# Chapter –IV Alkanes

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**Chapter** –**IV** Alkanes

**Introduction:** Alkanes are organic compounds that consist entirely of single-bonded carbon and hydrogen atoms and lack any other functional groups. Alkanes have the general formula  $CnH_{2n+2}$ ,

Alkanes, also called paraffin's. Alkanes can be subdivided into the following three groups: A) Linear straight-chain alkanes

B) Branched alkanes and

#### C)Cycloalkanes.

Alkanes are also *saturated hydrocarbons*. Cycloalkanes are cyclic hydrocarbons, meaning that the carbons of the molecule are arranged in the form of a ring.

The first four alkanes are methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>) and butane (C<sub>4</sub>H<sub>10</sub>). The simplest alkane is the gas methane, whose molecular formula is CH<sub>4</sub>. Methane exists as a tetrahedral shape. Due to the valence configuration of carbon, there are a variety of alkane isomers, which are commonly separated into linear and branched structure.

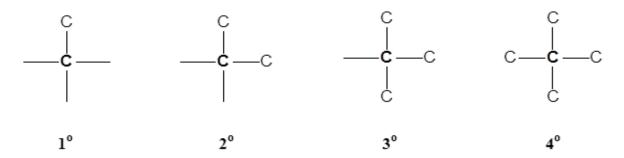
**Nomenclature for Alkanes:** Alkanes are named with the suffix "-ane" following the hydrocarbon prefixes. The series contains methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>), butane (C<sub>4</sub>H<sub>10</sub>), pentane (C<sub>5</sub>H<sub>12</sub>), and so on. For carbon chains with length of 6, 7, 8, 9, and 10 atoms, the prefixes are "hex-," "hept-," "oct-," "non-," and "dec-," respectively.

For the higher molecular weight compounds, the four bonds formed by carbon allow for a number of variations on the carbon skeleton. These multiple forms, which share the same molecular formula, are known as isomers. The prefix "n-," for normal, is reserved for the linear, unbranched forms of these alkanes.

| Seri<br>al<br>No. | Formula   | Name of<br>alkane | Isomers | Melting<br>point [°C] |
|-------------------|---|-------------------|---------|-----------------------|
| 01                | $CH_4$  | Methane           | 01      | -182                  |
| 02                | C <sub>2</sub> H <sub>6</sub> (CH <sub>3</sub> CH <sub>3</sub> )                                    | Ethane            | 01      | -183                  |
| 03                | C <sub>3</sub> H <sub>8</sub> (CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> )                    | Propane           | 01      | -188                  |
| 04                | C <sub>4</sub> H <sub>10</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> )   | Butane            | 02      | -138                  |
| 05                | C <sub>5</sub> H <sub>12</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> )   | Pentane           | 03      | -130                  |
| 06                | C <sub>6</sub> H <sub>14</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> )   | Hexane            | 05      | -95                   |
| 07                | C7H16 (CH3(CH2)5CH3)  | Heptane           | 09      | -91                   |
| 08                | C <sub>8</sub> H <sub>18</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub> )   | Octane            | 18      | -57                   |
| 09                | C9H20(CH3(CH2)7CH3)   | Nonane            | 35      | -54                   |
| 10                | C10H22 (CH3(CH2)8CH3)   | Decane            | 75      | -30                   |
| 11                | C <sub>11</sub> H <sub>24</sub> (CH <sub>3</sub> (CH <sub>2</sub> )9CH <sub>3</sub> )               | Undecane          | 159     | -26                   |
| 12                | C <sub>12</sub> H <sub>26</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub> ) | Dodecane          | 159     | -10                   |
| 13                | C <sub>13</sub> H <sub>28</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> CH <sub>3</sub> ) | Tridecane         | 355     | -5.4                  |
| 14                | C <sub>14</sub> H <sub>30</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> CH <sub>3</sub> ) | Tetradecane       | 802     | 5.9                   |
| 15                | C <sub>15</sub> H <sub>32</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> CH <sub>3</sub> ) | Pentadecane       | 1858    | 10                    |
| 16                | C <sub>16</sub> H <sub>34</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CH <sub>3</sub> ) | Hexadecane        |         | 18                    |
| 17                | C <sub>17</sub> H <sub>36</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> CH <sub>3</sub> ) | Heptadecane       |         | 22                    |
| 18                | C <sub>18</sub> H <sub>38</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CH <sub>3</sub> ) | Octadecane        | 1       | 28                    |
| 19                | C <sub>19</sub> H <sub>40</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>17</sub> CH <sub>3</sub> ) | Nonadecane        |         | 32                    |
| 20                | C <sub>20</sub> H <sub>42</sub> (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>18</sub> CH <sub>3</sub> ) | Eicosane          |         | 37                    |

