24

HYDROCARBONS

You have studied in the previous lesson that hydrocarbons are the compounds containing carbon and hydrogen. You also know that they are classified as aliphatic, alicyclic and aromatic hydrocarbons. They constitute a very important class of organic compounds and are widely used as fuels, lubricants and dry cleaning agents. They are also used as important ingredients in medicines and in dyes. Petroleum and coal are the major sources of various types of hydrocarbons. The products obtained from fractional distillation of petroleum and destructive distillation of coal are used almost in every sphere of life. Hydrocarbons are considered to be the parent organic compounds, from which other organic compounds can be derived by replacing one or more hydrogen atoms with different functional groups. In this lesson, you will study about the preparation, important physical and chemical properties of hydrocarbons.

OBJECTIVES

After reading this lesson, you will be able to :
- list different methods of preparation of alkanes;
- explain the reasons for variation in physical properties of alkanes;
- draw the conformations of ethane and compare their relative stability;
- describe different chemical properties of alkanes;
- list different methods of preparation of alkenes;
- explain the physical properties of alkenes;
- describe the chemical properties of alkenes;
- list different methods of preparation of alkynes;
- explain physical and chemical properties of alkynes;
- discuss the cause of greater reactivity of alkenes and alkynes over alkanes;

Notes

- distinguish alkanes, alkenes and alkynes;
- list various fractions obtained by destructive distillation of coal;
- explain the stability of various aromatic compounds using resonance;
- state Huckel rule and its use;
- describe methods of preparation, physical properties and chemical properties of benzene;
- list various uses of hydrocarbons; and
- explain the term carcinogenicity and Toxicity.

24.1 ALKANES (PARAFFINS)

Alkanes are saturated hydrocarbons. They are very less reactive towards various reagents; hence, they are also referred to as *paraffins* (*parum* means little, *affins* means affinity).
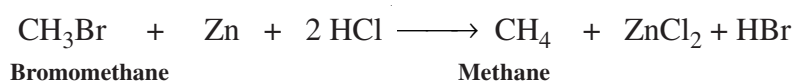
24.1.1 Methods of Preparation

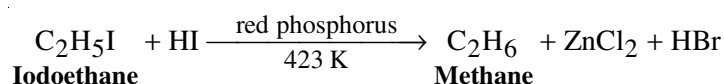Some important methods of preparation of alkanes are as follows:

1. **From Haloalkanes (Alkyl Halides):** Monohaloalkanes can be converted to alkanes by following three methods :

    a) By reduction of haloalkanes: The replacement of halogen atom of haloalkanes with hydrogen is called the reduction and can be carried out by the following reagents :
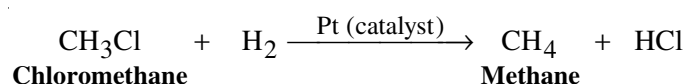
    (i)   Zinc and dilute HCl

    $$CH_3Br \quad + \quad Zn \ + \ 2\,HCl \longrightarrow CH_4 \quad + \quad ZnCl_2 + HBr$$
    Bromomethane   **Methane**

    (ii) HI in the presence of red phosphorus

    $$C_2H_5I \quad + HI \xrightarrow[\text{423 K}]{\text{red phosphorus}} C_2H_6 \ + ZnCl_2 + HBr$$
    Iodoethane   **Methane**

    (iii) Catalytic reduction

    $$CH_3Cl \quad + \quad H_2 \xrightarrow{\text{Pt (catalyst)}} CH_4 \quad + \quad HCl$$
    Chloromethane   **Methane**

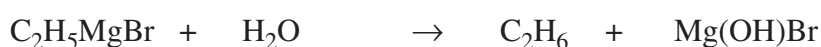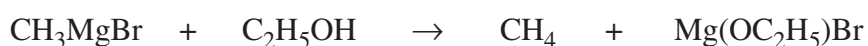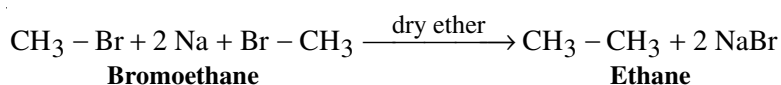   **b) By using Grignard's Reagent :** A Grignard reagent is a compund of the type RMgX which is prepared by reacting a haloalkane with magnesium metal in the presence of dry ether.

    $$C_2H_5Br + Mg \xrightarrow{\text{dry ether}} C_2H_5MgBr$$
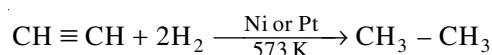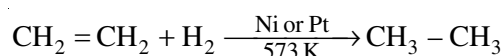   **Bromoethane**   **Ethyl Magnesium Bromide**
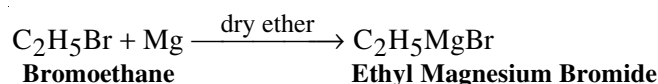
The Grignard's reagents are used to prepare various compounds like hydrocarbons, ethers, alcohols and carboxylic acids. It reacts with the compounds containing active hydrogen and forms alkanes. An easily replaceable hydrogen atom present in the compounds is called *active hydrogen*. An active hydrogen is present in (i) alcohols and (ii) water and (iii) acids.

$$CH_3MgBr \ + \ C_2H_5OH \ \rightarrow \ CH_4 \ + \ Mg(OC_2H_5)Br$$

$$C_2H_5MgBr \ + \ H_2O \ \rightarrow \ C_2H_6 \ + \ Mg(OH)Br$$

c) **By Wurtz Reaction :** In this reaction, an alkyl halide reacts with sodium metal in the presence of dry ether and forms the higher alkanes.

$$CH_3 - Br + 2\,Na + Br - CH_3 \xrightarrow{\text{dry ether}} CH_3 - CH_3 + 2\,NaBr$$
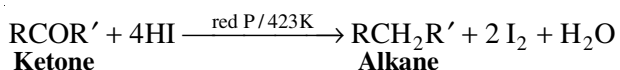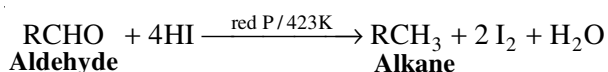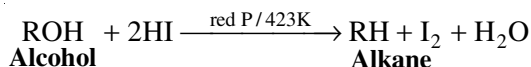$$\quad\quad\text{\textbf{Bromoethane}} \quad\quad\quad\quad\quad\quad\quad\quad \text{\textbf{Ethane}}$$

2. **From Unsaturated Hydrocarbons :** The unsaturated hydrocarbons (i.e. alkenes and alkynes) can be converted to alkanes by the addition of hydrogen in the presence of a catalyst like nickel, platinum or palladium.

$$CH_2 = CH_2 + H_2 \xrightarrow[573\,K]{\text{Ni or Pt}} CH_3 - CH_3$$

$$CH \equiv CH + 2H_2 \xrightarrow[573\,K]{\text{Ni or Pt}} CH_3 - CH_3$$

This reaction is also called **hydrogenation** and is used to prepare vegetable ghee from edible oils (by converting unsaturated fats to saturated ones.)

3. **From Alcohols, Aldehydes and Ketones :** Alcohols, aldehydes and ketones on reduction with HI, in presence of red phosphorus, give alkanes. The general reactions are as shown below.

$$\underset{\textbf{Alcohol}}{ROH} \ + 2HI \xrightarrow{\text{red P / 423K}} \underset{\textbf{Alkane}}{RH} + I_2 + H_2O$$

$$\underset{\textbf{Aldehyde}}{RCHO} \ + 4HI \xrightarrow{\text{red P / 423K}} \underset{\textbf{Alkane}}{RCH_3} + 2\,I_2 + H_2O$$

$$\underset{\textbf{Ketone}}{RCOR'} + 4HI \xrightarrow{\text{red P / 423K}} \underset{\textbf{Alkane}}{RCH_2R'} + 2\,I_2 + H_2O$$

4. **From Carboxylic Acids :** Carboxylic acids can produce alkanes in a number of ways as shown below :

i) **Heating with soda lime :** $RCOONa + NaOH \xrightarrow[\Delta]{\text{CaO}} RH + Na_2CO_3$

In this reaction, an alkane with one carbon less than those present in the parent carboxylic acid is obtained.

Notes

ii) By Reduction of carboxylic acid:
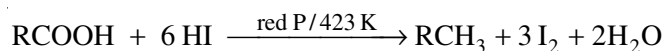
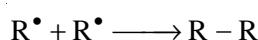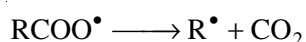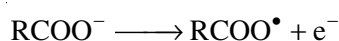$$RCOOH + 6HI \xrightarrow{\text{red P/423 K}} RCH_3 + 3I_2 + 2H_2O$$

Here, an alkane with same number of carbon atoms as in the starting carboxylic acid is obtained.

iii) Kolbe's Electrolysis: Sodium or potassium salt of a carboxylic acid, on electrolysis, gives a higher alkane. The reaction takes place as follows.
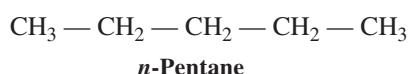
$$\underset{\textbf{Sodium salt of carboxylic acid}}{RCOONa} \xrightarrow{\text{electrolysis}} \underset{\textbf{Anion}}{RCOO^-} + \underset{\textbf{Cation}}{Na^+}$$

At Anode :

$$RCOO^- \longrightarrow RCOO^\bullet + e^-$$

$$RCOO^\bullet \longrightarrow R^\bullet + CO_2$$

$$R^\bullet + R^\bullet \longrightarrow R-R$$
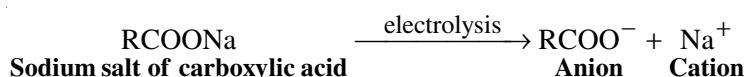
Thus, ethane can be obtained by the electrolysis of sodium ethonate.

$$\underset{\textbf{Sodium ethanote}}{2\,CH_3COONa} \longrightarrow \underset{\textbf{Ethane (at anode)}}{CH_3-CH_3}$$
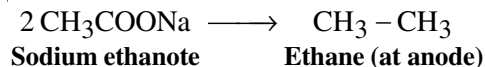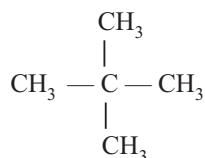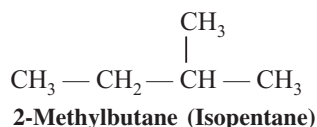
Note that the alkanes with even number of carbon atoms can easily be prepared by this method.

24.1.2 Physical Properties of Alkanes

Physical State: The physical state of alkanes depends upon the intermolecular forces of attraction present between molecules which in turn, depend upon the surface area of the molecules. *As the molecular mass of the alkanes increases, their surface area also increases, which in turn, increases the intermolecular forces of attraction, and accordingly, the physical state of alkanes changes from gaseous to liquid, and then to solid.* The alkanes containing 1 to 4 carbon atoms are gases, whereas those containing 5 to 17 carbon atoms are liquids, and the still higher ones are solids. In the case of isomeric alkanes, the straight chain alkanes will have maximum surface area, and hence, stronger intermolecular force of attraction. As the branching increases, surface area decreases. Hence the intermolecular forces of attraction decrease. Let us consider the isomers of pentane (C_5H_{12}).

$$\underset{\textit{n}\textbf{-Pentane}}{CH_3 — CH_2 — CH_2 — CH_2 — CH_3}$$

$$CH_3$$
$$|$$
$$CH_3 — CH_2 — CH — CH_3$$
2-Methylbutane (Isopentane)

$$CH_3$$
$$|$$
$$CH_3 — C — CH_3$$
$$|$$
$$CH_3$$
2,2-Dimethylpropane (Neopentane)

Amongst these three isomeric compounds, neopentane will have the weakest intermolecular forces of attraction due to the smallest surface area of its molecules.

