Chapter 13

Hydrocarbons

INTRODUCTION

Introduction to Hydrocarbons

It provides a comprehensive overview of the significance of hydrocarbons in various aspects of our daily life and industrial processes.
Let's summarize the key points:

1. **Definition of Hydrocarbons**
   Hydrocarbons are compounds composed of carbon and hydrogen only.

2. **Economic Importance of Hydrocarbons**
   Hydrocarbons play a crucial role in various industrial applications, contributing to economic development.

3. **Major Areas of Industrial Organic Chemistry**
   a. Polymers: Used in the production of various synthetic materials.
   b. Petrochemicals: Derivatives of petroleum used in the manufacturing of diverse products.
   c. Synthetic Materials (Other than Polymers): Various synthetic compounds beyond polymers.
   d. Miscellaneous Organic Materials: Other organic compounds used in various applications.

4. **Sources of Aliphatic and Aromatic Hydrocarbons**
   a. Aliphatic Hydrocarbons: Chiefly sourced from natural gas and petroleum.
   b. Aromatic Hydrocarbons: Majorly obtained from coal.

5. **Petroleum Composition**
   Petroleum is a complex mixture of organic compounds, primarily containing alkanes, cycloalkanes, and aromatic hydrocarbons.

6. **Fractional Distillation of Petroleum**
   The process yields essential fuels such as petrol, diesel, and kerosene oil.

7. **LPG, CNG and LNG (Liquefied Natural Gas)**
   a. LPG (Liquefied Petroleum Gas): Used in cooking, it is a mixture of hydrocarbons.
   b. CNG (Compressed Natural Gas): A form of natural gas used as fuel.

8. Coal Gas

Obtained through destructive distillation of coal, and it contains hydrocarbons.

9. Energy Source

Hydrocarbons serve as a valuable source of energy in the form of various fuels.

10. Industrial Applications of Hydrocarbons

a. Solvents for Paints: Higher hydrocarbons are utilized as solvents.
b. Starting Materials for Dyes and Drugs: Hydrocarbons are used as raw materials in the production of dyes and drugs.

11. Geostrategic Importance

Hydrocarbons, being valuable resources, can influence geopolitical relations and have implications for peace and conflict among nations.

Your description effectively highlights the diverse roles hydrocarbons play in our lives, from being essential energy sources to serving as building blocks for various industrial applications.

CLASSIFICATION

Classification of Hydrocarbons

1. Saturated Hydrocarbons: Contain carbon-carbon and carbon-hydrogen single bonds.
2. Unsaturated Hydrocarbons: Contain carbon-carbon multiple bonds, such as double bonds, triple bonds, or both.
3. Aromatic Hydrocarbons: A special type of cyclic compounds with a distinct structure.

1. Saturated Hydrocarbons

- Alkanes: Open-chain hydrocarbons with carbon-carbon single bonds.
- Cycloalkanes: Closed-chain or ring structures formed by carbon-carbon single bonds.

2. Unsaturated Hydrocarbons

- Contain one or more carbon-carbon double bonds, triple bonds, or a combination of both.
- Examples include alkenes (double bonds) and alkynes (triple bonds).

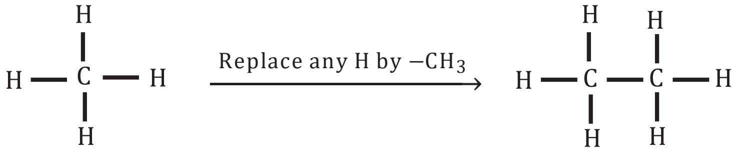
3. Aromatic Hydrocarbons

- Special cyclic compounds with a unique stability and resonance structure.
- Have a characteristic "aromatic" or pleasant odor.
- The most common example is benzene.

In summary, the classification is based on the nature of carbon-carbon bonds present in hydrocarbons. Saturated hydrocarbons have single bonds and include alkanes (open-chain) and cycloalkanes (closed-chain). Unsaturated hydrocarbons have double or triple bonds and include alkenes and alkynes. Aromatic hydrocarbons are a specific type of cyclic compounds with unique characteristics. Understanding these classifications is fundamental to exploring the diverse properties and applications of hydrocarbons in different chemical and industrial contexts.

