# **CLASS 11 Chemistry Chapter 13 Hydrocarbons**

Hydrocarbons are the organic compounds containing carbon and hydrogen only. Based on the types of carbon-carbon bonds present, hydrocarbons can be classified into three categories- (i) Saturated (ii) Unsaturated (iii) Aromatic hydrocarbons.

Saturated hydrocarbons contain carbon-carbon multiple bonds–double bonds, triple bonds or both.

**ALKANES:** Saturated open chain hydrocarbons containing carbon-carbon single bonds. These are inert under normal conditions i.e., do not react with acids, bases and other reagents. Alkanes exhibit Chain isomerism, Position isomerism and conformational isomerism.

#### General methods of preparation of alkanes:

1. From Unsaturated hydrocarbons: By hydrogenation in the presence of platinium, palladium or nickel as catalyst.

General Chemical Equation:  

$$R-CH=CH_2 + H_2 \xrightarrow{Ni} R - CH_2 - CH_3$$
  
[Where R is H or Alkyl group]  
*e.g.*  $CH_2=CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$   
Ethene Ni  $CH_3-C \equiv CH + H_2 \xrightarrow{Ni} CH_3 - CH = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_2 - CH_3$   
Propyne Propene

2. From alkyl halides: on reduction with Zinc and dilute hydrochloric acid

$$CH_3 - Cl + H_2 \xrightarrow{Zn, H^+} CH_4 + HCl$$
  
Chloromethane Methane

 $\begin{array}{c} C_2 H_5 - Cl + H_2 \\ Chloroethane \end{array} \xrightarrow{Zn, H^+} C_2 H_6 + HCl \\ Ethane \end{array}$ 

 $\begin{array}{c} CH CH CH CH Cl + H \\ 3 & 2 & 2 \\ 1 - Chloropropane \end{array} \xrightarrow{Zn, H^+} \begin{array}{c} CH CH CH \\ 3 & 2 & 3 \\ Propane \end{array} + HCl$ 

**3.** From alkyl halides by Wurtz reaction: Reaction of alkyl halide with sodium in dry ether, useful only for the preparation of symmetrical alkanes.

 $\begin{array}{c} CH_{3}CH_{2}Br+2Na+BrCH_{2}CH_{3} \xrightarrow{Dry Ether} CH_{3}CH_{2}CH_{2}CH_{3}\\ Bromoethane \\ CH_{3}CH_{2}DH_{2}Br+2Na+BrCH_{2}CH_{2}CH_{3} \xrightarrow{Dry Ether} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3}\\ 1-Bromopropane \\ CH_{3}CH_{2}Br+2Na+BrCH_{2}CH_{3} \xrightarrow{Dry Ether} CH_{3}CH_{2}CH_{2}CH_{2}CH_{3}\\ 1-Bromopropane \\ 1-Bromoethane \\ n-Pentane (desired) \end{array}$ 

- 4. From Carboxylic acids: By decarboxylation with soda lime CH COONa + NaOH 3Sodium acetate Sodium Hydroxide CH Hydroxide CH CH Hydroxide CH CH Hydroxide CH CH Hydroxide CH CH Hydroxide CH CH Hydroxide CH CH
- 5. By Kolbe's electrolytic method: Electrolysis of an aqueous solution sodium or potassium salt of carboxylic acid. Alkane containing even number of carbon atoms is formed at anode.

 $2CH_{3}COO Na + 2H_{2}O \xrightarrow{\text{Electrolysis}} CH_{3} - CH_{3} + 2CO_{2} + H_{2} + 2NaOH$ At Anode: (Oxidation)  $2CH_{3} - C - O^{-} \xrightarrow{-2e^{-}} 2CH_{3} - C - O^{-} \longrightarrow 2CH_{3} + 2CO_{2}$   $2CH_{3} \longrightarrow CH_{3} - CH_{3}$ At Cathode: (Reduction)  $2H_{2}O \longrightarrow 2OH^{-} + 2H^{+}$   $2H^{+} + 2e^{-} \longrightarrow H_{2}$ 

#### **Physical Properties of alkanes:**

- 1. Boiling point of alkanes decreases on branching due to decrease in surface area of molecule with branching which decreases magnitude of van der Waal'sforces of attraction.
- 2. Alkanes being non-polar in nature are soluble in non-polar solvents.

#### **Chemical properties of Alkanes:**

• Alkanes undergo substitution reactions. *e.g.*, Halogenation, Nitration, Sulphonation.