Density: *The density of alkanes increases with the increase in molecular mass which increases with the increase in the number of carbon atoms.* All alkanes are lighter than water i.e. their density is less than 1.0 g/cm^3. The maximum density in the case of alkanes is 0.89 g cm^3. The lower density of alkanes than water is due to the absence of strong intermolecular attractions in alkanes.

Boiling Point: *The boiling points of alkanes also increase with the increase in the molecular mass.* In straight chain alkanes, the increase in boiling points due to the increase in surface area of the molecules. Branching in a chain reduces the surface area and therefore, decreases the boiling point of alkanes. Thus, in the above example, isopentane and neopantane have a lower boiling point than pentane.

Melting Point: Similar to the boiling points, the melting points of alkanes also increase with the increase in their molecular mass, but there is no regular variation in melting point. The melting points of alkanes depend not only upon the size and shape of the molecules, but also on the arrangement (i.e. the packing) of the molecules in the crystal lattice.

In alkanes, each carbon atom is sp^3 hybridized which results in a bond angle of $109°28'$. In straight chain hydrocarbons the carbon atoms are arranged in a zig-zag way in the chain. If the molecule contains an odd number of carbon atoms, then the two terminal methyl groups lie on the same side. So the interaction between the alkane molecules, with odd number of carbon atoms, is less than the molecule with even number of carbon atoms, in which terminal methyl groups lie on the opposite sides.
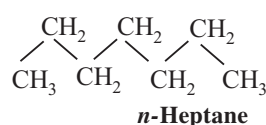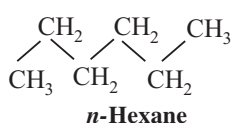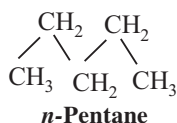
n-Pentane
(Carbon atoms = 5, m.p.142 K)

n-Hexane
(Carbon atoms =6, m.p. = 179 K)

n-Heptane
(carbon atoms = 7, m.p. = 183 K)

In the above structures, we find that alkanes containing even number of carbon atoms are more symmertical and can be more closely packed as compared with

alkanes containing odd number of carbon atoms and can be more closely packed. Van der Waal's force of attraction is stronger, due to which they have higher melting points. *Therefore, the alkanes with odd number of carbon atoms have lower melting point than those having even number of carbon atoms.*

24.1.3 Conformations of Ethane

You have studied section 25.3.2 that electronic displacements affect the physical and chemical properties of organic compounds. You will now study how the forces present within the molecules affect their structures and stabilities. In fact, these interactions make some geometric arrangements of atoms energetically *more favorable* than others.
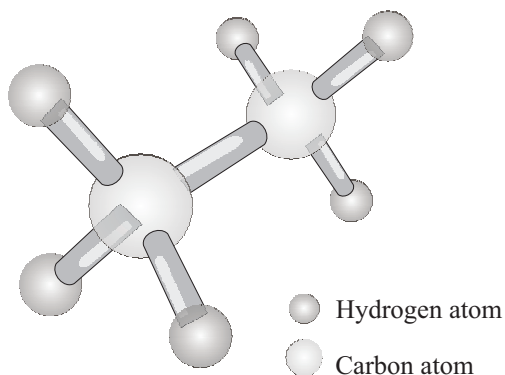
In ethane molecule, C_2H_6, the two carbon atoms are linked together by a single bond called *sigma* (σ) bond.
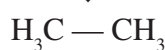
$$\text{sigma } (\sigma) \text{ bond}$$
$$\downarrow$$
$$H_3C - CH_3$$
$$\text{ethane}$$

If we make a model of ethane molecule showing the C — C bond and the hydrogens attached to carbon atoms, it will look like as follows :

○ Hydrogen atom

◯ Carbon atom

Model of ethane molecule

The groups bonded through a sigma bond can easily rotate with respect to each other. *i.e.* the two — CH_3 groups in ethane can rotate with respect to each other. The different arrangement of atoms resulting from such a rotation are called **conformations** and each such specific conformation is called a **conformer** (from *confor*mational iso*mer*).

The conformational isomers can be represented in the following two ways:

(i) Sawhorse representations

(ii) Newman projections

The **Sawhorse representations** show the carbon–carbon bond from an oblique angle and indicate the spatial arrangement of all C — H bonds.
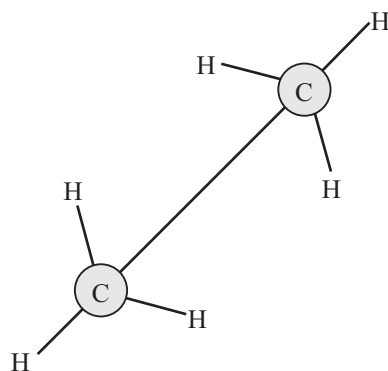
Sawhorse Projections

In **Newman projections** the two carbon atoms are viewed along the C — C bond axis. The front carbon and its bonds are represented as ⅄ whereas the back carbon and its bonds are represented as ⅄.
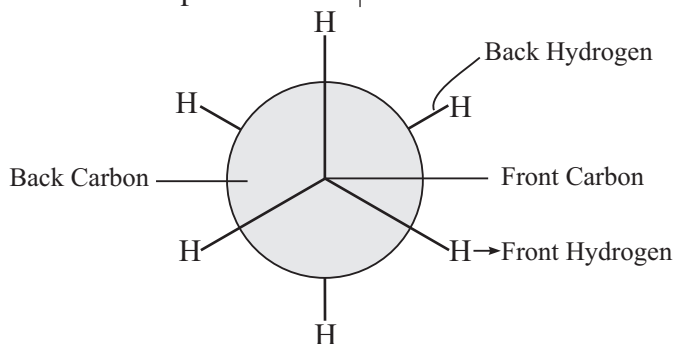
Newman Projection

The Newman projections are easier to draw and in such drawings, the relative positions of atoms are easily visualised. Therefore, we will use Newman projections to study the conformations of ethane.

Several conformations of ethane are possible. But, there are two extreme possibilities. These are discussed below:

(i)   In this conformation all the six C — H bonds are *as far away as possible*. This conformation is called **staggered conformation** and is shown below:
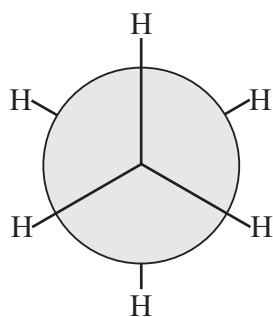
Staggered conformation of ethane

Notes

(ii) Another conformation in which all the six C — H bonds *are as close as possible is* shown below:

Eclipsed conformation of ethane

This is called **eclipsed conformation.** The three rear hydrogens are drawn little more rotated than the perfectly eclipsed positions to make them visible in the structure.

Remember that there are infinite number of possible conformations in between the staggered and the eclipsed conformations. All these conformations originate by the rotation of the C — C bond.

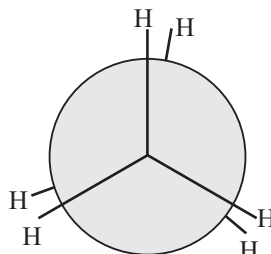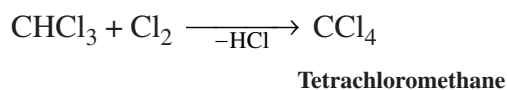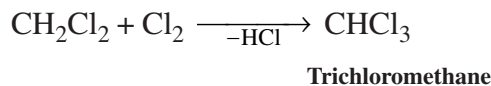The *staggered conformation* is the **most slable** conformation whereas the *eclipsed conformation* is the **least stable** conformation of ethane. The eclipsed conformation has about 12 kJ mol^{-1} higher energy than the staggered conformation.

24.1.4 Chemical Properties of Alkanes

1. Halogenation reactions: The chemical reactions in which a hydrogen atom of an alkane is replaced by a halogen atom are known as *halogenation*. Alkanes react with chlorine in the following way.

$$CH_4 + Cl_2 \xrightarrow[-HCl]{\text{Diffused Sunlight}} CH_3Cl$$
Methane   **Chloromethane**

$$CH_3Cl + Cl_2 \xrightarrow[-HCl]{} CH_2Cl_2$$
Dichloromethane

$$CH_2Cl_2 + Cl_2 \xrightarrow[-HCl]{} CHCl_3$$
Trichloromethane

$$CHCl_3 + Cl_2 \xrightarrow[-HCl]{} CCl_4$$
Tetrachloromethane
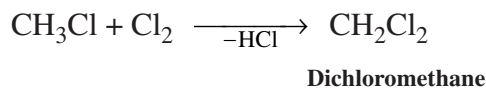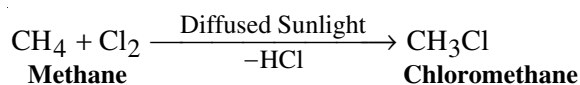
Chlorination of methane takes place via the **free radical mechanism**. When the reaction mixture is exposed to sunlight, chlorine molecules absorb energy from sunlight and get converted to free radicals i.e. chlorine atoms with an unpaired electron $(\overset{\bullet}{C}l)$. The chlorine radicals then combine with methane and form methyl radical $[\overset{\bullet}{C}H_3]$. The methyl radical further reacts with chlorine molecule and

produces chloromethane. This reaction continuously takes place till it is stopped or the reactants completely react to form the products. The free radical mechanism involves the following three steps.

(i) **Chain Initiation Step:** It involves the formation of free radicals.

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet} \qquad (h\nu = \text{energy of light})$$
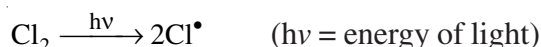
(ii) **Chain Propagation Step :** The free radicals give rise to the formation of more free radicals as is shown in the following reaction.

$$CH_4 + \overset{\bullet}{C}l \longrightarrow \overset{\bullet}{C}H_3 + HCl$$

$$\overset{\bullet}{C}H_3 + Cl_2 \longrightarrow CH_3Cl + \overset{\bullet}{C}l$$
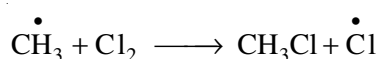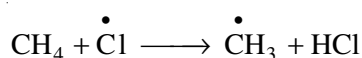
(iii) **Chain Termination Step :** In this step, free radicals combine with one another and the further reaction stops.

$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}l \longrightarrow CH_3Cl$$

$$\overset{\bullet}{C}l + \overset{\bullet}{C}l \longrightarrow Cl_2$$

$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3 \longrightarrow CH_3 - CH_3$$
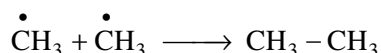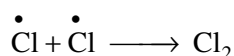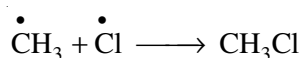
The reactivity of halogens is in the order of $F_2 > Cl_2 > Br_2 > I_2$.

