UNIT 13

11083CH13

HYDROCARBONS

Objectives

After studying this unit, you will be able to

- name hydrocarbons according to IUPAC system of nomenclature;
- recognise and write structures of isomers of alkanes, alkenes, alkynes and aromatic hydrocarbons;
- learn about various methods of preparation of hydrocarbons;
- distinguish between alkanes, alkenes, alkynes and aromatic hydrocarbons on the basis of physical and chemical properties;
- draw and differentiate between various conformations of ethane;
- appreciate the role of hydrocarbons as sources of energy and for other industrial applications;
- predict the formation of the addition products of unsymmetrical alkenes and alkynes on the basis of electronic mechanism;
- comprehend the structure of benzene, explain aromaticity and understand mechanism of electrophilic substitution reactions of benzene;
- predict the directive influence of substituents in monosubstituted benzene ring;
- learn about carcinogenicity and toxicity.

"Hydrocarbons are the important sources of energy."

The term 'hydrocarbon' is self-explanatory which means compounds of carbon and hydrogen only. Hydrocarbons play a key role in our daily life. You must be familiar with the terms 'LPG' and 'CNG' used as fuels. LPG is the abbreviated form of liquified petroleum gas whereas CNG stands for compressed natural gas. Another term 'LNG' (liquified natural gas) is also in news these days. This is also a fuel and is obtained by liquifaction of natural gas. Petrol, diesel and kerosene oil are obtained by the fractional distillation of petroleum found under the earth's crust. Coal gas is obtained by the destructive distillation of coal. Natural gas is found in upper strata during drilling of oil wells. The gas after compression is known as compressed natural gas. LPG is used as a domestic fuel with the least pollution. Kerosene oil is also used as a domestic fuel but it causes some pollution. Automobiles need fuels like petrol, diesel and CNG. Petrol and CNG operated automobiles cause less pollution. All these fuels contain mixture of hydrocarbons, which are sources of energy. Hydrocarbons are also used for the manufacture of polymers like polythene, polypropene, polystyrene etc. Higher hydrocarbons are used as solvents for paints. They are also used as the starting materials for manufacture of many dyes and drugs. Thus, you can well understand the importance of hydrocarbons in your daily life. In this unit, you will learn more about hydrocarbons.

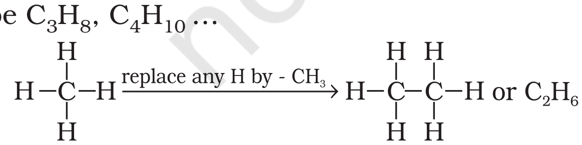
13.1 CLASSIFICATION

Hydrocarbons are of different types. Depending upon the types of carbon-carbon bonds present, they can be classified into three main categories – (i) saturated

(ii) unsaturated and (iii) aromatic hydrocarbons. Saturated hydrocarbons contain carbon-carbon and carbon-hydrogen single bonds. If different carbon atoms are joined together to form open chain of carbon atoms with single bonds, they are termed as alkanes as you have already studied in Unit 12. On the other hand, if carbon atoms form a closed chain or a ring, they are termed as cycloalkanes. Unsaturated hydrocarbons contain carbon-carbon multiple bonds – double bonds, triple bonds or both. Aromatic hydrocarbons are a special type of cyclic compounds. You can construct a large number of models of such molecules of both types (open chain and close chain) keeping in mind that carbon is tetravalent and hydrogen is monovalent. For making models of alkanes, you can use toothpicks for bonds and plasticine balls for atoms. For alkenes, alkynes and aromatic hydrocarbons, spring models can be constructed.

13.2 ALKANES

As already mentioned, alkanes are saturated open chain hydrocarbons containing carbon - carbon single bonds. Methane (CH_4) is the first member of this family. Methane is a gas found in coal mines and marshy places. If you replace one hydrogen atom of methane by carbon and join the required number of hydrogens to satisfy the tetravalence of the other carbon atom, what do you get? You get C_2H_6. This hydrocarbon with molecular formula C_2H_6 is known as ethane. Thus you can consider C_2H_6 as derived from CH_4 by replacing one hydrogen atom by $-CH_3$ group. Go on constructing alkanes by doing this theoretical exercise i.e., replacing hydrogen atom by $–CH_3$ group. The next molecules will be C_3H_8, C_4H_{10} ...



