1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 2)
Module Name/Title	Hydrocarbons: Part 1
Module Id	kech_21301
Pre-requisites	Knowledge about hybridization and orbital overlap, sigma and pi bonds, Rules of IUPAC nomenclature, Substitution reactions
Objectives	After going through this lesson, the learners will be able to: • Classify hydrocarbons into saturated, unsaturated and aromatic compounds • Name alkanes according to IUPAC system of nomenclature. • Recognize and write structures of different isomers of alkanes. • Write the various methods of preparation of alkanes. • Understand the physical and chemical properties of alkanes. • Draw and differentiate between various conformations of ethane. • Learn to draw Sawhorse and Newman projections and also differentiate between the stability of various conformers.
keywords	Covalent bond, sigma bond, Pi bond, single, double and triple bonds, Saturated and unsaturated hydrocarbons, Aromaticity, Chain isomerism , position isomerism, Conformations

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1. Introduction

The term ‘hydrocarbon’ 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. 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.

2. 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 hydrocarbons

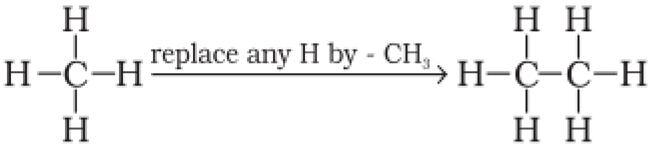
(ii) unsaturated hydrocarbons and

(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 . 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.

3. 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, you get C_2H_6, which 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.



You can go on constructing alkanes by 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). The general formula for alkanes is C_nH_{2n+2}, where n stands for number of carbon atoms and 2n+2 for number of hydrogen atoms in the molecule. According to VSEPR theory , methane has a tetrahedral structure (Fig.1) which is multiplanar, 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°.

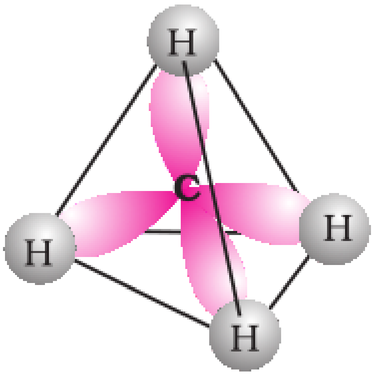
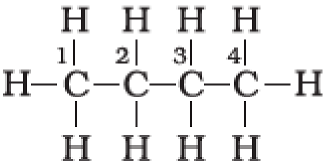


Fig.1 *Structure of methane*

4. Nomenclature and Isomerism

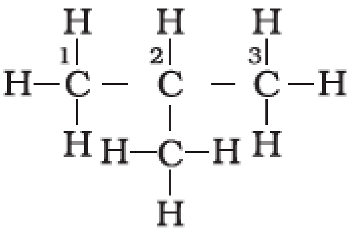
You have already read about nomenclature of different classes of organic compounds . Nomenclature and isomerism in alkanes can further be understood with the help of a few more examples. Common names are given in parenthesis. First three alkanes – methane, ethane and propane have only one possible structure 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)

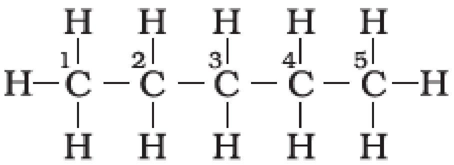
II



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

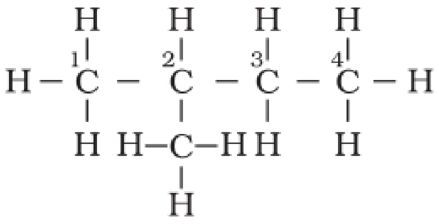
Similarly five carbon atoms and twelve hydrogen atoms of C_5H_{12} can be arranged in three ways as shown in structures III–V