2. **Oxidation:** Alkanes undergo oxidation (combustion) in excess of oxygen and produce carbon dioxide and water. This reaction is highly exothermic in nature. For example :

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + 890\,KJ\,mol^{-1}$$
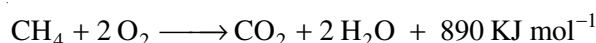
If the combustion is carried out in the presence of an insufficient supply of air or O_2, then *incomplete combustion takes place forming carbon monoxide* instead of carbon dioxide.

$$2C_2H_6 + 5O_2 \xrightarrow{\text{heat}} 4CO + 6H_2O$$
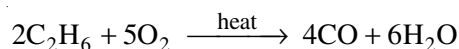
3. **Cracking or Pyrolysis:** At very high temperature and in the absence of air, the alkanes break apart into smaller fragments. For example,

$$CH_3 - CH_2 - CH_3 \xrightarrow{873\,K} CH_3CH = CH_2 + H_2$$

or
$$CH_2 = CH_2 + CH_4$$
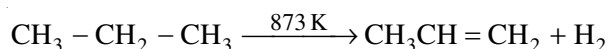
4. **Isomerisation :** *n*-Alkanes, in the presence of aluminium halide and HCl, are converted to their branched isomers.

$$\underset{n\textbf{-butane}}{CH_3 - CH_2 - CH_2 - CH_3} \xrightarrow{AlCl_3\,/\,HCl} \underset{\textbf{isobutane}}{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3}$$
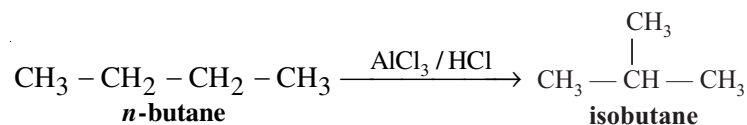
24.1.4 Uses of Alkanes

Alkanes are used as fuel gases, solvents, drycleaning agents, lubricants and in ointments (paraffin wax). Methane is used for illuminating and domestic fuel and also for the production of other organic compounds such as haloalkanes, methanol, formaldehyde and acetylene. Propane is used as a fuel, refrigerant and as raw material in the petrochemical industry. Butane and its isomer–isobutane, are the major constituents of LPG .

INTEXT QUESTIONS 24.1

1. List four important uses of hydrocarbons.

2. What is Grignard's reagent in a molecule?

3. What is an active hydrogen in a molecule?

4. What makes the physical properties of various hydrocarbons different?

5. Name two alkanes which are gases and two alkanes which are liquids at room temperature.

6. Name three isomers of pentane.

7. Which one has higher b.p. *n*-butane or *n*-pentane? Explain.

8. Write the balanced chemical equation for the complete combustion of propane.

24.2 Alkenes

These are unsaturated hydrocarbons containing at least one double bond between two carbon atoms. The hydrocarbons of this class are also called **olefines** (*olefiant* = oil forming).

24.2.1 Methods of Preparation

In the laboratory, alkenes are generally prepared either from haloalkanes (alkyl halides) or alcohols.

1. From Haloalkanes: Halaoalkanes are converted to alkenes by dehydrohalogenation. The process of removal of halogen acid like HCl, HBr or HI from the adjacent carbon atoms of alkyl halides, when reacted with alcoholic solution of potassium hydroxide, is called *dehydrohalogenation*.

$$CH_3 — CH_2 — Cl + KOH(alc.) \rightarrow CH_2 = CH_2 + KCl + H_2O$$
Chloroethane   **Ethene**

$$CH_3CH_2\underset{\underset{\textstyle \text{2-Chlorobutane}}{|}}{\underset{\textstyle Cl}{CHCH_3}} \xrightarrow{\text{2KOH(alc.)}} \underset{\text{But-2-ene (Major)}}{CH_3CH=CHCH_3} + \underset{\text{But-1-ene (Minor)}}{CH_3CH_2CH=CH_2}$$
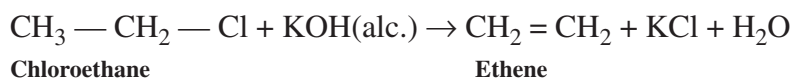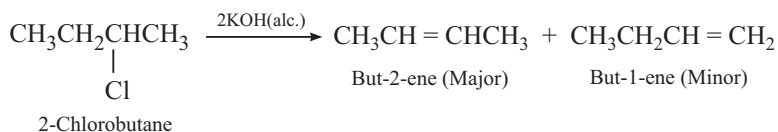
The major product is formed according to the Saytzeff's Rule.

Saytzeff's Rule : *It states that when an alkyl halide reacts with alcoholic solution of potassium hydroxide and if two alkenes are possible, then the one which is more substituted, will be the major product.* In the above example, but-2-ene is the major product because it contains two alkyl groups attached to the $-C=C-$ group.

2. From Alcohols : Alkenes can be prepared from alcohols by dehydration in the presence of a suitable dehydrating agent such as (i) Al_2O_3 or (ii) concentrated H_2SO_4.

$$\underset{\textbf{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[623-633K]{Al_2O_3} \underset{\textbf{Ethene}}{CH_2=CH_2} + H_2O$$

$$\underset{\textbf{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[433K]{\text{conc. } H_2SO_4} \underset{\textbf{Ethene}}{CH_2=CH_2} + H_2O$$
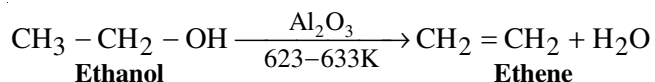
In the dehydration of higher alcohols, the major product obtained is according to the Saytzeff's Rule.

24.2.2 Physical Properties of Alkenes

Some important physical properties of alkanes are as follows:

Physical State : Unbranched alkenes containing upto four carbon atoms are gases and containing five to sixteen carbon atoms are liquids while those with more than 16 carbon atoms are solids.

Boiling Points : The boiling points of alkenes increase with molecular mass as is shown in Table 24.1.
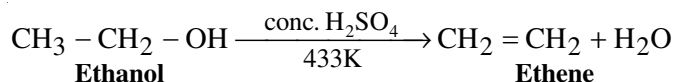
<div align="center">

Table 24.1 : Boiling points of Alkenes

</div>

Alkene	Ethene	Propene	But-1-ene	Pent-1-ene	Hex-1-ene
b.p. (K)	169	226	267	303	337

The increase in boiling point can be attributed to the van der Waals forces which increases with number of carbon atoms of the alkene. The branched chain alkenes have lower boiling points than those of straight chain isomers.

Melting Point : In alkenes, there is increase in the melting point with the increase in molecular mass. In the case of isomeric alkenes, the *cis* and *trans* isomers have different melting points.

For example

$$CH_3 \diagdown \qquad \diagup H$$
$$C = C$$
$$H \diagup \qquad \diagdown CH_3$$

$$CH_3 \diagdown \qquad \diagup CH_3$$
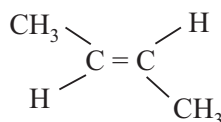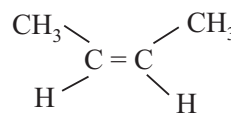$$C = C$$
$$H \diagup \qquad \diagdown H$$

trans-**But-2-ene**
(m.p. 167 K)

cis-**But-2-ene**
(m.p. = 134 K)

24.2.3 Chemical Properties of Alkenes

1. **Addition Reactions :** The chemical reactions in which a molecule adds to another molecule are called an *addition reaction*. These reactions are characteristic of unsaturated compounds like alkenes and alkynes. The following reactions illustrate the addition reactions of alkenes.

    (i) **Addition of Hydrogen :** Addition of hydrogen to unsaturated hydrocarbons takes place in the presence of a catalyst like Ni, Pt or Pd.

    $$CH_2 = CH_2 + H_2 \xrightarrow[573K]{\text{Ni (Pt or Pd)}} CH_3 - CH_3$$
    Ethene   **Ethane**
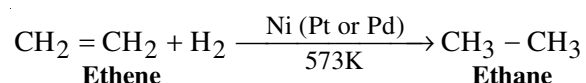
    (ii) **Addition of Halogens :** Halogens on addition to alkenes, form 1,2-dihaloalkanes.

    $$CH_2 = CH_2 + Br_2 \text{ (in } CCl_4) \longrightarrow CH_2 - CH_2$$
    Ethene | |
                                                  Br   Br
    1, 2-Dibromoethane
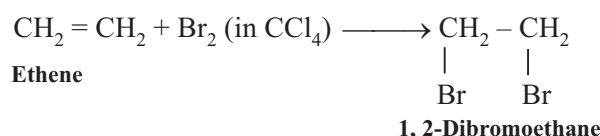
    As a result of this addition reaction, the reddish-brown colour of Br_2 gets discharged. This reaction is also used as test for unsaturation in hydrocarbons.

    (iii) **Addition of Halogen Acids (HX) :** When halogen acids are added to alkenes , hydrogen adds to one carbon atom whereas halogen atom adds to the second carbon atom of the double bond.

    $$CH_2 = CH_2 \ + \ HBr \longrightarrow CH_3 - CH_2 - Br$$
    Ethene   **Bromoethane**
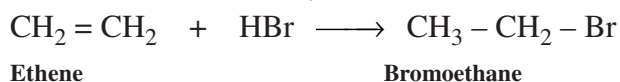
    In case of unsymmetrical alkenes (which contain unequal number of H-atoms attached to the carbon atoms of the double bonds), the addition of HX takes place according to the **Markownikoff's rule. This rule states that in the addition of halogen acids to unsymmetrical alkenes, the halogen of HX goes to that carbon atom of C = C bond which already has less H-atoms attached to it.** In other words, hydrogen

atom of HX goes to the carbon atom with more number of H-atoms attached to it.
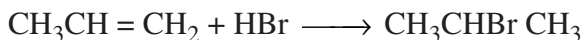
$$CH_3CH = CH_2 + HBr \longrightarrow CH_3CHBr\ CH_3$$
Propene   **2-Bromopropane**

Mechanism of Electrophilic Addition: You have studied earlier that the electron cloud of the pi bond is present above and below the plane of the molecule in alkenes. Various electron seeking species and reagents thus react with the alkenes. For example, H$^+$ of HX(HBr) can add to the double bond to yield a carbocation.

Carbocation
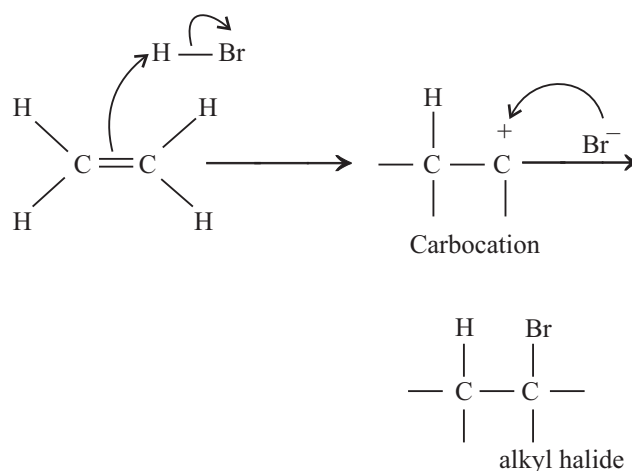
alkyl halide

The carbocation being highly reactive reacts with the halide ion in the second step to yield an alkyl halide (alkyl bromide).