ALKANES

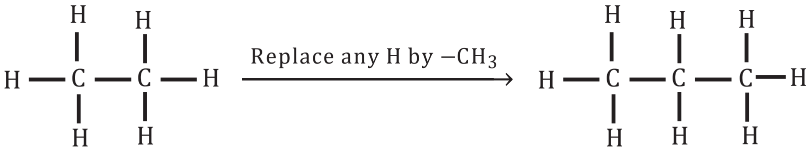
These represent the saturated hydrocarbon chains characterized by carbon-carbon single bonds. The initial member of this group is methane (CH_4), consisting of a solitary carbon atom. Recognized as 'marsh gas,' methane is commonly found in coal mines and marshy regions. The subsequent member in the alkane series is ethane (C_2H_6), comprised of two carbon atoms connected by a single bond. By substituting one hydrogen atom in CH_4 with a methyl group (-CH_3), ethane can be derived.



Methane (CH_4) Methane (CH_4)

It can be affirmed that substituting a hydrogen atom with a methyl group consistently leads to the generation of a higher alkane member.

To illustrate, when a methyl group replaces one hydrogen atom in ethane, the resulting hydrocarbon is propane. This substitution pattern, involving the exchange of hydrogen for a methyl group, serves as a reliable method for progressing to higher members within the alkane series.



Ethane (C_2H_6) Propane (C_3H_6)

These hydrocarbons demonstrate limited reactivity or inertness under standard conditions when exposed to acids, bases, and other reagents. Historically recognized as paraffins, a term derived from the Latin words "partum" (little) and "affine" (affinity), these compounds were identified for their minimal chemical responsiveness.

The general formula governing alkanes is C_nH_{2n+2}, where 'n' denotes the number of carbon atoms present in the molecule. All carbon-carbon (C-C) bonds in alkanes are sigma (σ) bonds formed through sp^3 hybridization, imparting considerable strength to the molecular structure. Alkanes exhibit three-dimensional configurations wherein all four bonds are tetrahedrally arranged, creating a regular angle of 109°28'.

	Properties	C–C	C–H
(i)	Overlapping	sp3 – sp3	sp3 – s
(ii)	Bond length	1.54 Aº	1.112 Aº
(iii)	Bond energy	80 – 85 kcal	98.6 kcal

Nomenclature and Isomerism

The process of nomenclature involves the systematic naming of chemical compounds, providing a structured and universally accepted method for the identification and communication of information about diverse compounds. It serves as an essential tool in standardizing the nomenclature of organic compounds, ensuring precision and consistency in scientific communication.

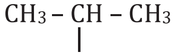
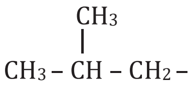
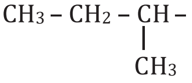
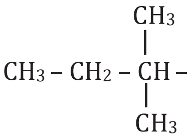
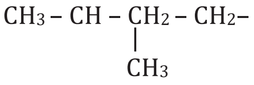
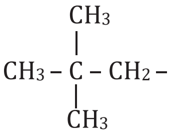
Additionally, within the alkane series, the first three members share identical common as well as IUPAC names. However, as we move to higher members in this hydrocarbon family, a multitude of structural forms or isomers emerge. Isomers are compounds possessing the same molecular formula but differing in their structures. The International Union of Pure and Applied Chemistry (IUPAC) system is widely utilized for nomenclature, offering a comprehensive set of rules for naming organic compounds based on their molecular structure.

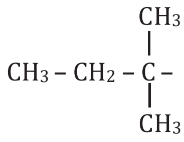
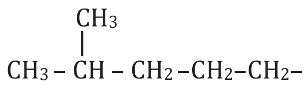
Isomerism is a phenomenon observed when two or more chemical compounds share the same molecular formula but exhibit different structural arrangements or spatial orientations of atoms. Structural isomerism involves compounds with identical molecular formulas but distinct bond connectivity, encompassing chain isomers, positional isomers, and functional group isomers.

On the other hand, stereoisomerism occurs when compounds possess the same molecular formula and identical atom connectivity but vary in the spatial arrangement of their atoms. This category includes geometric isomers and optical isomers. In summary, while nomenclature focuses on the systematic naming of compounds to ensure clarity and consistency in communication, isomerism explores the diverse structural arrangements or spatial orientations of compounds that share the same molecular formula.

Alkyl Group

When a hydrogen atom is substituted in an alkane, the resulting entity is referred to as an alkyl group. The alkyl group follows a general formula denoted as C_nH_{2n+1}. Since alkyl groups are derivatives of alkanes, their nomenclature is determined in accordance with specific naming conventions.