Halogenation: For example, Chlorination of methane

 $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$   $CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$  Dichloromethane  $CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$  Trichloromethane  $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$  Tetrachloromethane

Rate of reaction of alkanes with halogens is  $F_2 > Cl_2 > Br_2 > I_2$ . Rate of replacement of hydrogen in alkanes is  $3^\circ > 2^\circ > 1^\circ$ . Fluorination is too violent to be controlled. Iodination is reversible and it is therefore carried out in the presence of oxidising agent like HNO<sub>3</sub>.

Mechanism of halogenation: Free radical mechanism

 $Cl - Cl \xrightarrow{hv} Cl \cdot + \cdot Cl$ Initiation  $Cl \cdot + CH_4 \longrightarrow H - Cl + \cdot CH_3$ Propagation  $\cdot CH_3 + Cl - Cl \longrightarrow CH_3 Cl + \cdot Cl$ Propagation  $Cl \cdot + \cdot CH_3 \longrightarrow CH_3 Cl$ Termination

Combustion: Complete combustion gives carbon dioxide and water.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

**Isomerisation:** 

$$CH_{3}CH_{2}CH_{2}CH_{3} \xrightarrow{AlCl_{3} + HCl} CH_{3}CH_{3}CH_{2}CH_{3} \xrightarrow{CH_{3}} CH_{3}CHCH_{3}$$
  
n-Butane Isobutane

#### Aromatisation:



# (vi) Reaction with steam $CH + H O \xrightarrow{Ni} CO + 3H$ $4 2 \xrightarrow{A} 2$

Pyrolysis: Decomposition of higher alkanes to lower alkanes on heating.

$$C H \xrightarrow{773K} C_{6}H_{12} + H_{2}$$

$$C H \xrightarrow{773K} C_{4}H + C H$$

$$C H \xrightarrow{4} C_{3}H_{6} + C_{2}H_{4+}CH_{4}$$

#### **Conformations:**

Different spatial arrangement of atoms arising due to rotation around C-C single bond.

#### Conformation of ethane, CH<sub>3</sub>CH<sub>3</sub>

Two conformational isomers or conformers.

Eclipsed form = all hydrogen atoms nearest to each other.

**Staggered form** = all hydrogen atoms are farthest apart.



Stability of eclipsed conformation is least while staggered conformation is most stable. The energy difference between two extreme forms is 12.5kJmol<sup>-1</sup>. Due to this small energy difference the two forms are easily inter-convertible at ordinary temperature and cannot be separated and isolated.

### **ALKENES**

These are unsaturated non-cyclic hydrocarbons which have  $\mathrm{sp}^2$  -hybridisation with  $120^\circ$  bond angle.

Alkenes are also called olefins [oil. Forming] which indicates their high reactive nature.

Alkenes have general formula  $C_n H_{2n}$ , where  $n = 2, 3, 4, \dots$ 

 $C_2H_4$  (ethene),  $C_3H_6$  (propene), etc.

#### • Methods of Preparation of Alkenes

(i) From alkynes

 $R - C \equiv C - R' + H_2 \xrightarrow{Pd/C} \begin{array}{c} R \\ H \\ cis-alkene \end{array} = C - \begin{array}{c} R \\ H \\ cis-alkene \end{array}$ 

#### (ii) From alkyl halide [Dehydrohalogenational]

(iii) From *vicinal* dihalides

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$$\begin{array}{cccc} \mathrm{CH}_{2}\mathrm{Br}-\mathrm{CH}_{2}\mathrm{Br}+\mathrm{Zn} & \stackrel{\Delta}{\longrightarrow} & \mathrm{CH}_{2}=\mathrm{CH}_{2}+\mathrm{Zn}\mathrm{Br}_{2}\\ \mathrm{CH}_{3}--\mathrm{CH}--\mathrm{CH}_{2}+\mathrm{Zn} & \stackrel{\Delta}{\longrightarrow} & \mathrm{CH}_{3}--\mathrm{CH}=\mathrm{CH}_{2}+\mathrm{Zn}\mathrm{Br}_{2}\\ \mathrm{Br} & \mathrm{Br} \end{array}$$

#### (iv) From alcohols by acidic dehydrogenation

$$\begin{array}{cccc} H & H \\ | & | \\ H & C & C \\ | & | \\ H & OH \\ Ethanol \end{array} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{CH}_2 = \text{CH}_2 + \text{H}_2 \\ \hline \Delta & \text{Ethene} \end{array}$$

• Chemical Properties of Alkenes:

#### 1. Addition of Halogens:



2. Addition of hydrogen halides HCl, HBr, Hl: Add up to alkenes to form alkyl halides as per their reactivity order in HI>HBr>HCl.