In case, the starting alkene is unsymmetrical *e.g.* propene, then in the first step of formation of a carbocation, there are two possibilities of attachment of H$^+$ of HX which are shown below:

$$:\ddot{X}\!-\!H\ CH_3\ OH\!=\!CH_2 \longrightarrow CH_3\ \overset{H}{\underset{|}{C}}H\!-\!CH_2 + :\ddot{X}\!:^-$$
(I) primayr
carbocation
(less stable)

$$CH_3\ OH\!=\!CH_2 + H\!-\!\ddot{X}\!: \longrightarrow CH_3\ \overset{+}{C}H\!-\!CH_2\!-\!H + :\ddot{X}\!:^-$$
(II) secondary
carbocation
more stable
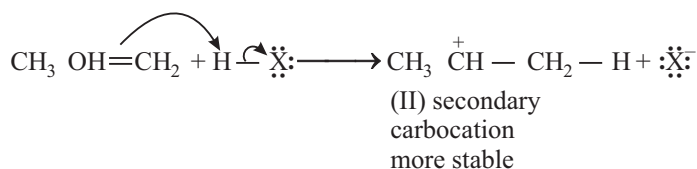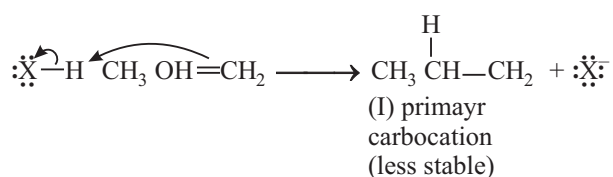
This would lead to the formation of two carbocations as shown above.

The two possible carbocations have different stabilities *i.e.* the secondary carbocation (II) is more stable than the primary carbocation (I). Therefore, the secondary carbocation (II) is formed preferentially in the first step. Further reaction, *i.e.* attack of Br$^-$ on the carbocation, thus yields 2-bromopropane as the major product.

$$CH_3\overset{+}{C}H\,CH_3 \quad \xrightarrow[\text{fast}]{\overset{-}{Br}} \quad CH_3CH\,CH_3$$

$$\uparrow_H \qquad\qquad\qquad\qquad |$$

$$\qquad\qquad\qquad\qquad\qquad Br$$

2-bromopropare
(main product)

$$CH_3CH=CH_2 \quad \overset{HBr}{\underset{slow}{\Big|}}$$

$$\xrightarrow{\quad X\quad} CH_3CH\,\overset{+}{C}H_2 \quad \xrightarrow{\overset{-}{Br}} \quad CH_3CH_2CH_2Br$$

1-bromopropare
little amount

Thus, the above explanation describes for the formation of 2-bromopropane as the major product as per the Markownikoff's rule.

If the addition of HBr is carried out in the presence of peroxides such as benzoyl peroxide, then the reaction takes place contrary to Markownikoff's rule. This is also known as **Anti-Markownikoff's addition** or **peroxide effect**.
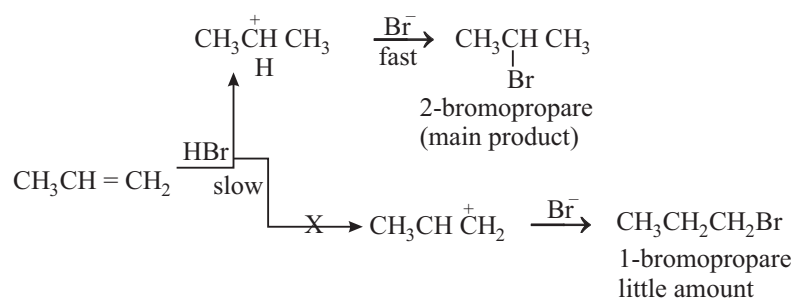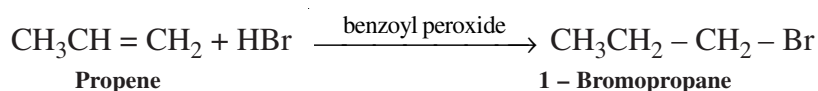
$$CH_3CH=CH_2 + HBr \xrightarrow{\text{benzoyl peroxide}} CH_3CH_2 - CH_2 - Br$$

Propene   **1 – Bromopropane**

(iv) Addition of Water : Addition of water takes place in the presence of mineral acids like H_2SO_4.

$$CH_2 = CH_2 + H_2O \xrightarrow[\text{Heat}]{H_2SO_4} CH_3 - CH_2 - OH$$

Ethene   **Ethanol**

(v) Addition of H_2SO_4

$$CH_2 = CH_2 + \text{conc. } H_2SO_4 \longrightarrow CH_3 - CH_2 - HSO_4$$

Ethene   **Ethyl hydrogen sulphate**
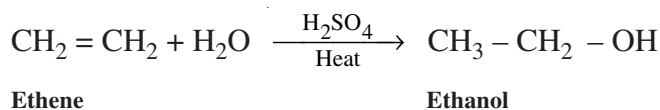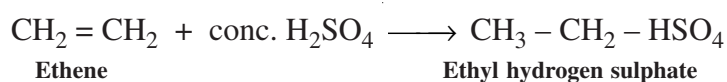
(vi) Addition Polymerization : The process in which many molecules of an alkene add together to form a larger molecule is called **addition polymerization.**

$$n\,(CH_2=CH_2) \xrightarrow{\text{heat, pressure}} (-CH_2-CH_2-)_n$$

Ethene   **Polyethene**
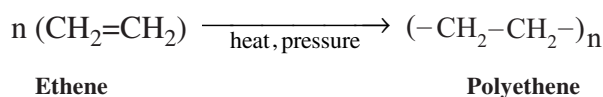
2. **Oxidation :** The oxidation of alkenes can be done by using different oxidizing agents like $KMnO_4$, oxygen and ozone.

(i) Oxidation with $KMnO_4$

Alkenes are unsaturated hydrocarbons having Pi (π)-bond(s) between the carbon atoms, so they are easily oxidized by cold dilute alkaline solution of $KMnO_4$.

$$\begin{array}{c} CH_2 \\ \parallel \\ CH_2 \end{array} \xrightarrow[\text{cold alkaline}]{KMnO_4} \begin{array}{c} CH_2 - OH \\ \mid \\ CH_2 - OH \end{array}$$

Ethene   **Ethanediol**
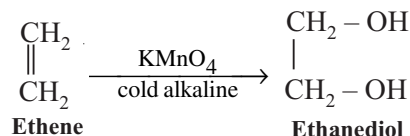
When an alkaline solution of $KMnO_4$ (Baeyer's Reagent) is added to an alkene, the purple colour of $KMnO_4$ gets discharged. This reaction is used to test unsaturation in hydrocarbons. On treatment with hot alkaline $KMnO_4$ the alkene gets oxidized to ketones or further to acids depending upon its structure. This happens due to the breaking of carbon-carbon double bond.

$$\begin{array}{c} CH_3 \\ \mid \\ CH_3 - C = CH_2 \end{array} + 3[O] \xrightarrow[\text{hot}]{\text{alk. } KMnO_4} \begin{array}{c} CH_3 \\ \\ CH_3 \end{array} \!\!\! > C = O \quad + \quad HCOOH$$

2-Methylpropene   **(Acetone)**   **(Formic Acid)**
                                          Propanone   Methanoic acid

(ii) Oxidation with Oxygen : Ethene on oxidation with oxygen in the presence of silver (Ag) gives epoxyethane. The reaction is shown below:

$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow[\text{Ag}]{585\ K} \begin{array}{c} CH_2 - CH_2 \\ \diagdown O \diagup \end{array}$$
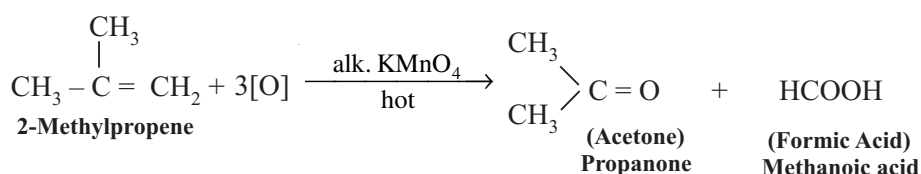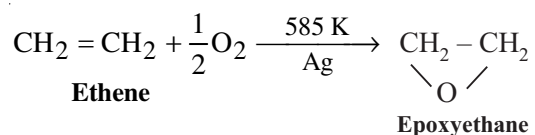
Ethene

Epoxyethane

(iii) Combustion : The oxidation reaction, in which carbon dioxide and water are formed along with the liberation of heat and light, is called **combustion.**

$$CH_2 = CH_2 + 3\ O_2 \xrightarrow{\text{heat}} 2\ CO_2 + 2\ H_2O \quad \Delta H = -1411\ KJ\ mol^{-1}$$

(iv) Oxidation with Ozone : Ozone adds to the alkene forming ozonide. The ozonide when further reacted with water in the presence of zinc dust, forms aldehydes or ketones, or both.

$$CH_2 = CH_2 + O_3 \rightarrow \qquad \xrightarrow{Zn\,/\,H_2O} 2HCHO$$

Ethene   **Ozonide**   **Ethene**
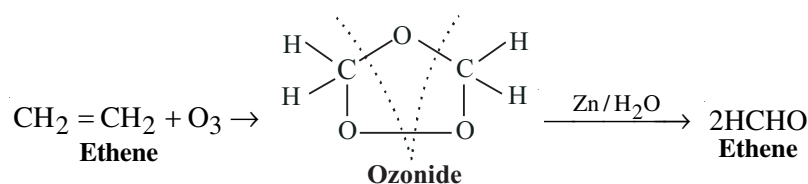
This process of addition of ozone to an unsaturated hydrocarbon followed by hydrolysis is called **ozonolysis.**

Ozonolysis can be used for the determination of the position of double bonds in alkenes by analysing the products formed i.e. aldehydes and ketones. This is explained below.