Structural formula	**IUPAC accepted common name**
CH_3-	Methyl
CH_3-CH_2 or C_2H_5-	Ethyl
CH_3-CH_2-CH_2- or C_2H_7-	Propyl
CH_3-CH_2-CH_2-CH_2- or C_4H_9-	Butyl
 $CH_3-\underset{\vert}{CH}-CH_3$	Isopropyl
 $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-$	Isobutyl group
 $CH_3-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-$	Secondary butyl group
 $CH_3-CH_2-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{CH}}-$	Tertiary butyl group
 $CH_3-CH-\underset{\underset{CH_3}{\vert}}{CH_2}-CH_2-$	Isopentyl group
 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_2-$	Neopentyl group

 $CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-$	Tertiary pentyl group
 $CH_3-\overset{CH_3}{CH}-CH_2-CH_2-CH_2-$	Isohexyl group

Ensuring precision in depicting chemical structures from their corresponding IUPAC names is as crucial as accurately assigning IUPAC names to given structures. To achieve the correct representation of a structure based on a provided IUPAC name, it is imperative to adhere to a specific set of rules. These guidelines facilitate the systematic and accurate portrayal of molecular configurations. In the case of 3-Ethyl-2,2-dimethylpentane, these rules are applied to ensure a clear and correct representation of the molecular composition.

Procedure:

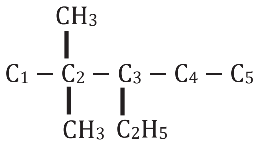
(i) Commence the process by illustrating a chain comprising five carbon atoms, as dictated by the root word 'pent' in the provided name, signifying the inclusion of a five-carbon atom chain.

$$C-C-C-C-C$$

(ii) Sequentially assign numbers to the carbon atoms within the chain, ensuring each carbon atom is uniquely identified for subsequent positioning of branches.

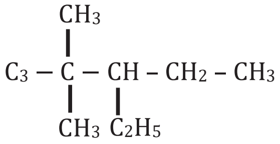
$$\overset{1}{C}-\overset{2}{C}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$$

(iii) Affix an ethyl group to carbon 3 and introduce two methyl groups at carbon 2.



$$C_1-\overset{CH_3}{\underset{CH_3}{C_2}}-\underset{C_2H_5}{C_3}-C_4-C_5$$

(iv) Satisfy the valency of each carbon atom by adding the requisite number of hydrogen atoms.



$$C_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{C_2H_5}{CH}-CH_2-CH_3$$

By systematically adhering to this set of rules, the accurate structures of the compound can be deduced.

Preparation of Alkanes

Although petroleum and natural gas stand out as primary sources of alkanes, there are several alternative methods for their synthesis.

1. From Unsaturated Hydrocarbons

Alkanes can be obtained through the addition of dihydrogen to unsaturated hydrocarbons such as alkenes and alkynes. This process, known as hydrogenation, occurs in the presence of a suitable catalyst under specific conditions. Catalysts such as nickel, platinum, or palladium in finely divided form are utilized to enhance the surface area and catalyze the reaction. While platinum and palladium can initiate the reaction at room temperature, a relatively higher temperature and pressure are required when nickel is employed as the catalyst.

$$\underset{\text{Ethene}}{CH_3} = CH_2 + H_2 \xrightarrow{\substack{\underline{pt}\\ \underline{pd}\\ Ni}} \underset{\text{Ethene}}{CH_3 - CH_3}$$

$$\underset{\text{Propene}}{CH_3 - CH = CH_2} + H_2 \xrightarrow{\substack{\underline{pt}\\ \underline{pd}\\ Ni}} \underset{\text{Propane}}{CH_3 - CH_2 - CH_3}$$

$$\underset{\text{Propyne}}{CH_3 - C \equiv C - H} + 2H_2 \xrightarrow{\substack{\underline{pt}\\ \underline{pd}\\ Ni}} \underset{\text{Propane}}{CH_3 - CH_2 - CH_3}$$

When the catalytic hydrogenation reaction described earlier occurs in the presence of nickel, it is recognized as the Sabatier-Senderen's reaction. It is important to note that methane cannot be synthesized using this specific method.

2. From Alkyl Halides

(a) Reduction:

Alkyl halides can be transformed into alkanes through a reduction process using zinc and dilute hydrochloric acid. In a broad sense, the reaction can be denoted as follows:

$$C_nH_{2n+1}X \xrightarrow{Zn,H^+} C_nH_{2n+2}$$

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

$$\underset{\text{Chloroethane}}{C_2H_5 - Cl} \xrightarrow{Zn,H^+} \underset{\text{Ethane}}{C_2H_6}$$

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

The reaction described is not observed with alkyl fluorides, primarily due to the presence of a robust bond exhibiting low dissociation. In terms of reactivity, among the halogens, the order is as follows: iodides demonstrate higher reactivity compared to bromides, and bromides exhibit higher reactivity than chlorides.