III



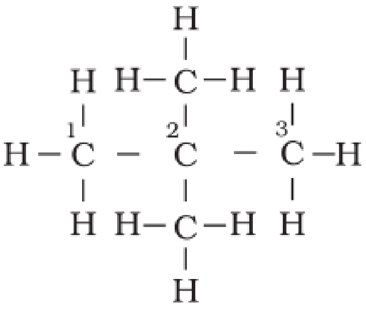
Pentane (*n*-pentane)
(b.p. 309 K)

IV



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

V



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

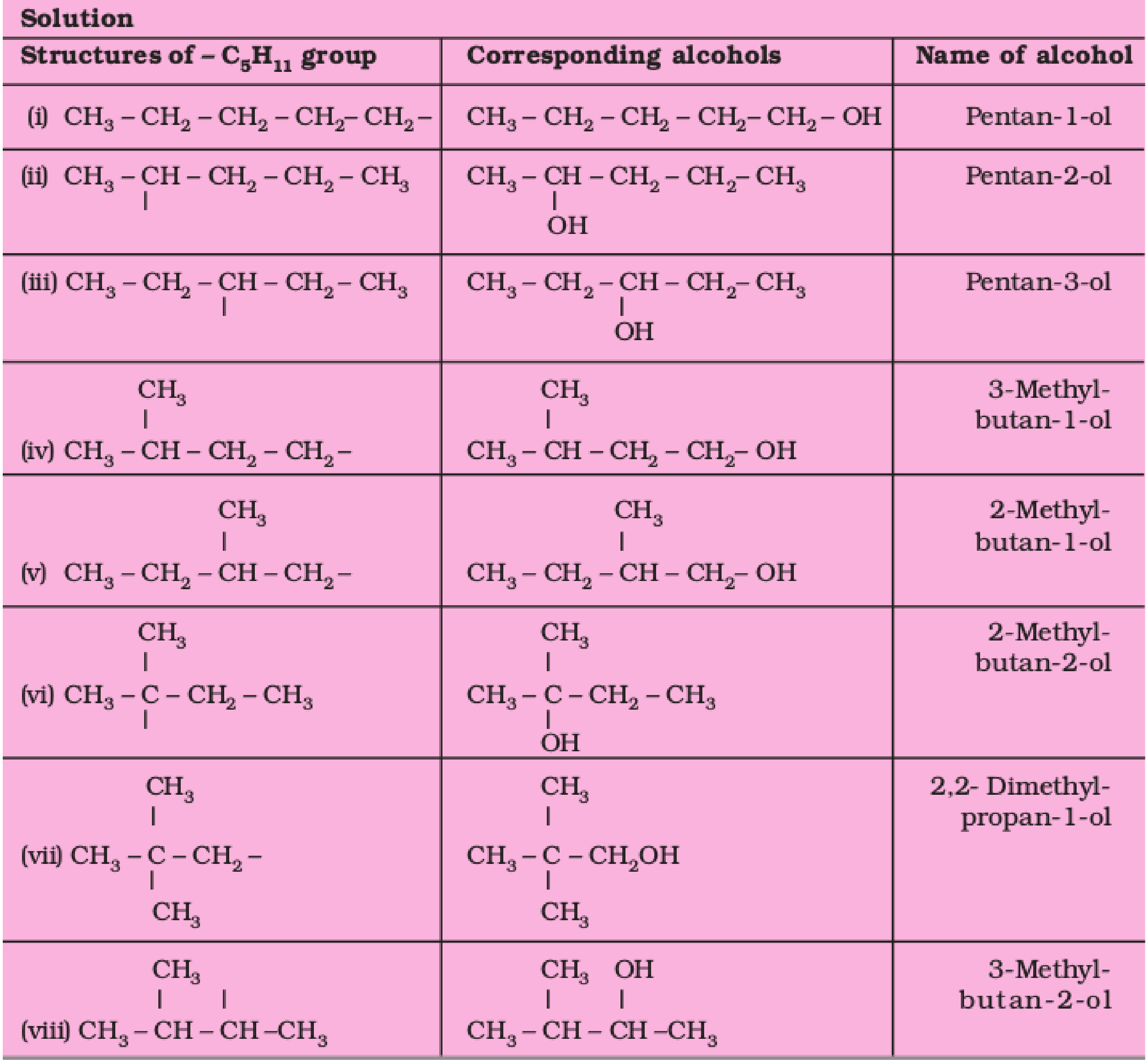
Structures I and II possess same molecular formula but differ in their boiling points and other properties. Similarly structures III, IV and V possess the same molecular formula but have different properties. Structures I and II are isomers of butane, whereas structures III, IV and V are isomers of pentane. 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.