Notes

$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH}=\overset{1}{CH_2} \xrightarrow{O_3} CH_3CH_2-C\underset{O----O}{\overset{O}{\diagdown \diagup}}CH_2$$
But-1-ene

$$\xrightarrow{Zn/H_2O} CH_3CH_2CHO + HCHO$$
Propanal **Methanal**

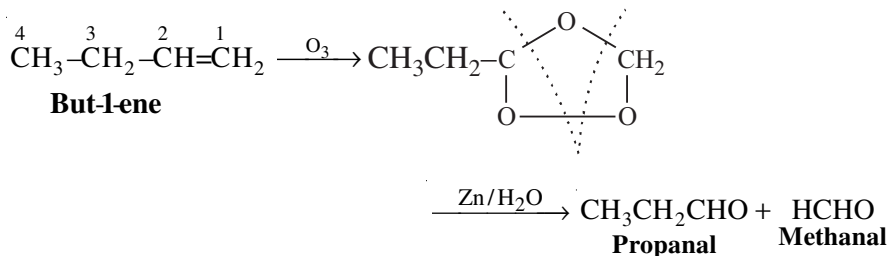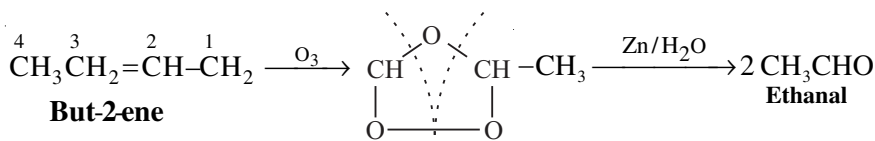When but-1-ene is oxidized with ozone and the ozonide formed is hydrolysed, we get one mole of propanal and one mole of methanal, showing that the double bond is between carbon atom 1 and 2. Whereas but-2-ene on oxidation with ozone, followed by hydrolysis, gives two moles of ethanal, showing that the double bond is present between carbon atoms 2 and 3 as shown below.

$$\overset{4}{CH_3}\overset{3}{CH_2}=\overset{2}{CH}-\overset{1}{CH_2} \xrightarrow{O_3} CH\underset{O----O}{\overset{O}{\diagdown \diagup}}CH-CH_3 \xrightarrow{Zn/H_2O} 2\,CH_3CHO$$
But-2-ene **Ethanal**

24.2.4 Uses of Alkenes

Ethene is used for making mustard gas, which is a poisonous gas used in warfare. It is also used for artificial ripening of fruits, as a general anaesthetic and for producing other useful materials such as polythene, ethanal, ethylene glycol (antifreeze), ethylene oxide (fumigant) etc.

INTEXT QUESTIONS 24.2

1. Which one has higher boiling point: *cis* but-2-ene or *trans* but-2-ene?

2. Name the products formed when ethene is oxidized with cold alkaline solution of $KMnO_4$.

3. Write the conditions for hydrogenation of alkenes.

4. What happens when ethene reacts with oxygen at 575 K in presence of Ag?

24.3 ALKYNES

These are also unsaturated hydrocarbons which contain atleast one triple bond between two carbon atoms. Some examples are as follows :

$$CH \equiv CH, \quad CH_3 - C \equiv CH, \quad CH_3 - C \equiv C - CH_3$$
Ethyne **Propyne** **But-2-yne**
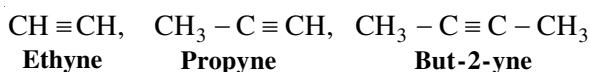
24.3.1 Preparation of Ethyne (Acetylene)

Some important methods for preparation of ethyne are explained below.

1. From Calcium Carbide: Ethyne can be prepared in the laboratory, as well as on a large scale, by the action of water on calcium carbide.

$$\underset{\textbf{Calcium carbide}}{CaC_2} \quad + \quad \underset{\textbf{Water}}{2\,H_2O} \longrightarrow \underset{\textbf{Ethyne}}{H-C \equiv C - H} + Ca(OH)_2$$
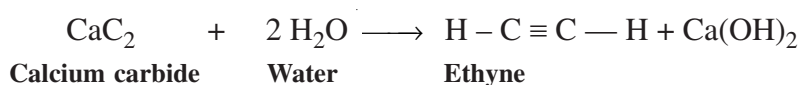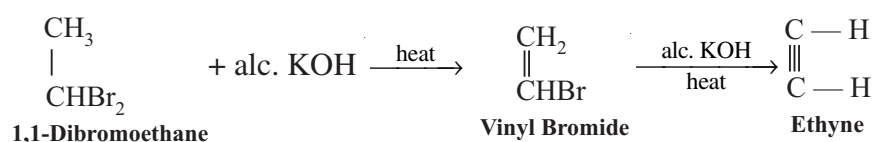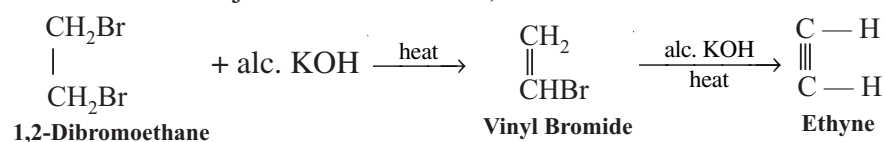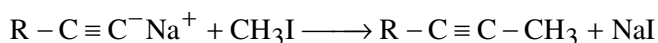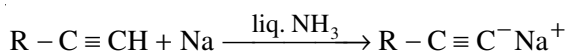
Ethyne prepared by this method generally contains the impurities of hydrogen sulphide and phosphine due to the impurities of calcium sulphide and calcium phosphide in calcium carbide.

2. Preparation of Ethyne from Dihaloalkanes

Ethyne can be prepared by refluxing *geminal* dihaloalkanes (having both halogens attached to the same carbon atom) or *vicinal* dihaloalkanes (having halogen atoms attached to the adjacent carbon atoms) with alcoholic solution of KOH.

$$\underset{\textbf{1,2-Dibromoethane}}{\overset{CH_2Br}{\underset{CH_2Br}{|}}} + alc.\ KOH \xrightarrow{\ heat\ } \underset{\textbf{Vinyl Bromide}}{\overset{CH_2}{\underset{CHBr}{\|}}} \xrightarrow[heat]{alc.\ KOH} \underset{\textbf{Ethyne}}{\overset{C-H}{\underset{C-H}{\||}}}$$

$$\underset{\textbf{1,1-Dibromoethane}}{\overset{CH_3}{\underset{CHBr_2}{|}}} + alc.\ KOH \xrightarrow{\ heat\ } \underset{\textbf{Vinyl Bromide}}{\overset{CH_2}{\underset{CHBr}{\|}}} \xrightarrow[heat]{alc.\ KOH} \underset{\textbf{Ethyne}}{\overset{C-H}{\underset{C-H}{\||}}}$$

3. Preparation of higher alkynes : Higher alkynes can be prepared by the reaction of alkynides of lower alkynes with primary alkyl halides.

$$R - C \equiv CH + Na \xrightarrow{\ liq.\ NH_3\ } R - C \equiv C^- Na^+$$

$$R - C \equiv C^- Na^+ + CH_3I \longrightarrow R - C \equiv C - CH_3 + NaI$$

24.3.2 Physical Properties of Alkynes

1. First three members of alkynes are gases, the next eight members are liquids and members having more than twelve carbon atoms are solids.

2. They are colourless and odourless, except ethyne which has a garlic odour.

3. The melting points, boiling points and densities of alkynes increase with the increasing molar mass. In alkynes, there are π(pi)-electrons due to which these molecules are slightly polar. So charge separation takes place in alkynes, and hence dipoles are formed. The presence of dipoles increases the inter molecular force of attraction, and hence the boiling points of alkynes are higher than those of the corresponding alkanes.

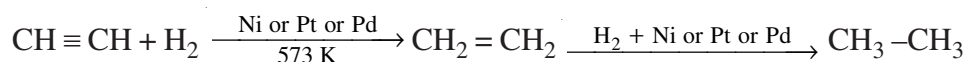4. Alkynes are very slightly soluble in water and soluble in acetone.

Notes

24.3.3 Chemical Properties of Alkynes

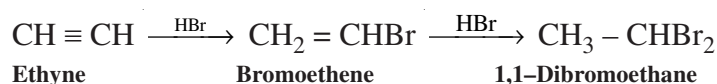1. **Addition Reactions** : Some of the addition reactions of alkynes are as follows.

    (i) Addition of Hydrogen : Addition of hydrogen to alkynes takes place in the presence of a catalyst like Ni, Pt or Pd.
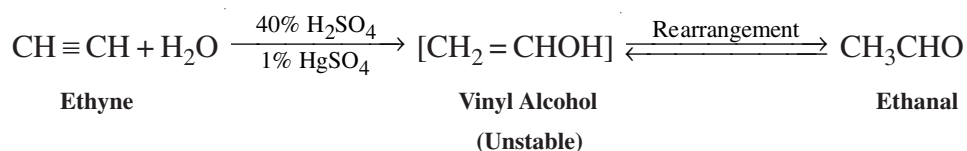
    $$CH \equiv CH + H_2 \xrightarrow[573\ K]{\text{Ni or Pt or Pd}} CH_2 = CH_2 \xrightarrow{\text{H}_2 + \text{Ni or Pt or Pd}} CH_3 - CH_3$$

    (ii) Addition of Halogens : When halogens are added to alkynes, they form 1,2-dihaloalkenes and 1,1,2,2-tetrahaloalkanes.

    $$CH \equiv CH \xrightarrow{\text{Br}_2\ \text{in CCl}_4} CHBr = CHBr \xrightarrow{\text{Br}_2\ \text{in CCl}_4} CHBr_2 - CHBr_2$$
    Ethyne 1,2-Dibromoethene 1,1,2,2-Tetrabromoethane

    (iii) Addition of Halogen Acids (HX) : Addition of HBr to ethyne is as follows :

    $$CH \equiv CH \xrightarrow{\text{HBr}} CH_2 = CHBr \xrightarrow{\text{HBr}} CH_3 - CHBr_2$$
    Ethyne **Bromoethene** **1,1–Dibromoethane**

    (iv) Addition of Water : Addition of water takes place in the presence of mineral acids like H_2SO_4 and in the presence of Hg^{2+} as the catalyst.
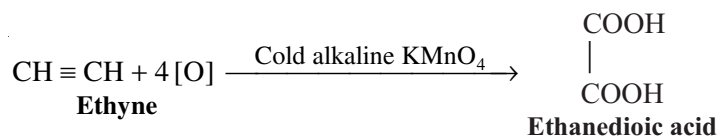
    $$CH \equiv CH + H_2O \xrightarrow[1\%\ \text{HgSO}_4]{40\%\ \text{H}_2\text{SO}_4} [CH_2 = CHOH] \underset{\longleftarrow}{\xrightarrow{\text{Rearrangement}}} CH_3CHO$$
    Ethyne **Vinyl Alcohol** **Ethanal**
    (Unstable)

    (v) Addition of H_2SO_4: Conc. H_2SO_4 adds to ethyne as shown below.

    $$CH \equiv CH \xrightarrow{\text{conc. H}_2\text{SO}_4} CH_2 = CHHSO_4 \xrightarrow{\text{H}_2\text{SO}_4} CH_3 - CH\ (HSO_4)_2$$
    Vinyl hydrogen sulphate **Ethylidene hydrogen sulphate**

2. **Oxidation** : Alkynes undergo oxidation with oxygen, $KMnO_4$ and ozone.