(b) Wurtz Reaction:

Alkyl halides, when subjected to treatment with sodium metal in dry ether (devoid of moisture), result in the formation of higher alkanes. This chemical transformation is recognized as the Wurtz reaction. Notably, the product generated in this reaction involves the establishment of new carbon-carbon bonds. The Wurtz reaction is commonly employed to produce alkanes characterized by an even number of carbon atoms.

$$CH_3Br + 2Na + BrCH_2 \xrightarrow{\text{dry ether}} \underset{\text{Ethane}}{CH_3 - CH_3} + 2NaBr$$

$$C_2H_5Br + 2Na + BrC_2H_5 \xrightarrow{\text{dry ether}} \underset{\text{n-Butane (major)}}{C_2H_5 - C_2H_3} + \underset{\text{(minor)}}{CH_3 - CH_3 + CH_2 = CH_2}$$

When two distinct varieties of alkyl halides are utilized, the outcome is a blend of three alkanes featuring both odd and even numbers of carbon atoms.

$$2CH_3 - CH_2 - Br + 4Na + 2Br - CH_3 \xrightarrow{\text{dry ether}} CH_3 - CH_2 - CH_2 - CH_3 + CH_3 - CH_2 - CH_3 + CH_3 - CH_3 + 4NaBr$$

(c) Corey-House Synthesis:

The Corey-House Synthesis involves a series of reactions as described below:

$$R - X + 2Li \rightarrow RLi + LiX$$

$$2RLi + CuI \rightarrow R_2CuLi + LiI$$

(a) $R_2LCu + 2R - X \rightarrow 2R - R + LX + CuX$

(b) $R_2LUCu + 2R' - X \rightarrow 2R - R' + LX + CuX$ etc.

This technique is versatile and can be employed to produce both symmetrical and unsymmetrical alkanes.

3. From Carboxylic Acids:

(a) Decarboxylation of Carboxylic Acids:

Alkanes can be derived from carboxylic acids through the process of decarboxylation. When sodium salts of carboxylic acids are heated with soda lime (a mixture of sodium hydroxide and calcium oxide), the resulting alkanes have one carbon atom fewer than the original carboxylic acid. This reaction involves the elimination of a molecule of carbon dioxide, which dissolves in NaOH to produce sodium carbonate.

$$\underset{\text{Sodium ethanoate}}{CH_3COO^-Na^+ + NaOH} \xrightarrow[\Delta]{\text{Cao}} \underset{\text{Methane}}{CH_4 + Na_2CO_3}$$

Note: The inclusion of CaO in soda lime serves the purpose of maintaining the dryness of NaOH, owing to its hygroscopic nature.

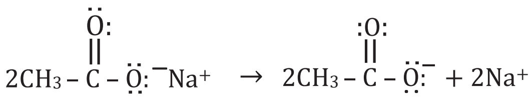
(b) Kolbe's Electrolytic Method:

In Kolbe's electrolytic method, an aqueous solution containing the sodium or potassium salt of a carboxylic acid undergoes electrolysis. This process results in the production of an alkane containing an even number of carbon atoms at the anode.

$$\underset{\text{Sodium ethanoate}}{2CH_3COO^-Na^+ + 2N_2O} \xrightarrow{\text{Electrolysis}} \underset{\text{Ethane}}{CH_3 - CH_3} + 2CO_2 + H_2 + 2NaOH$$

Mechanistic:

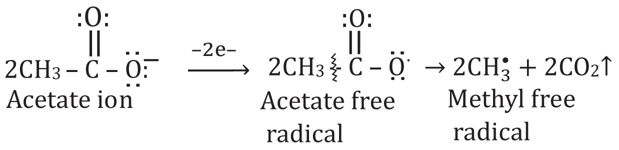
The reaction proceeds through a mechanism characterized by free radicals.



$$2CH_3 - \overset{\overset{\ddot{O}:}{||}}{C} - \underset{..}{\ddot{O}}:^{-}Na^{+} \rightarrow 2CH_3 - \overset{\overset{:O:}{||}}{C} - \underset{..}{\ddot{O}}:^{-} + 2Na^{+}$$

At anode:

(1)



$$\underset{\text{Acetate ion}}{2CH_3 - \overset{\overset{:O:}{||}}{C} - \underset{..}{\ddot{O}}:^{-}} \xrightarrow{-2e-} \underset{\text{Acetate free radical}}{2CH_3 \wr \overset{\overset{:O:}{||}}{C} - \underset{..}{\ddot{O}}^{\cdot}} \rightarrow \underset{\text{Methyl free radical}}{2CH_3^{\bullet}} + 2CO_2\uparrow$$