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. 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 $C_{10}H_{22}$. Nomenclature of substituted alkanes can further be understood by considering some problems:

Problem 1

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



Solution

Structures of – C_5H_{11} group	**Corresponding alcohols**	**Name of alcohol**
(i) $CH_3-CH_2-CH_2-CH_2-CH_2-$	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$	Pentan-1-ol
(ii) $CH_3-\underset{\vert}{CH}-CH_2-CH_2-CH_3$	$CH_3-\underset{\underset{OH}{\vert}}{CH}-CH_2-CH_2-CH_3$	Pentan-2-ol
(iii) $CH_3-CH_2-\underset{\vert}{CH}-CH_2-CH_3$	$CH_3-CH_2-\underset{\underset{OH}{\vert}}{CH}-CH_2-CH_3$	Pentan-3-ol
(iv) $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-CH_2-$	$CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-CH_2-OH$	3-Methyl-butan-1-ol
(v) $CH_3-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-$	$CH_3-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-OH$	2-Methyl-butan-1-ol
(vi) $CH_3-\underset{\vert}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-CH_3$	$CH_3-\underset{\underset{OH}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-CH_3$	2-Methyl-butan-2-ol
(vii) $CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2-$	$CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_2OH$	2,2- Dimethyl-propan-1-ol
(viii) $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-\overset{\vert}{CH}-CH_3$	$CH_3-\overset{\overset{CH_3}{\vert}}{CH}-\overset{\overset{OH}{\vert}}{CH}-CH_3$	3-Methyl-butan-2-ol

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 :

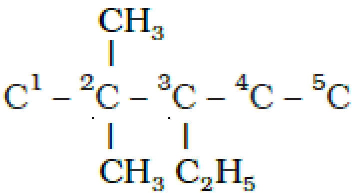
i) Draw the chain of five carbon atoms:

C – C – C – C – C

ii) Give number to carbon atoms:

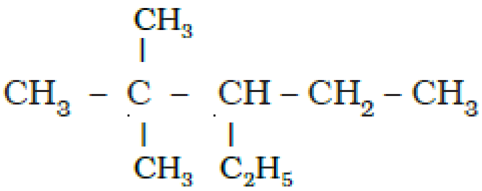
$C^1 - C^2 - C^3 - C^4 - C^5$

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



$$C^1 - {}^2\underset{CH_3}{\overset{CH_3}{C}} - {}^3\underset{C_2H_5}{C} - {}^4C - {}^5C$$

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



$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - \underset{C_2H_5}{CH} - CH_2 - CH_3$$

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

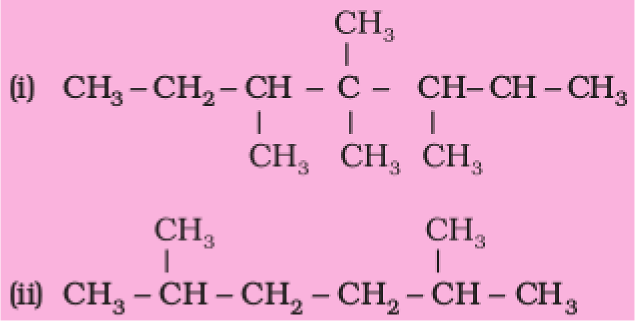
Problem 2

Write structural formulas of the following compounds :