    (i) **Oxidation with $KMnO_4$**

    $$CH \equiv CH + 4\,[O] \xrightarrow{\text{Cold alkaline KMnO}_4} \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$
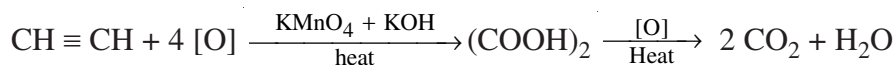   **Ethyne** **Ethanedioic acid**

   The colour of alkaline solution of $KMnO_4$ is discharged on reaction with alkynes. Alkynes on heating with alkaline $KMnO_4$ give carboxylic acids.

    $$R - C \equiv C - R' \xrightarrow[\text{heat}]{\text{KMnO}_4 + \text{KOH}} RCOOH + R'\,COOH$$
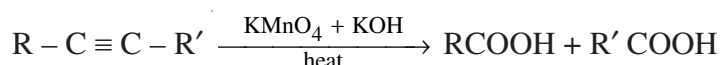
However, ethyne, on similar treatment, gives carbon dioxide and water.

$$CH \equiv CH + 4\ [O] \xrightarrow[\text{heat}]{\text{KMnO}_4 + \text{KOH}} (COOH)_2 \xrightarrow[\text{Heat}]{[O]} 2\ CO_2 + H_2O$$

Combustion : Combustion of ethyne in excess of oxygen or air gives carbon dioxide and water as shown below :

$$2\ C_2H_2 + 5\ O_2 \xrightarrow{\text{heat}} 4\ CO_2 + 2\ H_2O \quad \Delta H = -1300\ KJ\ mol^{-1}$$
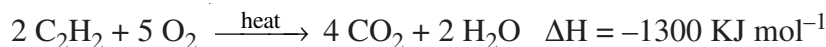
Ozonolysis : On ozonolysis, alkynes give dicarbonyl compounds at the position of C≡C without breaking the chain of carbon atoms as shown below:
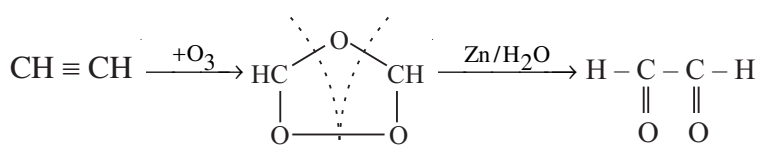
3. **Formation of Acetylides :** Ethyne forms precipitates of copper and silver acetylides when passed through ammonical solution of cuprous chloride and ammonical silver nitrate, respectively.

$$CH \equiv CH + 2Cu(NH_3)_2 \longrightarrow CuC \equiv CCu + 2\ NH^+_4 + 2\ NH_3$$
Cuprous acetylide (red)

$$CH \equiv CH + 2Ag(NH_3)_2 \longrightarrow AgC \equiv CAg + 2\ NH^+_4 + 2\ NH_3$$
Silver acetylide (white)
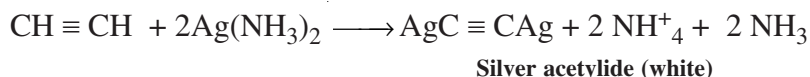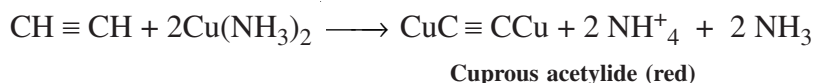
24.3.4 Acidic Nature of Ethyne

The acidic nature of hydrocarbons can be determined with the help of the percentage (%) of *s*-character of the hydrocarbon. The greater the percentage of *s*-character of a hydrocarbon, the more will be its acidic nature.

Table 24.2 : % *s*-Character of hyrid orbitals in Hydrocarbons

Hydrocarbon	Type of hybridization	(%) s-character
Alkanes	sp^3	25%
Alkenes	sp^2	33.3%
Alkynes	sp	50%

As alkynes have 50% *s*- character, they are the most acidic in nature. An *sp*-hybridized carbon atom is more electronegative than sp^2 or sp^3 carbon atoms. Due to greater electronegativity of *sp* hybridized carbon atom in ethyne, hydrogen atom is less tightly held by the carbon and hence, it can be removed as a proton (H^+) by a strong base like sodium metal and sodamide. **The following reactions**
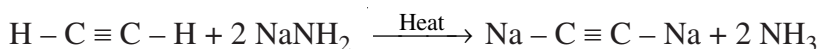
of ethyne with sodium and sodamide confirm its acidic nature. In these reactions, disodium acetylide is formed.

$$H - C \equiv C - H + 2\, Na \xrightarrow{\text{Heat}} Na - C \equiv C - Na + H_2$$

Ethyne (Acetylene)   **Disodium Acetylide**

$$H - C \equiv C - H + 2\, NaNH_2 \xrightarrow{\text{Heat}} Na - C \equiv C - Na + 2\, NH_3$$

Ethyne   **Sodamide**   **Disodium Acetylide**

24.3.5 Uses of Alkynes

Ethyne (acetylene) is used for producing oxyacetylene flame (2800ºC) which is used for for welding and cutting of iron and steel. It is also used for artificial ripening of fruits and vegetables. It also finds use in the production of a number of other organic compounds such as ethanal, ethanoic acid, ethanol, synthetic rubbers and synthetic fibre *orlon*.

24.3.6 Distinction Between Alkanes, Alkenes and Alkynes

The folloiwng table shows different tests for distinction between alkanes, alkenes and alkynes :

Table 24.3 : Tests for identification of alkanes, alkenes and alkynes

S.No	Test	Alkanes	Alkenes	Alkynes
1.	Add bromine dissolved in carbon tetrachloride.	No change	Reddish brown colour of Br_2 is discharged	Reddish brown colour of Br_2 is discharged
2.	Add alkaline solution of $KMnO_4$ (Baeyer's reagent)	No change	Purple colour of $KMnO_4$ is discharged	Purple colour of $KMnO_4$ is discharged
3.	Add ammonical solution of silver nitrate	No change	No change	White ppt. of silver acetylide is formed
4.	Add ammonical solution of cuprous chloride (Cu_2Cl_2)	No change	No change	Red ppt. of cuprous acetylide is formed

INTEXT QUESTIONS 24.3

1. How is ethyne prepared from calcium carbide?
2. Give one reaction to confirm the acidic nature of ethyne.
3. What is the percentage of *s*-character in ethane, ethene and ethyne?

24.4 AROMATIC HYDROCARBONS

Till now, we have explained various methods of preparation of aliphatic hydrocarbons. Now, we shall deal with an aromatic hydrocarbon (benzene) in detail. It is one of the major components obtained by the destructive distillation of coal as shown in Fig. 24.1
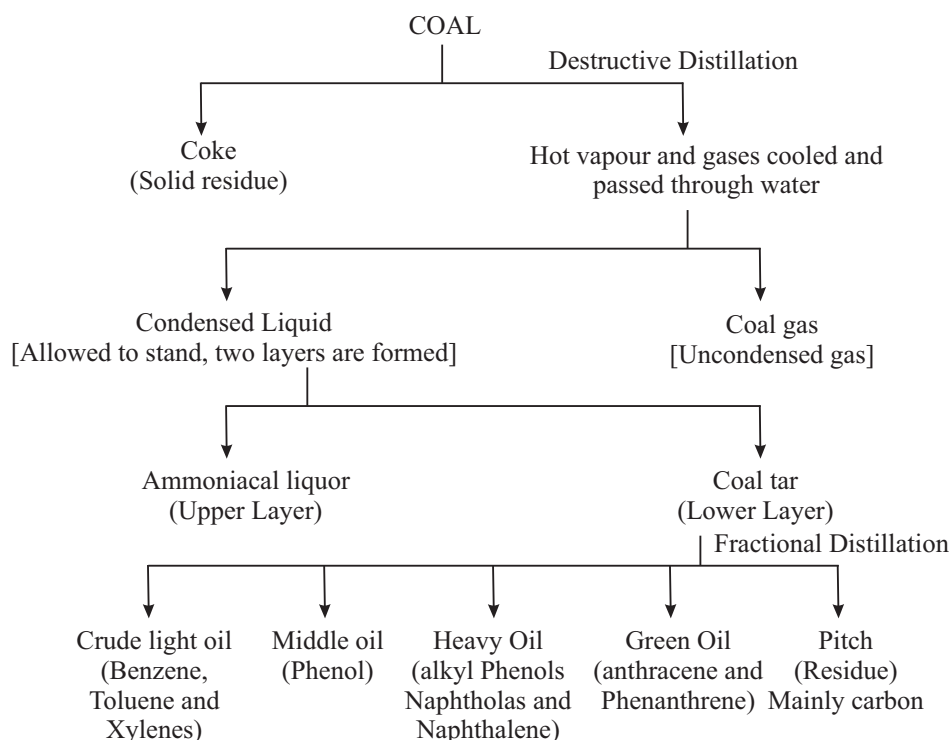
COAL

Destructive Distillation

Coke
(Solid residue)

Hot vapour and gases cooled and
passed through water

Condensed Liquid
[Allowed to stand, two layers are formed]

Coal gas
[Uncondensed gas]

Ammoniacal liquor
(Upper Layer)

Coal tar
(Lower Layer)

Fractional Distillation

Crude light oil
(Benzene,
Toluene and
Xylenes)

Middle oil
(Phenol)

Heavy Oil
(alkyl Phenols
Naphtholas and
Naphthalene)

Green Oil
(anthracene and
Phenanthrene)

Pitch
(Residue)
Mainly carbon

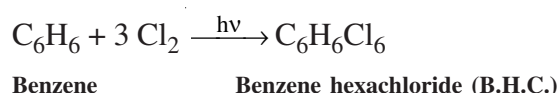**Fig. 24.1 :** *Destructive Distillation of coal*

24.4.1 Structure of Benzene

The molecular formula of benzene is C_6H_6 which indicates that benzene is an unsaturated hydrocarbon. The unsaturation in benzene can be verified by the following reactions.

(i) Benzene undergoes the addition of H_2 in the presence of Ni or Pt as catalyst.

$$C_6H_6 + 3H_2 \xrightarrow{\text{Ni or Pt}} C_6H_{12}$$

Benzene   **Cyclohexane**
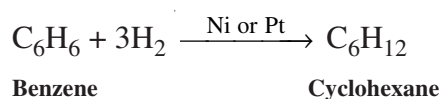
(ii) Benzene undergoes the addition of chlorine in the presence of sunlight.

$$C_6H_6 + 3\,Cl_2 \xrightarrow{h\nu} C_6H_6Cl_6$$

Benzene   **Benzene hexachloride (B.H.C.)**

Notes

Benzene does not respond to the tests of unsaturation which are shown by alkenes and alkynes i.e., both the alkenes and the alkynes decolourize bromine water and alkaline solution of potassium permanganate (Bayer's Reagent). However, benzene undergoes substitution reactions.

e.g.
$$C_6H_6 + Br_2 \xrightarrow{\text{Fe or FeCl}_3} C_6H_5Br + HBr$$

Benzene   **Bromobenzene**

Notes
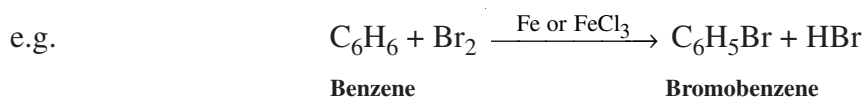
Kekule Structure : A ring structure for benzene was proposed by Kekule in 1865. According to him, six carbon atoms are joined to each other by alternate single and double bonds to form a hexagon ring. As the proposed structure of benzene has three double bonds, so its properties should resemble with the properties of alkenes. But the chemical properties of benzene are different from alkenes.


or
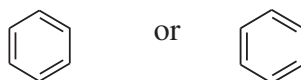
As Kekule's structure contains three single bonds and three double bonds, one may expect that in benzene there should be two different bond lengths i.e. 154 pm for C-C single bond and 134 pm for C=C double bond. But the experimental studies show that benzene is regular hexagon with an angle of 120^0 and all the carbon-carbon bond lengths are equal i.e. 139 pm.