(2) $CH_3^{\bullet} + CH_3^{\bullet} \rightarrow CH_3 - CH_3$

At cathode:

(1) $2H_2O + 2e^- \rightarrow 2OH^- + 2H^{\bullet}$

$2H^{\bullet} \rightarrow H_2$

(2) $2Na^+ + 2OH^- \rightarrow 2NaOH$

This approach is specifically suitable for generating symmetrical alkanes and is not viable for the synthesis of methane. Kolbe's electrolytic method consistently yields higher alkanes because the formation of carbon-carbon (C-C) bonds limits the production of methane through this process.

Properties of Alkanes

Physical Properties

Alkanes exhibit nearly non-polar characteristics owing to the covalent nature of the C-C and C-H bonds and the minimal difference in electronegativity between carbon and hydrogen atoms. The intermolecular forces of attraction within alkanes are notably weak, predominantly attributed to van der Waals forces.

(i) Physical State: Due to this weak van der Waals forces, the initial four members (C_1 to C_4), namely methane, ethane, propane, and butane, exist in the gaseous state. Alkanes ranging from C_5 to C_{17} are liquids, while those with 18 carbon atoms or more assume a solid state at 298 K. Regardless of their physical state, all alkanes are characterized by being colorless and odorless.

(ii) Solubility: Alkanes typically demonstrate low solubility in water and polar solvents. However, they readily dissolve in non-polar solvents such as ether, benzene, and carbon tetrachloride. This solubility behavior aligns with the principle "Like Dissolves Like," as alkanes, being non-polar, find affinity with organic or non-polar solvents.

(iii) Boiling Point: The boiling points of straight-chain alkanes exhibit a consistent increase with the augmentation of the carbon atom count. This phenomenon can be attributed to the escalating intermolecular van der Waals forces correlated with the enlargement of molecular size or surface area. Notably, among isomeric alkanes, straight-chain alkanes tend to have higher boiling points compared to their branched-chain counterparts. The increased symmetry of the molecule due to branching results in decreased surface area, thereby reducing van der Waals interactions.

Table: Variation of Melting Point and Boiling Point in Alkanes

Molecular formula	Name	Molecular mass/u	b.p./(K)	m.p./(K)
CH_4	Methane	16	111.0	90.5
C_2H_6	Ethane	30	184.4	101.0
C_3H_8	Propane	44	230.9	85.3
C_4H_{10}	Butane	58	272.4	134.6
C_5H_{12}	Pentane	72	309.1	143.3
C_6H_{14}	Hexane	86	341.9	178.5
C_7H_{16}	Heptane	100	371.4	182.4
C_8H_{18}	Octane	114	398.7	216.2
C_9H_{20}	Nonane	128	423.8	222.0
$C_{10}H_{22}$	Decane	142	447.1	243.3

Chemical Properties

1. Stability

Although alkanes are chemically unreactive under ordinary conditions due to the presence of strong C – C and C – H sigma σ bonds, yet they give following reactions under special conditions

2. Substitution Reaction

Halogenation

$$R - H + X_2 \xrightarrow{hv} R - X + HX$$

➢ Reactivity order of hydrogen atoms in alkanes is

$$3°H > 2°H > 1°H$$

$$3ºH > 2ºH > 1ºH$$

- Reactivity order of halogens is

$$F_2 >> Cl_2 > Br_2 > I_2$$

Fluorine can react in dark. Cl_2 and Br_2 require light energy. I2 does not show any reaction at room temperature, on heating it shows iodination.

Fluorination

- Direct-fluorination of alkanes is usually explosive.

$$CH_4 + F_2 \longrightarrow \text{Carbon black (explosive reaction)}$$

- It is carried out successfully by diluting fluorine with nitrogen (Inert gas).

$$CH_4 + F_2 \longrightarrow CH_3F + HF$$

Chlorination

$$CH_4 + Cl_2 \longrightarrow CH_3Cl \xrightarrow{Cl_2} CH_2Cl \xrightarrow{Cl_2} 2CHCl_3 \xrightarrow{Cl_2} CCl_4$$

The monochorea derivative of alkane is obtained as a major product by taking alkane in excess.

Ex.

$$\underset{\substack{\text{Methane}\\\text{(excess)}}}{CH_4} + Cl_2 \xrightarrow{hv} \underset{\text{Methyl chloride}}{CH_3Cl + HCl}$$

- When chlorine is in excess, carbon tetrachloride will be the major product.