(i) 3, 4, 4, 5–Tetramethylheptane

(ii) 2,5-Dimethyhexane

Solution



(i) $CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\underset{CH_3}{\underset{|}{CH}}-CH-CH_3$

(ii) $CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3$

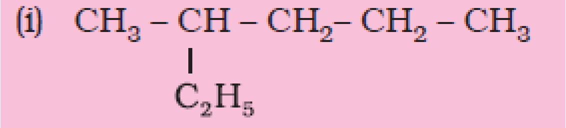
Problem 3

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

(i) 2-Ethylpentane

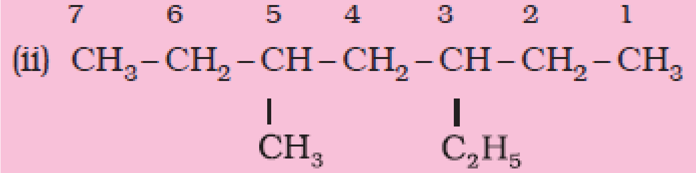
(ii) 5-Ethyl – 3-methylheptane

Solution



(i) $CH_3-\underset{C_2H_5}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

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



(ii) $\overset{7}{CH_3}-\overset{6}{CH_2}-\underset{CH_3}{\underset{|}{\overset{5}{CH}}}-\overset{4}{CH_2}-\underset{C_2H_5}{\underset{|}{\overset{3}{CH}}}-\overset{2}{CH_2}-\overset{1}{CH_3}$

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

5. Preparation of Alkanes

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

1. From unsaturated hydrocarbons

Hydrogen 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 hydrogen 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.

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

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

2. From alkyl halides

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

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

$$\underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl}+H_2\xrightarrow{Zn,H^+}\underset{\text{Propane}}{CH_3CH_2CH_3}+HCl$$

(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.

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

$$\underset{\text{Bromoethane}}{C_2H_5Br}+2Na+BrC_2H_5\xrightarrow{\text{dry ether}}\underset{\text{n-Butane}}{C_2H_5-C_2H_5}$$

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 4

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

Solution

Butanoic acid,

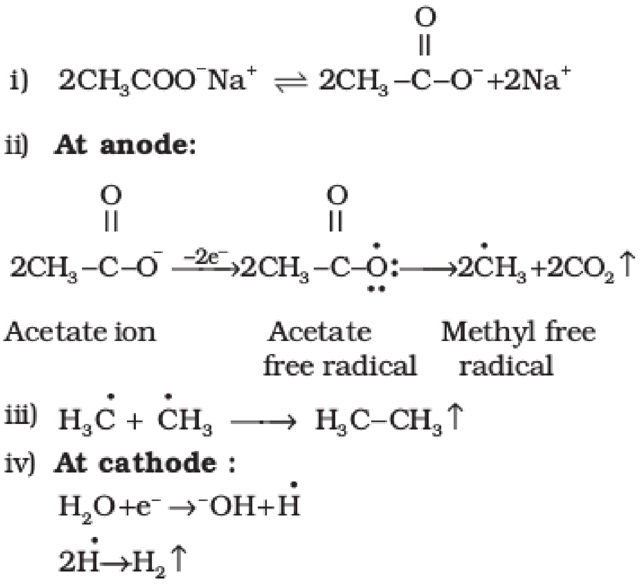
$$CH_3CH_2CH_2COO^-Na^+ + NaOH \xrightarrow{CaO} CH_3CH_2CH_3 + Na_2CO_3$$

(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.

$$\underset{\text{Sodium acetate}}{2CH_3COO^-Na^+} + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

The reaction is supposed to follow the following path :



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

ii) **At anode:**

$$\underset{\text{Acetate ion}}{2CH_3-\overset{\overset{O}{\parallel}}{C}-O^-} \xrightarrow{-2e^-} \underset{\text{Acetate free radical}}{2CH_3-\overset{\overset{O}{\parallel}}{C}-\underset{\cdot\cdot}{\dot{O}}:} \longrightarrow \underset{\text{Methyl free radical}}{2\dot{C}H_3} + 2CO_2\uparrow$$

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.