Addition reaction of HBr to unsymmetrical alkenes (Markownikov's rule) According to Markownikovs' rule, the negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms.

$$H \qquad Br \\ -C - C = C - H + HBr \rightarrow H_3C - C - CH_3 \\ -H H H H H H 2-Bromopropane$$

Anti Markownikov addition or peroxide effect or Kharasch effect in the presence of organic peroxide, addition of only HBr molecule on unsymmetrical alkene takes place contrary to the Markownikov's rule. Peroxide effect is not observed in case of HF, HCl and HI.

$$CH_3$$
— $CH=CH_2 + HBr$   $(C_6H_5CO)_2O_2$   $CH_3CH_2CH_2Br$   
1-bromopropane

#### 3. Addition of sulphuric acid

$$CH_{3} - CH = CH_{2} + HOSO_{2}OH \rightarrow CH_{3}CH(OSO_{3}H) CH_{3}$$
[cold and conc.]  $\rightarrow$  propyl hydrogen sulphate

4. Addition of water

$$CH_{3} - C = CH_{2} + H_{2}O \xrightarrow{H^{+}} CH_{3} - CH_{3} - CH_{3} - CH_{3}$$

$$CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$2-Methylpropan-2-ol$$

5. Oxidation: Alkenes decolourise cold dilute aqueous solution potassium permanganate (Baeyer's reagent). It is used as a test for unsaturation.

$$\begin{array}{rcl} \mbox{CH}_2 = \mbox{CH}_2 + \mbox{H}_2 \mbox{O} + \mbox{O} & \mbox{dil.KMnO}_4 \mbox{O}_4 \mbox{OH}_2 - \mbox{CH}_2 \mbox{CH}_2 - \mbox{CH}_2 \mbox{OH}_2 \mbox{I} & \mbox{OH} & \mbox{O$$

Acidic  $KMnO_4$  or acidic  $K_2Cr_2O_7$  oxidises alkenes to ketones and/or acids depending upon the nature of alkene and the experimental conditions.



6. Ozonolysis: Reaction of ozone with alkene to form ozonide which on subsequent reductive cleavage with zinc dust and water give carbonyl compounds (aldehydes & ketones).



# **ALKYNES**

These are unsaturated hydrocarbons with general formula  $C_nH_{2n-2}$  e.g.,  $C_2H_2$  (ethyne),  $C_3H_4$  (propyne).

Alkynes also exhibit electrophilic addition reaction but less reactive than alkenes because the dissociation of  $\pi$ -electron cloud requires more energy.

H–C=C–H contins  $3\sigma$  and  $2\pi$  -bonds and bond length is 120 pm. In acetylene. H–C–C bond angle is 180°.

#### • Methods of Preparation of Alkynes

1.

2.

From calcium carbide  $CaCO_3 \longrightarrow CaO + CO_2$   $CaO + C \longrightarrow CaC_2 + CO$   $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$ From vicinal dihalides

$$\begin{array}{c|c} H & C & -CH \\ 2 & | & | & 2 \\ Br & Br & -KBr \\ -H_2O \end{array} \xrightarrow{H} C = C \\ H & Br \\ -H_2O \end{array}$$

#### **Physical Properties of Alkynes:**

- 1. The first two members are gases next eight members  $(C_5 C_{12})$  are liquids and higher members are solids.
- 2. They are all colorless and odorless with the exception of acetylene which has slightly garlic odour due to the presence of PH<sub>3</sub> and H<sub>2</sub>S as impurities.
- 3. Alkynes are insoluble in water but soluble in organic solvents like ethers, carbon tetrachloride and benzene.
- 4. Melting point, boiling point and density increase with increase in molar mass.

#### • Chemical properties of Alkynes

Alkynes show electrophilic as well as nucleophilic addition reactions.

#### (i) Acidic character of alkyne

$$HC \equiv CH + Na \longrightarrow HC \equiv CNa + \frac{1}{2}H_{2}$$
  
monosodium  
acetylides  
$$H - C \equiv CNa^{+} + Na \longrightarrow Na^{+}C \equiv \overline{C}Na^{+} + \frac{1}{2}H_{2}$$
  
disodium acetylide  
$$CH_{3} - C \equiv C - H + NaNH_{2} \longrightarrow CH_{3} - C \equiv \overline{C}Na^{+} + NH_{3}$$
  
sodium propynide

These reactions are not shown by alkenes, alkanes and non-terminal alkynes, hence used for distinction between alkane, alkene and alkyne.