If Kekule's structure is to be taken as a true structure, then benzene should form only one monosubstitution product and two ortho distubstitution products, shown below as (a) and (b).
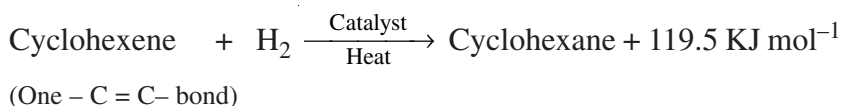

(a)   (b)

In structure (a), the two halogen atoms are on the doubly bonded carbon atoms, whereas in structure (b), the two halogen atoms are on the singly bonded carbon atoms. As per the Kekule's structure these two isomers (a and b) should exist and show different properties. But, in reality, only one ortho disubstituted product exists. In order to explain this, Kekule proposed a dynamic equilibrium between the two structures.
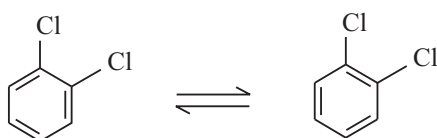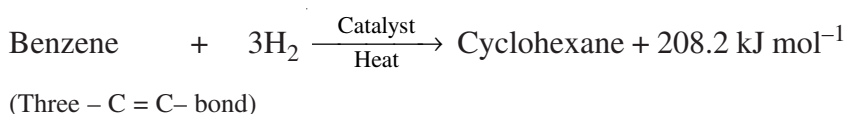

Kekule's structure does not explain the stability of benzene and its some unusual reactions. Resonance can explain the unusual behaviour of benzene. Let us now study about resonance.

Resonance : *The phenomenon by virtue of which a single molecule can be represented in two or more structures is called resonance.* The actual structure is the resonance hybrid of all the canonical or resonating structure. (see lesson 25)

Heat of hydrogenation data provides proof for resonance stabalization in benzene. **The heat of hydrogenation is the amount of heat liberated when hydrogen is added to one mole of an unsaturated compound in the presence of a catalyst.**

$$\text{Cyclohexene} \quad + \quad H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 119.5 \text{ KJ mol}^{-1}$$

(One – C = C– bond)

If the three double bonds in benzene do not interact, then it should behave like cyclohexatriene and the amount of heat liberated on adding there molecules of hydrogen should be 358.5 KJ mol^{-1}. But, the actual heat of hydrogenation of benzene is 208.2 kJ mol^{-1}.

$$\text{Benzene} \quad + \quad 3H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 208.2 \text{ kJ mol}^{-1}$$

(Three – C = C– bond)

This difference of (358.5 – 208.2) 150.3 kJ mol^{-1} in the heat of hydrogenation is the measure of stability of benzene. Benzene acquires stability due to resonance and hence, this energy is called resonance energy of benzene.

Thus, the structure of benzene can be described as a resonance hybrid of two equivalent forms, (I) and (II). None of these two forms is correct by itself.

I   II   III

Resonance forms of benzene   Resonance hybrid structure showing delocalisation of electrons
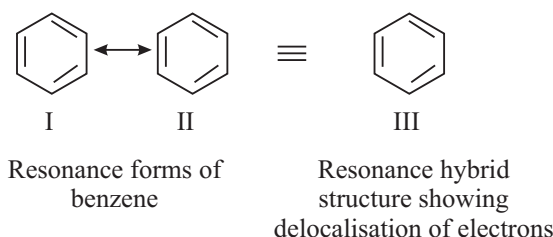
and the actual structure is intermediate of these two forms. This can be represented as III where the circle inside the ring indicates the equivalence of the carbon-carbon bonds. The carbon-carbon bond length has been found to be 139 pm. which is same for all the carbon-carbon bonds in benzene. Also, this value of bond length is intermediate between the typical C—C single (154 pm) and C=C double bond (134 pm) lengths.

Notes

Notes

Molecular Orbital Picture of Benzene

All the six carbon atoms of benzene are sp^2 hybridised. All C—C—C bond angles are 120° and there is a p orbital on each carbon atom. All the six p-orbitals are perpendicular to the plane of the six-membered carbon ring. The overlap of these p orbitals leads to a delocalised electron cloud above and below the place of the carbon ring. This is shown below in IV and V.

IV   V
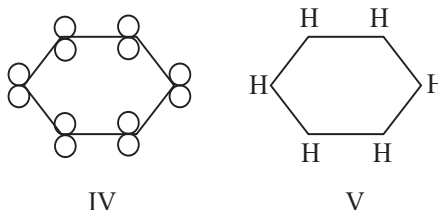
24.4.2 Aromaticity

So far you have studied that benzene

- is a cyclic conjugated molecule.

- is unusually stable.

- is planar in nature and its all C — C bond lengths are equal.

- can be represented as a resonance hybrid of two structures.

- undergoes substitution reactions rather than addition reactions.

Though the above properties indicate that benzene is *aromatic* in nature. But to complete the argument for its aromatic nature, we have to check whether it follows **Huckel's rule** or not. According to **Huckel rule** – a molecule is aromatic only if it has a planar, monocyclic system of conjugated $4n + 2$ π electrons where $n = 0$, 1, 2, 3, …. Thus, molecules with 2, 6, 10, 14 π … electrons can be aromatic.

For example, in Benzene, C_6H_6

No. of π electrons = $6e^-$ (3π bonds $\times$ $2e^-$ = $6e^-$)

Using formula,

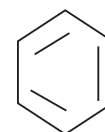$4n + 2$ = No. of π electrons

$4n + 2 = 6$ gives n = 1

Hence, benzene is aromatic.
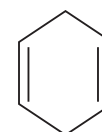
Let us take another example, i.e. 1,4-hexadiene

For this compound, No. of π electron = $4e^-$ (2π bond $\times$ $2e^-$)

Using formula,

$4n + 2$ = No. of π electrons


Benzene

Hex-1, 4-diene

$4n + 2 = 4$

$$n = \frac{2}{4} = 0.5$$

Hence, the value of n is 0.5. So, it does not obey Huckel rule and is non aromatic.

### 24.4.3 Physical Properties of Aromatic Hydrocarbons

1. Benzene and its homologues are colourless liquids having a characteristic odour.

2. They are immiscible in water but are miscible in all proportions with organic solvents such as alcohol, ether, petrol, etc. They dissolve fats and many other organic substances.

3. Most of the aromatic hydrocarbons are lighter than water.

4. Their boiling points show a gradual increase with increasing molecular mass e.g. benzene (b.p. 353 K), toluene (b.p. 383 K) and ethylbenzene (b.p. 409 K) and so on.

Notes

Benzene
(b.p. 353 K)

Toluene
**(b.p. 383 K)**

Ethylbenzane
(b.p. 409 K)
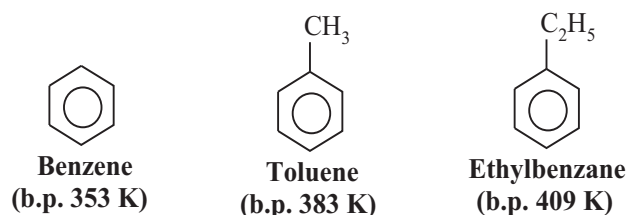
24.4.4 Chemical Properties of Aromatic Hydrocarbons

Aromatic hydrocarbons generally undergo electrophilic substitution reactions in which hydrogen atom of the aromatic ring is replaced by an electrophile. Such reactions are discussed below in detail taking benzene as an example.

(i)   Halogenation : The reaction in which a hydrogen atom of benzene is replaced by a halogen atom is called halogenation of benzene. Halogenation takes place in the presence of iron, or ferric halides (FeX_3, where X = Cl or Br).

$$\text{Benzene} + X_2 \xrightarrow{\text{Fe or } FeX_3} \text{Halobenzene} + HX$$
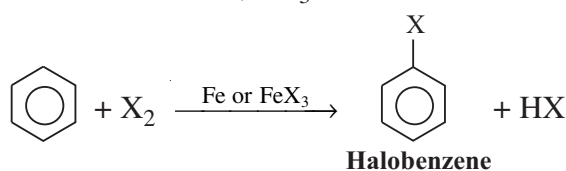
Halobenzene

In case of iodination the HI formed can reduce iodobenzene back to be benzene which is prevented by carrying out this reaction in the presence of HNO_3 or HIO_3. These acids react with HI as soon as it is formed.
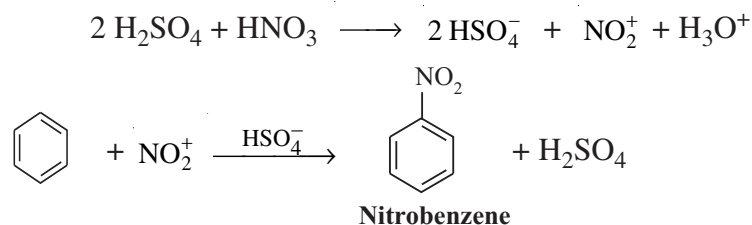
$$2 \text{ Benzene} + I_2 \xrightarrow{\text{conc. } HNO_3} 2 \text{ Iodobenzene}$$

Iodobenzene
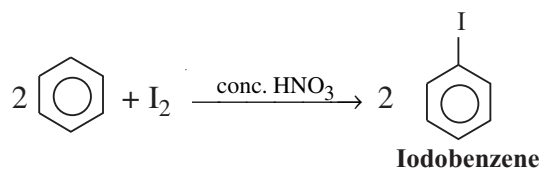
Notes

(ii) **Nitration :** The chemical reaction in which a hydrogen atom of benzene ring is replaced by $-NO_2$ group, is called nitration. It is carried out in the presence of nitrating mixture, i.e. a mixture of conc. HNO_3 and conc. H_2SO_4. Nitronium ion (NO_2^+) so formed acts as an electrophile.

$$2 H_2SO_4 + HNO_3 \longrightarrow 2 HSO_4^- + NO_2^+ + H_3O^+$$

Nitrobenzene

(iii) **Sulphonation :** The chemical reaction in which the hydrogen atom of benzene is replaced by $-SO_3H$ group when benzene is heated with fuming sulphuric acid (oleum), is called sulphonation.

**Fuming sulphuric acid**   **Benzenesulphonic acid**
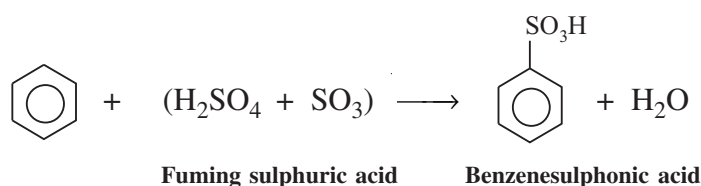
(iv) **Friedel–Craft's Reactions :** In Friedel-Craft's reaction, benzene is heated either with alkyl halide **(alkylation)** or acyl halide **(acylation)** in the presence of a catalyst (anhydrous $AlCl_3$). The products formed are alkyl or acyl derivatives of benzene.