6. Physical Properties of Alkanes

Alkanes are almost non-polar molecules because of the covalent nature of C-C and C-H bonds and due to very little difference of electronegativity between carbon and hydrogen atoms. They possess weak van der Waals forces. Due to the weak forces, the first four members, C1 to C4 are gases, C5 to C17 are liquids and those containing 18 carbon atoms or more are solids at 298 K. They are colourless and odourless. What do you think about solubility of alkanes in water based upon nonpolar 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 alkanes) is non-polar and, hence, hydrophobic in nature. It is generally observed that in relation to solubility of substances in solvents, polar substances are soluble in polar solvents, whereas the non-polar ones in non-polar solvents *i.e., like dissolves like*. Boiling point (b.p.) of different alkanes show a steady increase in boiling point with increase in molecular mass. This is due to the fact that the intermolecular van der Waals forces increase with increase of the molecular size or the surface area of the molecule. You can make an interesting observation by having a look on the boiling points of three isomeric pentanes viz., (pentane, 2-methylbutane and 2,2-dimethylpropane). It is observed that pentane having a continuous chain of five carbon atoms has the highest boiling point (309.1K) whereas 2,2 – dimethylpropane boils at 282.5K. With increase in number of branched chains, the molecule attains the shape of a sphere. This results in smaller area of contact and therefore weak intermolecular forces between spherical molecules, which are overcome at relatively lower temperatures.

7. Chemical Properties of Alkanes

As already mentioned, alkanes are generally inert towards acids, bases, oxidising and reducing agents. However, they undergo the following reactions under certain conditions.

1. Substitution reactions

One or more hydrogen atoms of alkanes can be replaced by halogens, nitro group and sulphonic acid group. **Halogenation** takes place either at higher temperature (573-773 K) or in the presence of diffused sunlight or ultraviolet light. Lower alkanes do not undergo nitration and sulphonation reactions. These reactions in which hydrogen atoms of alkanes are substituted are known as *substitution reactions*. As an example, chlorination of methane is given below:

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Chloromethane}}{CH_3Cl} + HCl \qquad (13.10)$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl \qquad (13.11)$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{Trichloromethane}}{CHCl_3} + HCl \qquad (13.12)$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{Tetrachloromethane}}{CCl_4} + HCl \qquad (13.13)$$

It is found that the rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$. Rate of replacement of hydrogens of alkanes is :

3° > 2° > 1°. Fluorination is too violent to be controlled. Iodination is very slow and a reversible reaction. It can be carried out in the presence of oxidizing agents like HIO_3 or HNO_3. These oxidising agents convert back the HI formed Into I_2, hence prevent the backward reaction.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O$$

Halogenation is supposed to proceed via free radical chain mechanism involving three steps namely initiation, propagation and termination as given below:

Mechanism

(i) *Initiation* : The reaction is initiated by homolysis of chlorine molecule in the presence of light or heat. The Cl–Cl bond is weaker than the C–C and C–H bond and hence, is easiest to break.

$$Cl{-}Cl \xrightarrow[\text{homolysis}]{h\nu} \underbrace{\dot{C}l \quad + \quad \dot{C}l}_{\text{Chlorine free radicals}}$$

(ii) *Propagation* : Chlorine free radical attacks the methane molecule and takes the reaction in the forward direction by breaking the C-H bond to generate methyl free radical with the formation of H-Cl.

$$CH_4 + \dot{C}l \xrightarrow{h\nu} \dot{C}H_3 + H{-}Cl$$

The methyl radical thus obtained attacks the second molecule of chlorine to form $CH_3 - Cl$ with the liberation of another chlorine free radical by homolysis of chlorine molecule.