These hydrocarbons are inert under normal conditions as they do not react with acids, bases and other reagents. Hence, they were earlier known as paraffins (*latin : parum,* little; *affinis,* affinity). Can you think of the general formula for alkane family or **homologous series**? If we examine the formula of different alkanes we find that the general formula for alkanes is C_nH_{2n+2}. It represents any particular homologue when *n* is given appropriate value. Can you recall the structure of methane? According to VSEPR theory (Unit 4), methane has a tetrahedral structure (Fig. 13.1), in which carbon atom lies at the centre and the four hydrogen atoms lie at the four corners of a regular tetrahedron. All H-C-H bond angles are of 109.5°.

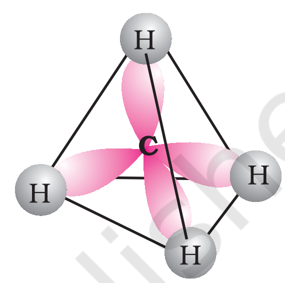


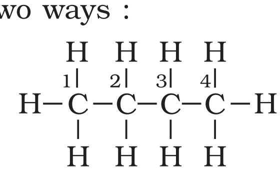
Fig. 13.1 *Structure of methane*

In alkanes, tetrahedra are joined together in which C-C and C-H bond lengths are 154 pm and 112 pm respectively (Unit 12). You have already read that C–C and C–H σ bonds are formed by head-on overlapping of sp^3 hybrid orbitals of carbon and 1*s* orbitals of hydrogen atoms.

13.2.1 Nomenclature and Isomerism

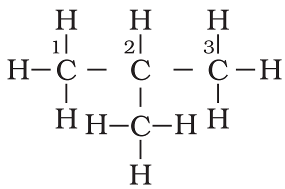
You have already read about nomenclature of different classes of organic compounds in Unit 12. Nomenclature and isomerism in alkanes can further be understood with the help of a few more examples. Common names are given in parenthesis. First three alkanes – methane, ethane and propane have only one structure but higher alkanes can have more than one structure. Let us write structures for C_4H_{10}. Four carbon atoms of C_4H_{10} can be joined either in a continuous chain or with a branched chain in the following two ways :

I



Butane (*n*- butane), (b.p. 273 K)

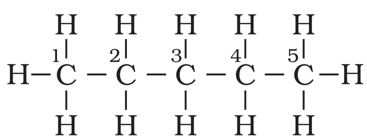
II



2-Methylpropane (isobutane)
(b.p.261 K)

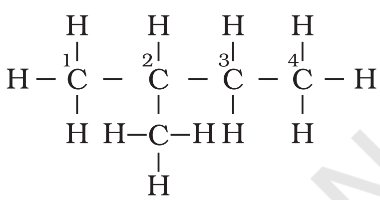
In how many ways, you can join five carbon atoms and twelve hydrogen atoms of C_5H_{12}? They can be arranged in three ways as shown in structures III–V

III



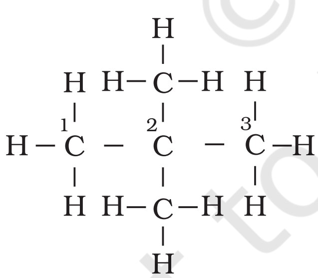
Pentane (*n*-pentane)
(b.p. 309 K)

IV



2-Methylbutane (isopentane)
(b.p. 301 K)

V



2,2-Dimethylpropane (neopentane)
(b.p. 282.5 K)

Structures I and II possess same molecular formula but differ in their boiling points and other properties. Similarly structures III, IV and V possess the same molecular formula but have different properties. Structures I and II are isomers of butane, whereas structures III, IV and V are isomers of pentane. Since difference in properties is due to difference in their structures, they are known as **structural isomers**. It is also clear that structures I and III have continuous chain of carbon atoms but structures II, IV and V have a branched chain. Such structural isomers which differ in chain of carbon atoms are known as **chain isomers**. Thus, you have seen that C_4H_{10} and C_5H_{12} have two and three chain isomers respectively.

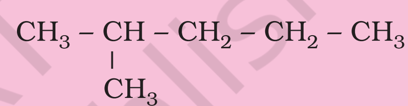
Problem 13.1

Write structures of different chain isomers of alkanes corresponding to the molecular formula C_6H_{14}. Also write their IUPAC names.