Ex.

$$\underset{\text{Methane (excess)}}{CH_4 + Cl_2} \xrightarrow{hv} \underset{\text{(Main)}}{CCl_4}$$

Chlorination of alkanes takes place in the following conditions.

- No reaction at room temperature in darkness.
- At 300ºC in darkness.
- At 100ºC in the presence of organic peroxides.
- At 150ºC in the presence of Tetra ethyl lead
- Chlorination of methane is based on free radical mechanism and it completes in the following three steps:
  - (a) Chain initiating (first) step

$$Cl_2 \xrightarrow{hv} Cl^{\bullet} + Cl^{\bullet}$$

  - (b) Chain propagating (second) step

$$Cl^{\bullet} + CH_4 \longrightarrow CH_3^{\bullet} + HCl$$
$$CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

  - (c) Chain terminating (third) step

$$CH_3^{\bullet} + {}^{\bullet}Cl \longrightarrow H_3Cl$$
$$CH_3^{\bullet} + {}^{\bullet}CH_3 \longrightarrow CH_3 - CH_3$$
$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

Bromination: Bromination of alkanes is similar to chlorination but not so vigorous.

Iodination: Iodination of alkanes is slow and reversible.

$$CH_4 + I_2 \overset{\triangle}{\rightleftharpoons} CH_3 - I + HI$$

- Iodination may be carried out in the presence of an oxidising agent such as HIO_3, HNO_3, HgO, etc. which destroys the HI as it is formed and so drives the reaction to the right.

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

Reactivity selectivity Principle

(i) **Probability factor:** The factor is based on the number of each kind of H atom in the molecule.
For example, is $CH_3–CH_2–CH_2–CH_3$ there are six equivalent 1° H's and four equivalent 2° H's.
The probability of abstracting 1° H's to 2° H's is 6 to 4. **i.e.,** 3 to 2

(ii) **Reactivity of halogen free radical:** The more reactive chlorine free radical is less selective and more influenced by the probability factor. On the other hand, the less reactive Br radical is more selective and less influenced by the probability factor (Reactivity selectivity principle).

(iii) **Reactivity of alkanes (ease of abstraction of 'H' atoms):** Since the rate determining step in halogenations is abstraction of hydrogen by a halogen atom be the formation of alkyl radical, halogenation of alkanes follows order of stability of free radical is

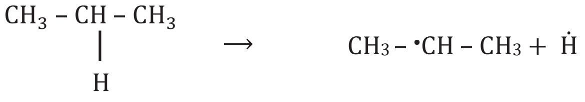
$$3° > 2° > 1° > CH_3.$$

Rapacity ratio of H atom for Chlorination (1° : 2° : 3° H)
1 : 3.8 : 5
Reactivity ration of H atom for bromination (1 : 82 : 1600)

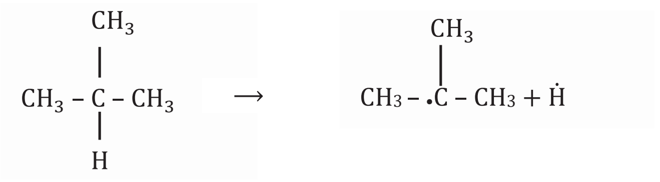
The above order of stability of radicals is due to the ease of their formation from the corresponding alkane which in turn is due to difference in the value of △H.

$$CH_3 – H \longrightarrow {}^{\bullet}CH_3 + H^{\bullet} \qquad \triangle H_1$$

$$CH_3– CH_2 – H \longrightarrow {}^{\bullet}CH_3– CH_2 + H^{\bullet} \qquad \triangle H_2$$



$$CH_3 – \underset{\underset{H}{|}}{CH} – CH_3 \longrightarrow CH_3 – {}^{\bullet}CH – CH_3 + \dot{H} \qquad \triangle H_3$$



$$CH_3 – \overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}} – CH_3 \longrightarrow CH_3 – \overset{\overset{CH_3}{|}}{{}^{\bullet}C} – CH_3 + \dot{H} \qquad \triangle H_4$$

Reactivity of any H-atom ∝ number of H atoms of that kind × reactivity of that H.

Thus, the amount of energy required to form the various classes of radicals decreases in the order $CH_3 > 1° > 2° > 3°$ ($\triangle H_1 > \triangle H_2 > \triangle H_3 > \triangle H_4$). Therefore, it easiest to form 3° radical and it is most difficult to form CH_3. We can also interpret this in an alternative way the case of abstraction of H atoms from hydrocarbon fallows the sequence $3° > 2° > 1°$ CH_4 which should also be the case of formation of free radicals.