$$\dot{C}H_3 + Cl - Cl \xrightarrow{h\nu} CH_3 - Cl \;+ \underset{\substack{\text{Chlorine}\\ \text{free radical}}}{\dot{C}l}$$

The chlorine and methyl free radicals generated above repeat steps (a) and (b) espectively and thereby setup a chain of reactions. The propagation steps (a) and (b) are those which directly give principal products, but many other propagation steps are possible and may occur. Two such steps given below explain how more highly halogenated products are formed.

$$CH_3Cl + \dot{C}l \rightarrow \dot{C}H_2Cl + HCl$$
$$\dot{C}H_2Cl + Cl - Cl \rightarrow CH_2Cl_2 + \dot{C}l$$

(iii) Termination: The reaction stops after some time due to consumption of reactants and / or due to the following side reactions :

The possible chain terminating steps are :

(a) $\dot{C}l + \dot{C}l \rightarrow Cl{-}Cl$

(b) $H_3\dot{C} + \dot{C}H_3 \rightarrow H_3C{-}CH_3$

(c) $H_3\dot{C} + \dot{C}l \rightarrow H_3C{-}Cl$

Though in (c), $CH_3 - Cl$, one of the products is formed but free radicals are consumed and the chain is terminated. The above mechanism helps us to understand the reason for the formation of ethane as a byproduct during chlorination of methane.

2. Combustion

Alkanes on heating in the presence of air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of large amount of heat.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \qquad \Delta_c H^\ominus = -890\ \text{kJ mol}^{-1}$$

The general combustion equation for any alkane is :

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)\,H_2O$$

Due to the evolution of large amount of heat during combustion, alkanes are used as fuels. During incomplete combustion of alkanes with insufficient amount of air or oxygen, carbon black is formed which is used in the manufacture of ink, printer ink, black pigments and as filters.

$$CH_4(g)+O_2(g)\xrightarrow[\text{combustion}]{\text{Incomplete}}C(s)+2H_2O(l)$$

3. Controlled oxidation

Alkanes on heating with a regulated supply of oxygen or air at high pressure and in the presence of suitable catalysts give a variety of oxidation products.

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

$$\text{(ii)}\quad CH_4 + O_2\xrightarrow[\Delta]{Mo_2O_3}\underset{\text{Methanal}}{HCHO} + H_2O$$

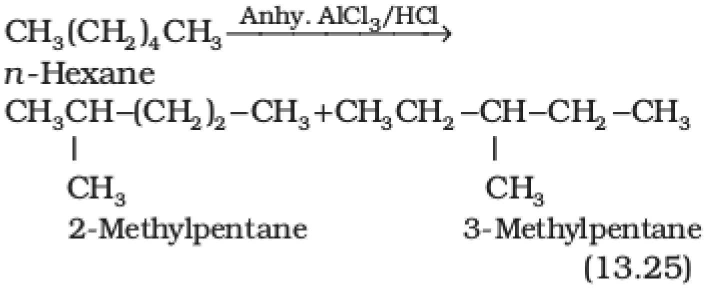
$$\text{(iii)}\quad 2CH_3CH_3+3O_2\xrightarrow[\Delta]{(CH_3COO)_2Mn}\underset{\text{Ethanoic acid}}{2CH_3COOH} + 2H_2O$$

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

$$\underset{\text{2-Methylpropane}}{(CH_3)_3CH}\xrightarrow[\text{Oxidation}]{KMnO_4}\underset{\text{2-Methylpropan-2-ol}}{(CH_3)_3COH}$$

