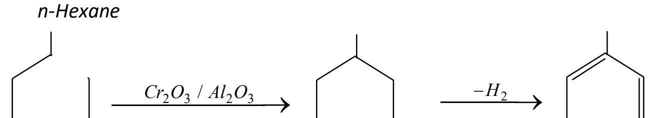
Note: This reaction is of great importance to petroleum industry.

(v) **Isomerization**: $\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[200^o C,35\,atm]{AlCl_3+HCl} \underset{\text{Isobutane}}{CH_3\overset{\overset{CH_3}{|}}{C}HCH_3}$;



(vi) **Aromatization:**





(vii) **Step up reaction**

(a) Reaction with CH_2N_2 : $R-CH_2-H+CH_2N_2 \xrightarrow{hv} R-CH_2-CH_2-H$

(b) Reaction with $CHCl_3 / NaOH$: $R-CH_2-H \xrightarrow[:CCl_2]{CHCl_3 / OH^-} R-CH_2-CHCl_2$

(c) Reaction with $CH_2=\underset{\underset{O}{\|}}{C}$: $R-CH_2-H \xrightarrow[:CH_2 /-CO]{CH_2=\overset{\overset{O}{\|}}{C} / \Delta} R-CH_2-CH_3$

(viii) **HCN formation:** $2CH_4 \xrightarrow{N_2 / electric\,arc} 2HCN+3H_2$ or $CH_4+NH_3 \xrightarrow[700^o C]{Al_2O_3} HCN+3H_2$

(ix) **Chloro sulphonation/Reaction with SO_2+Cl_2**

$$CH_3-CH_2-CH_3+SO_2+Cl_2 \xrightarrow{u.v\,light} CH_3-CH_2-CH_2SO_2Cl+HCl$$

This reaction is known as reed's reaction.

Note: This is used in the commercial formation of detergent.

(x) **Action of steam:** $CH_4+H_2O \xrightarrow[800^o C]{Ni / Al_2O_3} CO+3H_2$