The above order of stability is in accordance with the stability of free radicals on the basis of delocalization of odd electron. Order of stability of free radical is:

Allyl, benzyl > 3° > 2° > 1° > methyl, vinyl.

(a) Nitration:

When a mixture of vapour of alkane nitric acid is heated at high temperature (400°C – 450°C) a mixture of all possible nitroalkanes is obtained (The reaction involves both C–C and C–H bond cleavage).

$$R – \boxed{H + HO} – NO_2 \xrightarrow{\text{high temp.}} R – NO_2 + H_2O$$

(b) Sul phonation:

In this reaction, hydrogen atom of the C–H bond is replaced by $–SO_3H$ group.

$$R-\boxed{H + HO}-SO_3H \xrightarrow{\triangle} R-SO_3H + H_2O$$

(Fluming) Alkane sulphonic acid

- ➢ Fuming H_2SO_4 = mixture of SO_3 + Conc. H_2SO_4 = $H_2S_2O_7$ **(Oleum)**
- ➢ Alkanes containing 6 or more carbon atom and lower branched alkenes (not lower unbranded) can be sulphonated).

(c) Chlor sulphuration (Reed reaction):

Reaction with a mixture of SO_2 and Cl_2 at ordinary temp. in the presence of UV light is called Chlor sulphuration.

$$C_3H_7SO_2Cl \xrightarrow{UV} C_3H_7SO_2Cl + HCl$$

Propane sulphonyl Chloride

Further hydrolysis of alkane sulphonyl chloride gives alkane sulphonic acid.

$$C_3H_7SO_2Cl \xrightarrow{H_2O} C_3H_7SO_3H + HCl$$

Propane sulphonic acid

$$C_3H_7SO_3H + HCl \longrightarrow C_3H_7SO_3Na + HCl$$

Sodium salt of sulphonic acid (used as detergent)

(3) Oxidation

(a) Complete oxidation or combustion

All alkanes readily burn in excess of air or oxygen to form CO_2 and H_2O.

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

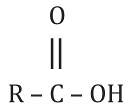
$$\frac{\text{Volume of alkane}}{\text{Volume of oxygen}} = \frac{2}{3n+1}$$

(b) Catalytic oxidation

(i) $CH_4 + \frac{1}{2}O_2 \xrightarrow[250^\circ C/100\ atm.]{\text{Red hot Cu or Fe tube}} CH_3OH$

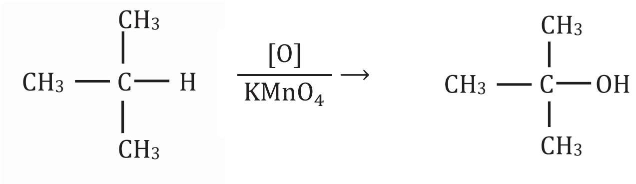
(ii) $CH_4 + O_2 \xrightarrow[250^\circ C/100\ atm.]{MO_2O_3} HCHO$

(iii) $R\text{-}CH_3 \xrightarrow{(CH_3COO)_3\,Mn, \triangle}$



$R-\overset{\overset{\large O}{\|}}{C}-OH$

Tertiary alkanes are oxidized to give tertiary alcohols by $KMnO_4$.

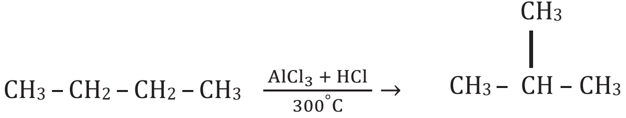


$$CH_3-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-H \xrightarrow[KMnO_4]{[O]} CH_3-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-OH$$

(4) Isomerization

Straight chain alkanes are converted into their branched chain isomers when heated in the presence of $AlCl_3 + HCl$ at 300°C.

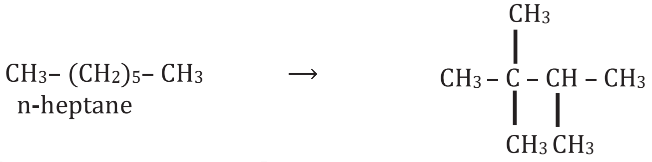
Ex.



$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[300^\circ C]{AlCl_3 + HCl} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$

"If we take n-heptane then it converts into highly branched alkane (triptane).