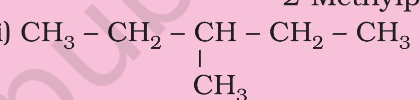
Solution

(i) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

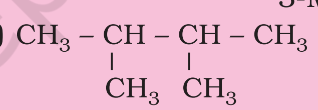
n-Hexane

(ii) 

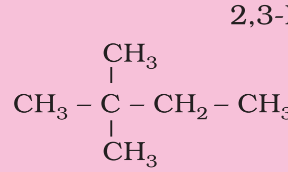
2-Methylpentane

(iii) 

3-Methylpentane

(iv) 

2,3-Dimethylbutane

(v) 

2,2 - Dimethylbutane

Based upon the number of carbon atoms attached to a carbon atom, the carbon atom is termed as primary (1°), secondary (2°), tertiary (3°) or quaternary (4°). Carbon atom attached to no other carbon atom as in methane or to only one carbon atom as in ethane is called primary carbon atom. Terminal carbon atoms are always primary. Carbon atom attached to two carbon atoms is known as secondary. Tertiary carbon is attached to three carbon atoms and neo or quaternary carbon is attached to four carbon atoms. Can you identify 1°, 2°, 3° and 4° carbon atoms in structures I to V ? If you go on constructing structures for higher alkanes, you will be getting still larger number of isomers. C_6H_{14} has got five isomers and C_7H_{16} has nine. As many as 75 isomers are possible for $C_{10}H_{22}$.

In structures II, IV and V, you observed that $–CH_3$ group is attached to carbon atom numbered as 2. You will come across groups like $–CH_3$, $–C_2H_5$, $–C_3H_7$ etc. attached to carbon atoms in alkanes or other classes of compounds. These groups or substituents are known as alkyl groups as they are derived from alkanes by removal of one hydrogen atom. General formula for alkyl groups is C_nH_{2n+1} (Unit 12).

Let us recall the general rules for nomenclature already discussed in Unit 12. Nomenclature of substituted alkanes can further be understood by considering the following problem:

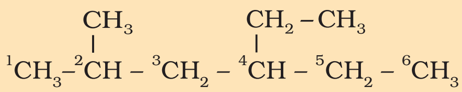
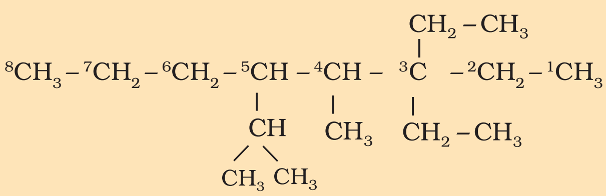
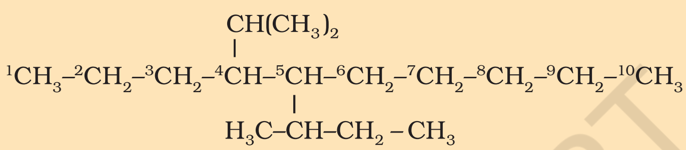
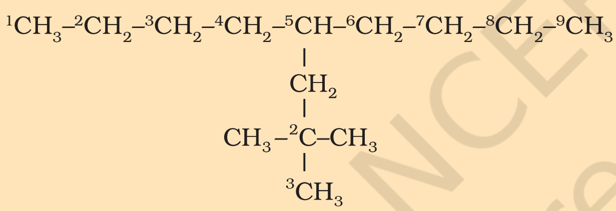
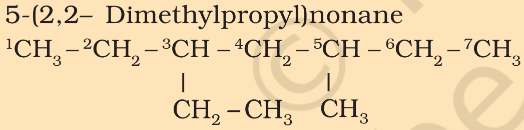
Problem 13.2

Write structures of different isomeric alkyl groups corresponding to the molecular formula C_5H_{11}. Write IUPAC names of alcohols obtained by attachment of –OH groups at different carbons of the chain.

Solution

<table>
<tr><th>Structures of – C_5H_{11} group</th><th>Corresponding alcohols</th><th>Name of alcohol</th></tr>
<tr><td>(i) $CH_3 – CH_2 – CH_2 – CH_2 – CH_2 –$</td><td>$CH_3 – CH_2 – CH_2 – CH_2 – CH_2 – OH$</td><td>Pentan-1-ol</td></tr>
<tr><td>(ii) $CH_3 – CH – CH_2 – CH_2 – CH_3$
|</td><td>$CH_3 – CH – CH_2 – CH_2 – CH_3$
|
OH</td><td>Pentan-2-ol</td></tr>
<tr><td>(iii) $CH_3 – CH_2 – CH – CH_2 – CH_3$
|</td><td>$CH_3 – CH_2 – CH – CH_2 – CH_3$
|
OH</td><td>Pentan-3-ol</td></tr>
<tr><td>CH_3
|
(iv) $CH_3 – CH – CH_2 – CH_2 –$</td><td>$CH_3$
|
$CH_3 – CH – CH_2 – CH_2 – OH$</td><td>3-Methyl-butan-1-ol</td></tr>
<tr><td>CH_3
|
(v) $CH_3 – CH_2 – CH – CH_2 –$</td><td>$CH_3$
|
$CH_3 – CH_2 – CH – CH_2 – OH$</td><td>2-Methyl-butan-1-ol</td></tr>
<tr><td>CH_3
|
(vi) $CH_3 – C – CH_2 – CH_3$
|</td><td>CH_3
|
$CH_3 – C – CH_2 – CH_3$
|
OH</td><td>2-Methyl-butan-2-ol</td></tr>
<tr><td>CH_3
|
(vii) $CH_3 – C – CH_2 –$
|
CH_3</td><td>CH_3
|
$CH_3 – C – CH_2OH$
|
CH_3</td><td>2,2- Dimethyl-propan-1-ol</td></tr>
<tr><td>CH_3
| |
(viii) $CH_3 – CH – CH – CH_3$</td><td>CH_3 OH
| |
$CH_3 – CH – CH – CH_3$</td><td>3-Methyl-butan-2-ol</td></tr>
</table>