Alkylation

Benzene   **Chloromethane**   **Toluene**

Acylation

**Benzene**   **acetyl chloride**   **Acetophenone**
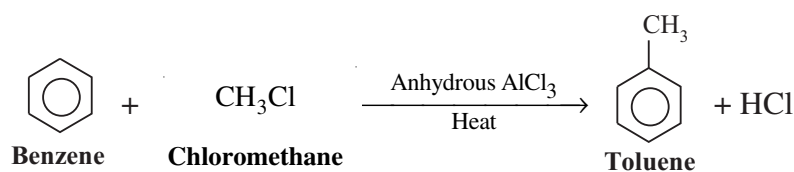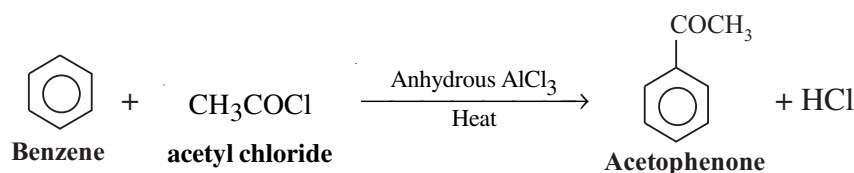
24.4.5 Directive Influence of Functional Groups

In case of substituted aromatic compounds, the functional group(s) already present directs the next incoming group to a particular position in the aromatic ring.. It is called directive influence of the group already attached to the benzene ring. For example, phenol on chlorination gives a mixture of *ortho* – chlorophenol and *para*– chlorophenol as – OH groups is an *ortho* and *para* directing group.
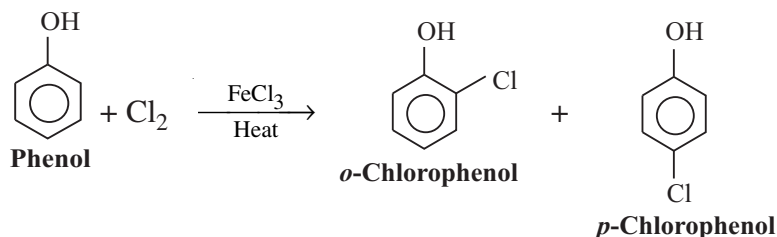
In case of nitrobenzene, we find that $-NO_2$ group is a *meta* directing group and hence, the product obtained on chlorination is *meta*-chloronitrobenzene.
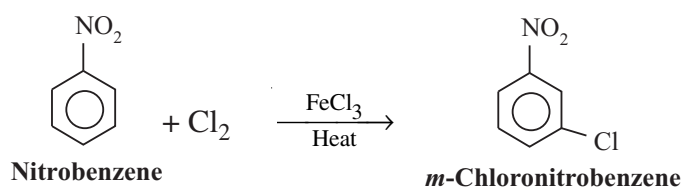
24.4.6 Carcinogenicity & Toxicity

There exist several aromatic compounds-many of them being very important for the life while there are some others which are harmful. A large number of them are toxic in nature. For example benzene is carcinogenic in nature.

Another such hydrocarbon, is benzo[α] pyrene which has been found in cigarette smoke and in the exhaust from automobiles. This compound is also carcinogenic and can cause skin cancer in mice.
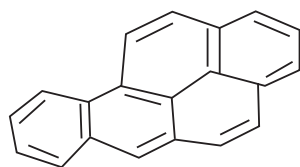
Benzo [a] pyrene

24.4.7 Uses of Aromatic Hydrocarbons

Benzene is used as a solvent for several organic compounds and thus, acts as a medium for carrying out synthetic reactions. It is the basic aromatic hydrocarbon and can be converted to other organic compounds by carrying out substitution in the benzene ring. **Toluene,** a higher homologue of the benzene, finds its uses for dry-cleaning, as a solvent, and as a starting material for the manufacture of dyes, drugs, explosive (trinitrotoluene, T.N.T.), benzaldehyde, benzoic acid etc.

Notes

INTEXT QUESTIONS 24.4

1. What is the value of resonance energy of benzene?

2. Name the product formed when :

    (i) benzene reacts with chlorine in the presence of light.

    (ii) phenol reacts with chlorine in the presence of $FeCl_3$.

    (iii) nitrobenzene reacts with chlorine in the presence of $FeCl_3$.

3. Classify the following into *o*-and *p*- or *m*-directing groups :

    $-NH_2$, $-NO_2$, $-Cl$, $-\overset{\overset{O}{\|}}{C}-R$, $-OH$, $-SO_3H$

WHAT YOU HAVE LEARNT

- Alkanes can be prepared by (i) the reduction of haloalkanes, (ii) action of water or alcohol on Grignard's reagent, (iii) Wurtz reaction and (iv) hydrogenation of unsaturated hydrocarbons.

- Physical properties of hydrocarbons depend on the intermolecular forces of attraction. which in turn depend upon the shapes of molecules and their surface area.

- The melting points of hydrocarbons depends upon the symmetry of the molecules i.e. hydrocarbons with even number of carbon atoms are more symmetrical and have higher melting points.

- Rotation about carbon-carbon single bond leads to various conformations of a molecule. Ethane has many conformations out of which the staggered conformation is the most stable one and the eclipsed conformation is the least stable one.

- Alkenes can be prepared by dehydrohalogenation of alkyl halides and by dehydration of alcohols.

- Alkenes and alkynes undergo addition reactions e.g. addition of hydrogen, halogens, halogen acids, water, sulphuric acid etc. due to the presence of carbon-carbon double or triple bonds.

- Addition of halogen acids and other unsymmetrical reagents to unsymmetrical alkenes and alkynes takes place according to the Markownikoff's rule.

- Alkenes undergo polymerization on heating under pressure.

- All hydrocarbons (saturated as well as unsaturated) form CO_2 and H_2O on combustion and liberate energy.

- An alkaline solution of $KMnO_4$ can oxidize alkenes and alkynes forming different products such as carboxylic acids, aldehydes and/or ketones and carbon dioxide.

- Ozone can oxidize unsaturated hydrocarbons (alkenes and alkynes) forming ozonides which when further reacted with water in the presence of zinc dust either form aldehydes or ketones or both.

- Reaction of ozone with alkenes can be used to determine the position of double bond.

- Ethyne can be prepared by the action of water on calcium carbide and by dehydrogenation of dihaloalkanes.

- Alkynes are acidic in nature due to sp-hybridization of carbon atoms. Because sp hybridized carbon atoms are more electronegative than sp^2 and sp^3, and the bond between C—H is weakened. Hence, hydrogen atoms in alkynes can be replaced by certain metal atoms.

- Alkanes, alkenes and alkynes can be distinguished by using:

    a) Br_2 dissolved in carbon tetrachloride.

    b)   Ammoniacal solution of $AgNO_3$

    c)   Ammoniacal solution of Cu_2Cl_2

    d)   Alkaline solution of $KMnO_4$

- Benzene is obtained by destructive distillation of coal.

- A ring structure of benzene was suggested by Kekule. Actual structure of benzene is the resonance hybrid of the canonical structures.

- Aromatic hydrocarbons undergo substitution reactions i.e. the reactions in which hydrogen atom of hydrocarbons is replaced by another atom or group of atoms. Halogenation, sulphonation, nitration and Friedel Craft's reaction are substitution reactions of benzene.

- The position of second substituent on a benzene ring depends upon the nature of the group already present.

Notes

TERMINAL EXERCISE

1.   What happens when : (Write chemical equations)

    (i)   Iodoethane is heated with HI in the presence of red phosphorus.

    (ii) 2-Chlorobutane reacts with sodium metal.

Notes

   (iii)   Ethyl magnesium bromide is reacted with methyl alcohol (methanol).

   (iv)   2-Chloropropane reacts with alcoholic solution of KOH.

   (v)   1,1-Dichloroethane reacts with alcoholic solution of KOH.

2.   Give reasons for the following :

   (i)   The boiling point of neopentane is less than that of n-pentane.

   (ii)   Stability of benzene ring

   (iii)   Boiling points of hydrocarbons decrease with the increase in branching.

3.   How will you prepare the following?

   (i)   Ethane from ethene

   (ii)   Ethene from ethanol

   (iii)   Cyclohexane from benzene

   (iv)   Methane from sodium acetate

   (v)   Butane from bromoethane

4.   What happens when (write balanced chemical equations):

   (i)   Hydrochloric acid is added to ethene.

   (ii)   Hydrobromic acid (HBr) is added to propene in the presence of benzoyl peroxide.

   (iii)   Benzene reacts with chloromethane in the presence of anhydrous $AlCl_3$.

   (iv) Br_2 is added to ethyne.

   (v)   Methane is oxidized with oxygen in the presence of copper at 475K and a high pressure of 120 atm.

5.   How are the following conversions carried out?

   (i)   Ethyne to ethane

   (ii)   Benzene to nitrobenzene

   (iii)   Ethyl alcohol (ethanol) to ethene

   (iv)   Ethyne to ethanedioic acid

   (v)   Benzene to *o*-nitrochlorobenzene.

6.   You are provided with three gas jars containing ethane, ethene and ethyne. Give the suitable chemical tests to identify the three hydrocarbons.

7.   What is ozonolysis? How is it used to determine the position of a double bond?

8.   Give reasons for the following :

   (i)   Alkanes do not undergo addition reactions like alkenes and alkynes.

   (ii)   Ethyne is more acidic than ethane.

(iii) Ethene undergoes polymerization but not ethane.

(iv) Benzene undergoes electrophilic substitution reactions.

ANSWERS TO INTEXT QUESTIONS

Notes

24.1

1. They are used as fuels and to prepare detergents, dyes, drugs, explosives etc. Hydrocarbons are used to prepare some important organic compounds like alcohols, aldehydes, carboxylic acids etc.

2. The alkyl magnesium halides (R-MgX) are called Grignard's reagent.

3. Easily replaceable hydrogen present in a molecule is called active hydrogen.

4. The physical properties of hydrocarbons differ from one another due to difference in molecular mass, surface area, intermolecular force of attraction.

5. Methane and ethane are gases, pentane and hexane are liquids.

6. Three isomers of pentane are : *n*-pentane, isopentane and neopentane.

7. *n*-pentane has higher boiling point than n-butane.

8. $C_3H_8 + 5 O_2 \longrightarrow 3 CO_2 + 4 H_2O$
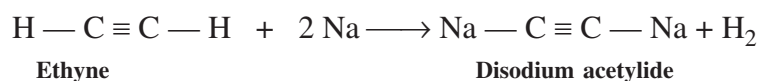
24.2

1. *Trans*-2-butene has higher boiling point than *cis*-isomer.

2. Ethane-1, 2-diol

3. Hydrogen in presence of catalist Ni, Pt or Pd

4. Epoxyethane is produced.

24.3

1. Calcium carbide is reacted with water to prepare ethyne.

    $CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$
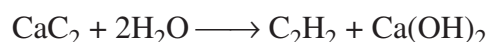
2. Reaction with sodium metal confirms the acidic nature of ethyne.

    $H-C \equiv C-H + 2 Na \longrightarrow Na-C \equiv C-Na + H_2$
    Ethyne   **Disodium acetylide**

3. The *s*-character in : Ethane = 25%,
    Ethene = 33%,
    Ethyne = 50%

Notes

24.4

1. The resonance energy of benzene is 150.3 KJ mol^{-1}.

2. (i) Benzene hexachloride (BHC).

    (ii) *o*-Chlorophenol and *p*-chlorophenol.

    (iii) *m*-Chloronitrobenzene.

3. *o* – and *p* – directing groups : –NH$_2$, –Cl, – OH
    m-directing groups : NO$_2$, $-\overset{\|}{\underset{O}{C}}-R$, – SO$_3$H