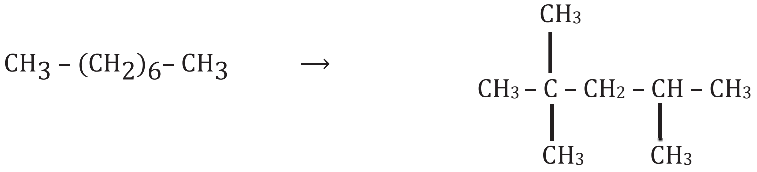
Ex.



$$\underset{\text{n-heptane}}{CH_3-(CH_2)_5-CH_3} \longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

Triptane [2,2,3-Trimethyl butane]

If we take n-octane then it converts into most stable form iso-octane.



$$CH_3-(CH_2)_6-CH_3 \longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

n-Octane iso-octane [2,2,4-Trimethyl pentane]

Isomerisation of alkanes is of great importance in petroleum industry to increase the octane number of petrol (gasoline).

(5) Pyrolysis of Cracking or Thermal Decomposition

When alkanes are heated to 500 700°C they are decomposed in to lower hydrocarbon. this decomposition is called pyrolysis. In petroleum industry it is also termed as cracking. Cracking is used for the manufacture of petrol, petrol gas/oil gas etc.

Ex. $CH_4 \xrightarrow{1000^\circ C} C + H_2$

$$CH_3-CH_3 \xrightarrow[\text{absence of air}]{500^\circ C} CH_2-CH_2 + H_2$$

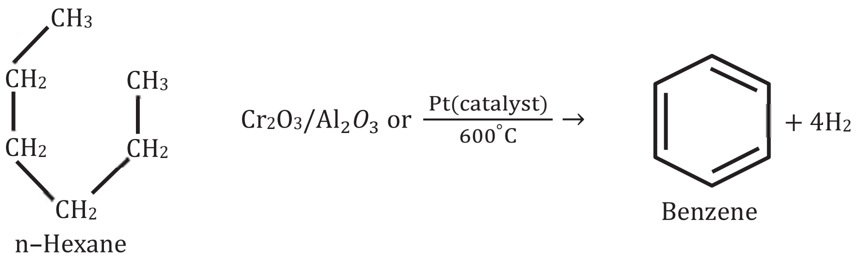
$$CH_3CH_2CH_3 \longrightarrow CH_2=CH_2 + CH_4$$
$$CH_3CH_2CH_3 \longrightarrow CH_3-CH_2=CH_2 + H_2$$

$$\text{n-Butane} \xrightarrow{\text{Cracking}} \text{1-Butane} + \text{2-Butene} + \text{Ethane} + \text{Ethene} + \text{Propene} + CH_4 + H_2$$

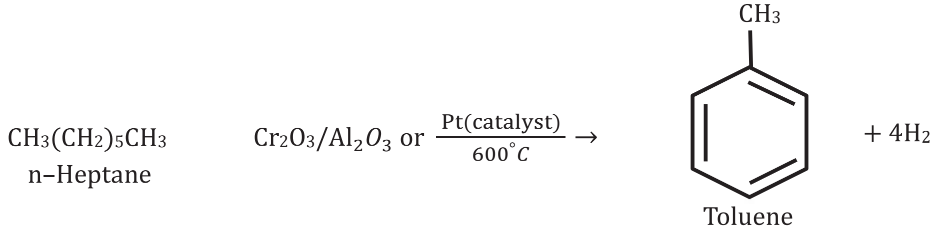
(6) Aromatization, Hydroforming or Catalytic Reforming

The conversion of aliphatic compounds into aromatic compounds is referred to as aromatization. Alkanes having six or more carbon atoms are heated at 600°C in the presence of a catalyst such as Cr_2O_3 supported over alumina or Pt, an aromatic hydrocarbon result.

Ex. (i)



(ii)



Aromatization involves cyclization and dehydrogenation.

Dehydrogenation

Ex. $\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow[600°C]{Cr_2O_3/AlO_3} \underset{\text{Propene}}{CH_3-CH=CH_2+H_2}$

(7) Special Properties of Ch_4

(i) $CH_4 + O_3 \xrightarrow{\triangle} HCHO + O_2 + H_2O$

(ii) $CH_4 + H_2O \longrightarrow CO + 3H_2$
Synthetic gas

(iii) $3CH_4 + O_2 \xrightarrow{1500°C} C_2H_2 + 5H_2 + CO_2$
acetylene

(iv) $CH_4 + N_2 \xrightarrow{\text{Electric arch}} HCN + H_2$

(v) $CH_4 + NH_3 \xrightarrow[\text{High temp.}]{Al_2O_3} HCN + H_2$