Acetylenic hydrogens are acidic in nature due to 50% s-character insphybridized orbitals. Acidity of alkynes is lesser than water.

#### Acidic behavior order

(i) 
$$HC \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$$
  
 $sp^{2} = sp^{2} - sp^{3} - CH_3$ 

(ii) 
$$HC = CH > CH_3 - C = CH >> CH_3 - C = C - CH_3$$

#### (ii) Electrophilic addition reactions

$$-C \equiv C - + HZ \xrightarrow{H^+} \xrightarrow{H^-} C \equiv C + Z^- \longrightarrow -C \equiv C - C = C$$
vinyl cation

The addition product formed depends upon the stability of vinylic cation. Addition on unsymmetrical alkynes takes place according to Markovnikov's rule.

$$CH_{3} - C \equiv C - H + H_{2} \xrightarrow{Pt/Pd/Ni} [CH_{3} - CH = CH_{2}] \xrightarrow{H_{2}} CH_{3}CH_{2}CH_{3}$$
propene
propene

# **Addition of halogens** $HC \equiv CH + Cl \longrightarrow [HCCl = CHCl]$ 1, 2-Dichloropropene $Cl_2 \downarrow$ Cl Cl HC-CH Cl Cl 1, 1, 2, 2-Tetrachloroethane or westron HCl CH=CCl<sub>2</sub> Cl westrosol (1, 1, 2-Trichloroethene) Addition of hydrogen halides Br $CH_{3} - C = CH \xrightarrow{HBr} CH_{3} - C = CH_{2} \xrightarrow{HBr} CH_{3} - C$ -CH<sub>3</sub> -C-Br Br 2-Bromopropene 2, 2-Dibromopropane

#### **Addition for water**

$$CH \longrightarrow C = CH + HOH \xrightarrow{Hg^{2+}/H^{+}}_{333K} 3 \xrightarrow{C}_{0} H \xrightarrow{C}_{1} CH_{3} \xrightarrow{C}_{1} CH_{3}$$

#### (iii) Cyclic polymerization of ethyne



# **AROMATIC HYDROCARBONS**

These hydrocarbons are also known as arenes. The parent member of the family aromatic hydrocarbons is benzene.

Aromatic compounds containing benzene ring are known as benzenoids.

**Structure of benzene:** Hexagonal ring of carbon atoms with alternate single and double bonds. Each carbon atom is sp<sup>2</sup> hybridized. Planar ring, bond angle 120°. All C-C bond lengths are equal due to complete delocalization of  $\pi$  electrons.



# **HUCKEL'S RULE**

- Huckel's rule, (based on calculations): a planar cyclic molecule with alternating double and single bonds has aromatic stability if it has  $(4n + 2\pi)$  electrons (n is 0, 1, 2, 3, 4)
- For n = 1 : 4n+2 = 6; benzene is stable and electrons are delocalized.

#### Benzene



Three double bonds; six  $\pi$  electrons

#### • METHODS OF PREPARATION

### 1. Cyclic polymerization of ethyne



### 2. Decarboxylation of aromatic acids



### 3. Reduction of phenol



# **Physical Properties of Benzene:**

- (i) Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma.
- (ii) Aromatic hydrocarbons are immiscible with water but readily miscible with organic solvents.
- (iii) Aromatic compounds burn with sooty flame.

# **Chemical Reactions of Benzene:**

- (i) Benzene gives electrophile substitution reactions.
- (ii) According to experimental evidences, electrophile substitution reaction involve following three steps:
  - Generation of electrophilie
  - Formation of carbocation intermediate.
  - Removal of proton from the carbocation intermediate.



#### (v) Friedel-Crafts acylation reaction



• COMBUSTION

 $2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$ 

#### Directing influence of substituents in monosubstituted benzene

- (i) **Ortho and para directing groups:** Ring activating groups *e.g.*,  $NH_2$ ,  $-CH_3$ ,  $-C_2H_5$ ,  $-OCH_3$  etc. (+R effect)
- (ii) Meta directing groups: Ring deactivating groups

e.g. -  $NO_2$ , - CN, - CHO, - COOH, -  $SO_3H$  (- R effect)

