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# **Hydrocarbons**

Hydrocarbon molecule contains only carbon and hydrogen. Hydrocarbons are further divided into several structural types called, alkanes, alkenes, alkynes and aromatics.

#### Composed of only carbon and hydrogen



Saturated hydrocarbons (Alkanes)

CH<sub>3</sub>·CH<sub>3</sub>



Unsaturated hydrocarbons (Alkenes, Alkynes & Aromatics)

H<sub>2</sub>C=CH<sub>2</sub>

HCECH



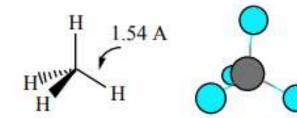
## **Alkane**

- A chain of carbon atoms that contains the maximum number of hydrogen atoms has the general formula  $C_nH_{2n}+2$  (n = number of carbon atoms).
- ☐ This type of hydrocarbon is called an alkane. Alkanes can exist in straight chains, chains with branching, and cycles.
- The alkanes are isolated from natural gas and petroleum. Natural gas contains mainly methane, with smaller amounts of other low-molecular-weight alkanes.
- ☐ Alkane names always end with -ane.

sp³ orbital ◄

(a) Methane, CH

- ☐ The carbon atom in an alkane has four sp³ hybridized and forms four single bonds that are equidistant from each other.
- The shape is referred to as tetrahedral with a C-C bond length of 1.54 Å and bond angles of 109.5°.



#### **Physical Properties of Alkanes**

- Alkanes are almost non-polar molecules because of the covalent nature of C-C and C-H bonds and due to very little difference of electronegativity between carbon and hydrogen atom.
- Polar molecules are soluble in polar solvents whereas non-polar molecules are soluble in non-polar solvents. Hence, alkanes are hydrophobic in nature that is, alkanes are insoluble in water.
- Alkanes possess weak vander Waals forces. Due to the weak forces, the first four members, C1 to C4 are gases, C5 to C17 are liquids and those containing 18 carbon atoms or more are solids at 298.
- ☐ They are colourless and odourles.

The boiling point and melting Point of alkanes increases with increasing molecular
weight. This is due to the fact that the intermolecular van der Waals forces
increase with increase of the molecular size or the surface area of the molecule.
The straight-chain alkanes are observed to have a higher boiling point and melting
Point in comparison to their structural isomers.
Even-numbered alkanes have higher trend in melting point in comparison to odd-
numbered alkanes.

## **Chemical Properties of Alkanes**

- Alkanes are generally inert towards acids, bases, oxidising and reducing agents.

  However, they undergo the following reactions under certain conditions.
- 1) <u>Combustion:</u> Alkanes on heating in the presence of air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of large amount of heat.

  Due to the evolution of large amount of heat during combustion, alkanes are used as fuels.

$$CH_4(g)+2O_2(g) \rightarrow CO_2(g)+2H_2O(l);$$
  
 $\Delta_c H^{\oplus} = -890 \text{ kJ mol}^{-1}$   
 $C_4H_{10}(g)+13/2 O_2(g) \rightarrow 4CO_2(g)+5H_2O(l);$   
 $\Delta_c H^{\oplus} = -2875.84 \text{ kJ mol}^{-1}$ 

During incomplete combustion of alkanes with insufficient amount of air or dioxygen, carbon black is formed which is used in the manufacture of ink, printer ink, black pigments and as filter.

$$CH_4(g)+O_2(g)$$
 Incomplete  $C(s)+2H_2O(l)$ 

2) <u>Controlled oxidation</u>: Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalysts give a variety of oxidation products.

(i) 
$$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} 2CH_3OH$$
  
Methanol

(ii) 
$$CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$$
  
Methanal

(iii) 
$$2CH_3CH_3 + 3O_2 \xrightarrow{(CH_3COO)_2Mn} 2CH_3COOH$$
  
Ethanoic acid  
 $+ 2H_2O$ 

(iv) Ordinarily alkanes resist oxidation but alkanes having tertiary H atom can be oxidized to corresponding alcohols by potassium permanganate.

$$(CH_3)_3 CH \xrightarrow{KMnO_4} (CH_3)_3 COH$$
2-Methylpropane 2-Methylpropan-2-ol

3) <u>Isomerisation</u>: n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.

$$\begin{array}{c} \operatorname{CH_3(CH_2)_4CH_3} \xrightarrow{\operatorname{Anhy.\ AlCl_3/HCl}} \\ n\text{-Hexane} \\ \operatorname{CH_3CH-(CH_2)_2-CH_3+CH_3CH_2-CH-CH_2-CH_3} \\ | & | & | \\ \operatorname{CH_3} & |$$

4) Reaction with steam: Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen. This method is used for industrial preparation of dihydrogen gas.

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

**Aromatization**: n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming.

$$\begin{array}{c|c} \operatorname{CH_3} & \operatorname{CH_2} & \operatorname{CH_3} & \operatorname{Cr_2O_3} \text{ or } \operatorname{V_2O_5} \\ \operatorname{CH_2} & \operatorname{CH_2} & \operatorname{Or Mo_2O_3} \\ \operatorname{CH_2} & \operatorname{CH_2} & 10\text{-}20 \text{ atm} \end{array} \longrightarrow \begin{array}{c} \\ \end{array}$$

6) Pyrolysis: Higher alkanes on heating to higher temperature decompose into lower alkanes, alkenes etc. Such a decomposition reaction into smaller fragments by the application of heat is called pyrolysis or cracking.

Pyrolysis of alkanes is believed to be a free radical reaction. Preparation of oil gas or petrol gas from kerosene oil or petrol involves the principle of pyrolysis. For example, dodecane, a constituent of kerosene oil on heating to 973K in the presence of platinum, palladium or nickel gives a mixture of heptane and pentene

$$C_{12}H_{26} \xrightarrow{Pt/Pd/Ni} C_7H_{16} + C_5H_{10} +$$
 other products