4. Isomerisation

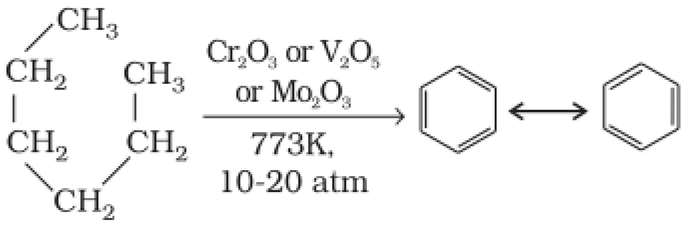
n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes. Major products are given below. Some minor products are also possible .



$$\underset{n\text{-Hexane}}{CH_3(CH_2)_4CH_3}\xrightarrow{\text{Anhy. }AlCl_3/HCl}\underset{\text{2-Methylpentane}}{CH_3\underset{\substack{|\\CH_3}}{CH}-(CH_2)_2-CH_3}+\underset{\text{3-Methylpentane}}{CH_3CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_2-CH_3}\qquad(13.25)$$

5. Aromatization

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



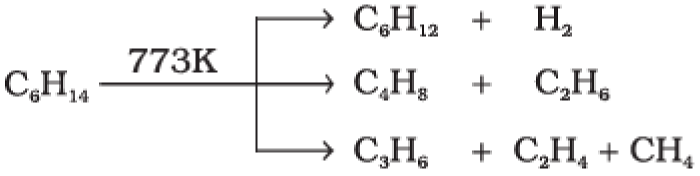
6. Reaction with steam

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

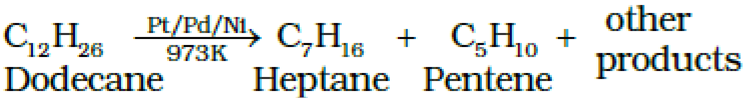
$$CH_4 + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2$$

7. Pyrolysis

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



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



$$\underset{\text{Dodecane}}{C_{12}H_{26}} \xrightarrow[973K]{Pt/Pd/Ni} \underset{\text{Heptane}}{C_7H_{16}} + \underset{\text{Pentene}}{C_5H_{10}} + \text{other products}$$

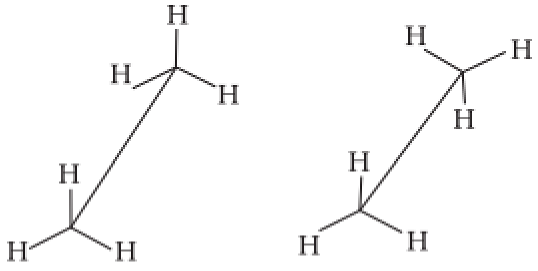
8. Conformations

Alkanes contain carbon-carbon sigma (σ) bonds. Electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C–C bond which is not disturbed due to rotation about its axis.This permits free rotation about C–C single bond. This rotation results into different spatial arrangements of atoms which can change into one another. Such spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called **conformations** or **conformers** or **rotamers**. Alkanes can thus have infinite number of conformations by rotation around C-C single bonds. However, it may be remembered that rotation around a C-C single bond is not completely free. It is hindered by a small energy barrier of 1-20 kJ mol–1 due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called **torsional strain**.

Conformations of ethane : Ethane molecule (C_2H_6) contains a carbon – carbon single bond with each carbon atom attached to three hydrogen atoms. Considering the ball and stick model of ethane, keep one carbon atom stationary and rotate the other carbon atom around the C-C axis. This rotation results into infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These are called **conformational isomers** (conformers). Thus there are infinite number of conformations of ethane. However, there are two extreme cases. One such conformation in which hydrogen atoms attached to two carbons are as close together as possible is called **eclipsed** conformation and the other in which hydrogens are as far apart as possible is known as the **staggered** conformation. Any other intermediate conformation is called a **skew** conformation.It may be remembered that in all the conformations, the bond angles and the bond lengths remain the same. Eclipsed and the staggered conformations can be represented by **Sawhorse** and **Newman projections**.