Table 13.1 Nomenclature of a Few Organic Compounds

	Structure and IUPAC Name	Remarks
(a)	 (4 – Ethyl – 2 – methylhexane)	Lowest sum and alphabetical arrangement
(b)	 (3,3-Diethyl-5-isopropyl-4-methyloctane)	Lowest sum and alphabetical arrangement
(c)	 5-*sec*– Butyl-4-isopropyldecane	*sec* is not considered while arranging alphabetically; isopropyl is taken as one word
(d)	 5-(2,2– Dimethylpropyl)nonane	Further numbering to the substituents of the side chain
(e)	 3–Ethyl–5–methylheptane	Alphabetical priority order

Problem 13.3

Write IUPAC names of the following compounds :

(i) $(CH_3)_3\,C\,CH_2C(CH_3)_3$

(ii) $(CH_3)_2\,C(C_2H_5)_2$

(iii) tetra – *tert*-butylmethane

Solution

(i) 2, 2, 4, 4-Tetramethylpentane

(ii) 3, 3-Dimethylpentane

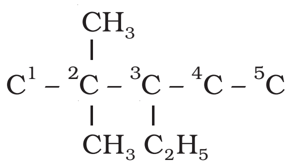
(iii) 3,3-Di-*tert*-butyl -2, 2, 4, 4 - tetramethylpentane

If it is important to write the correct IUPAC name for a given structure, it is equally important to write the correct structure from the given IUPAC name. To do this, first of all, the longest chain of carbon atoms corresponding to the parent alkane is written. Then after numbering it, the substituents are attached to the correct carbon atoms and finally valence of each carbon atom is satisfied by putting the correct number of hydrogen atoms. This can be clarified by writing the structure of 3-ethyl-2, 2–dimethylpentane in the following steps :

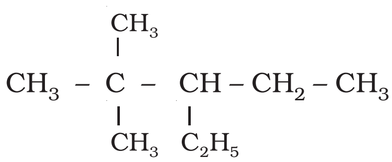
i) Draw the chain of five carbon atoms: C – C – C – C – C

ii) Give number to carbon atoms: $C^1 – C^2 – C^3 – C^4 – C^5$

iii) Attach ethyl group at carbon 3 and two methyl groups at carbon 2



iv) Satisfy the valence of each carbon atom by putting requisite number of hydrogen atoms :



Thus we arrive at the correct structure. If you have understood writing of structure from the given name, attempt the following problems.

Problem 13.4

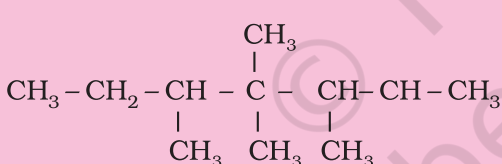
Write structural formulas of the following compounds :

(i) 3, 4, 4, 5–Tetramethylheptane

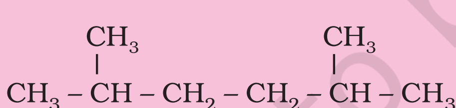
(ii) 2,5-Dimethyhexane

Solution

(i)



(ii)



Problem 13.5

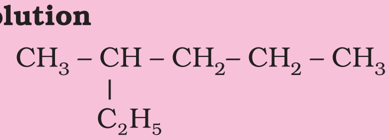
Write structures for each of the following compounds. Why are the given names incorrect? Write correct IUPAC names.

(i) 2-Ethylpentane

(ii) 5-Ethyl – 3-methylheptane

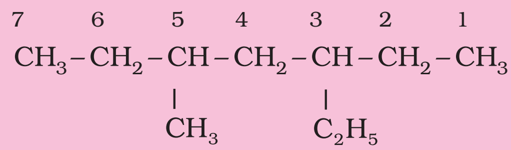
Solution

(i)



Longest chain is of six carbon atoms and not that of five. Hence, correct name is 3-Methylhexane.

(ii)



Numbering is to be started from the end which gives lower number to ethyl group. Hence, correct name is 3-ethyl-5-methylheptane.

13.2.2 Preparation

Petroleum and natural gas are the main sources of alkanes. However, alkanes can be prepared by following methods :

1. From unsaturated hydrocarbons

Dihydrogen gas adds to alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes. This process is called **hydrogenation**. These metals adsorb dihydrogen gas on their surfaces and activate the hydrogen – hydrogen bond. Platinum and palladium catalyse the reaction at room temperature but relatively higher temperature and pressure are required with nickel catalysts.

$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Ethane}}{CH_3-CH_3} \qquad (13.1)$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propane}}{CH_3-CH_2-CH_3} \qquad (13.2)$$

$$\underset{\text{Propyne}}{CH_3-C\equiv C-H} + 2H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{Propane}}{CH_3-CH_2-CH_3} \qquad (13.3)$$

2. From alkyl halides

i) Alkyl halides (except fluorides) on reduction with zinc and dilute hydrochloric acid give alkanes.

$$\underset{\text{Chloromethane}}{CH_3-Cl} + H_2 \xrightarrow{Zn,\ H^+} \underset{\text{Methane}}{CH_4} + HCl \qquad (13.4)$$

$$C_2H_5-Cl + H_2 \xrightarrow{Zn, H^+} C_2H_6 + HCl$$

Chloroethane Ethane (13.5)

$$CH_3CH_2CH_2Cl + H_2 \xrightarrow{Zn, H^+} CH_3CH_2CH_3 + HCl$$

1-Chloropropane Propane (13.6)

ii) Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as **Wurtz reaction** and is used for the preparation of higher alkanes containing even number of carbon atoms.

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} CH_3-CH_3 + 2NaBr$$

Bromomethane Ethane (13.7)

$$C_2H_5Br + 2Na + BrC_2H_5 \xrightarrow{\text{dry ether}} C_2H_5-C_2H_5$$

Bromoethane n-Butane (13.8)

What will happen if two different alkyl halides are taken?

3. From carboxylic acids

i) Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid. This process of elimination of carbon dioxide from a carboxylic acid is known as **decarboxylation**.

$$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Sodium ethanoate

Problem 13.6

Sodium salt of which acid will be needed for the preparation of propane ? Write chemical equation for the reaction.

Solution

Butanoic acid,

$$CH_3CH_2CH_2COO^-Na^+ + NaOH \xrightarrow{CaO} CH_3CH_2CH_3 + Na_2CO_3$$

ii) ***Kolbe's electrolytic method*** An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode.

$$2CH_3COO^-Na^+ + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH \quad (13.9)$$

Sodium acetate

The reaction is supposed to follow the following path :

i) $2CH_3COO^-Na^+ \rightleftharpoons 2CH_3-\overset{O}{\overset{\|}{C}}-O^- + 2Na^+$

ii) **At anode:**

$$2CH_3-\overset{O}{\overset{\|}{C}}-O^- \xrightarrow{-2e^-} 2CH_3-\overset{O}{\overset{\|}{C}}-\ddot{\underset{\cdot\cdot}{O}}: \longrightarrow 2\dot{C}H_3 + 2CO_2\uparrow$$

Acetate ion Acetate free radical Methyl free radical

iii) $H_3\dot{C} + \dot{C}H_3 \longrightarrow H_3C-CH_3\uparrow$

iv) **At cathode :**

$H_2O + e^- \rightarrow {}^-OH + \dot{H}$

$2\dot{H} \rightarrow H_2\uparrow$

Methane cannot be prepared by this method. Why?

13.2.3 Properties

Physical properties

Alkanes are almost non-polar molecules because of the covalent nature of C-C and C-H bonds and due to very little difference of electronegativity between carbon and hydrogen atoms. They possess weak van der Waals forces. Due to the weak forces, the first four members, C_1 to C_4 are gases, C_5 to C_{17} are liquids and those containing 18 carbon atoms or more are solids at 298 K. They are colourless and odourless. What do you think about solubility of alkanes in water based upon non-polar nature of alkanes? Petrol is a mixture of hydrocarbons and is used as a fuel for automobiles. Petrol and lower fractions of petroleum are also used for dry cleaning of clothes to remove grease stains. On the basis of this observation, what do you think about the nature of the greasy substance? You are correct if you say that grease (mixture of higher