1. Sawhorse projections

In this projection, the molecule is viewed along the molecular axis. It is then projected on paper by drawing the central C–C bond as a somewhat longer straight line. Upper end of the line is slightly tilted towards right or left hand side. The front carbon is shown at the lower end of the line, whereas the rear carbon is shown at the upper end. Each carbon has three lines attached to it corresponding to three hydrogen atoms. The lines are inclined at an angle of 120° to each other. Sawhorse projections of eclipsed and staggered conformations of ethane are depicted in Fig. 2.

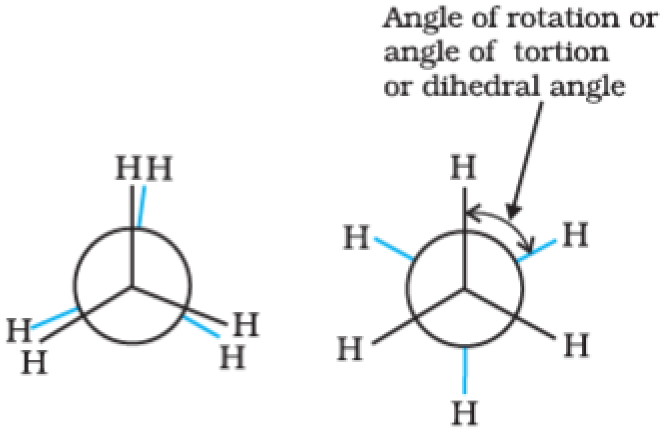


(i) Eclipsed (ii) Staggered

Fig. 2 *Sawhorse projections of ethane*

2. Newman projections

In this projection, the molecule is viewed at the C–C bond head on. The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 120° to each other. The rear carbon atom (the carbon atom away from the eye) is represented by a circle and the three hydrogen atoms are shown attached to it by the shorter lines drawn at an angle of 120° to each other. The Newman's projections are depicted in Fig.3.


Angle of rotation or angle of tortion or dihedral angle

(i) Eclipsed (ii) Staggered

Fig. 3 *Newman's projections of ethane*

Relative stability of conformations: As mentioned earlier, in staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon – hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions. To check the increased repulsive forces, molecule will have to possess more energy and thus has lesser stability. As already mentioned, the repulsive interaction between the electron clouds, which affects stability of a conformation, is called **torsional strain**. Magnitude of torsional strain depends upon the angle of rotation about C–C bond.This angle is also called **dihedral angle** or **torsional angle**. Of all the conformations of ethane, the *staggered form has the least torsional strain and the eclipsed form, the maximum torsional strain*. Thus it may be inferred that rotation around C–C bond in ethane is not completely free. The energy difference between the two extreme forms is of the order of 12.5 kJ mol^{-1}, which is very small. Even at ordinary temperatures, the ethane molecule gains thermal or kinetic energy sufficient enough to overcome this energy barrier of 12.5 kJ mol^{-1} through intermolecular collisions. Thus, it can be said that rotation about carbon-carbon single bond in ethane is almost free for all practical purposes. It has not been possible to separate and isolate different conformational isomers of ethane.

9. Summary

Hydrocarbons are the compounds of carbon and hydrogen only. Hydrocarbons are mainly obtained from coal and petroleum, which are the major sources of energy. Petrochemicals are the prominent starting materials used for the manufacture of a large number of commercially important products. LPG (liquefied petroleum gas) and CNG (compressed natural gas),the main source of energy for domestic fuels and the automobile industry, are obtained from petroleum. Hydrocarbons are classified as open chain saturated(alkanes) and unsaturated(alkenes and alkynes),cyclic(alicyclic) and aromatic, according to their structure.

The important reactions of alkanes are free radical substitution, combustion, oxidation and aromatization. Alkanes also show conformational isomerism due to free rotation along the C-C sigma bonds. Out of staggered and the eclipsed conformations of ethane, staggered conformation is more stable as hydrogen atoms here are farthest apart.