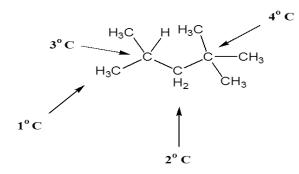
#### **Classification of alkanes:**

Carbons have a special terminology to describe how many other carbons they are attached to,



- Primary carbons (1°) attached to one other C atom
- Secondary carbons (2°) are attached to two other C's
- Tertiary carbons (3°) are attached to theree other C's
- Quaternary carbons (4°) are attached to four C's

For example, each of the three types of carbons are found in the 2,2 -dimethyl, 4methylpentane molecule,



#### **Properties of Alkanes:**

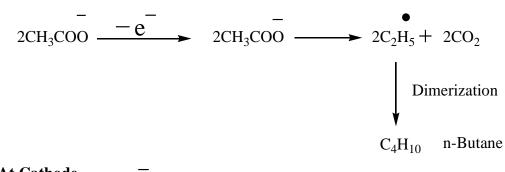
The smaller members of the alkane family are gases (C-1 to C-4), while the larger compounds are liquid(C-5 to C-16) and solid (C-17 onwards) compounds. They are commonly found in fuel sources, like natural gas and petroleum. The solid compounds are typically waxy in texture.

Alkanes have a number of industrial applications beyond fuels, including uses in cosmetics and plastics. Alkanes are generally less reactive than alkenes and alkynes because they lack the more reactive double and triple bonds. However, they do participate in reactions with oxygen (combustion) and halogens.

**Methods of formation of alkanes:** Alkanes are referred to as the saturated hydrocarbons, that is, hydrocarbons having all carbon atoms bonded to other carbon atoms or hydrogen atoms with sigma bonds only. As the alkanes possess weak Van Der Waals 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. Alkanes are prepared in laboratories and industries through various techniques.

**01)** Kolbe reaction: Sodium or potassium salts of a dicarboxylic acid on electrolysis give an alkane. An alkanes are generated when concentrated aqueous solution of sodium or potassium salt of a fatty acid (with adjacent carboxylic groups) on electrolysis. **Example** Propionate anions by losing electrons undergo anodic oxidation to form carboxylate radicals which decompose into ethyl radical and  $CO_2$ . Ethyl radicals dimerize to form n-butane. Symmetrical alkanes are obtained in good yields by this method.

#### At anode:



At Cathode +2e -  $2OH + H_2$  gain of electrons from cathode

**02)** Corey - House reaction: The reaction of an alkyl halide with a lithium dialkyl cuprate t form a new alkane, an organocopper compound and a lithium halide is Corey House synthesis. It is useful to synthesize alkane with an odd number of carbons that are not possible with the Wurtz reaction in which a mixture of alkanes is formed.

Step I: Alkyl halides react with lithium in dry ether to form alkyl lithium.

 $\textbf{R-X} + 2\textbf{Li} \twoheadrightarrow \textbf{R-Li} + \textbf{LiX}$ 

**Step II:** This alkyl lithium reacts with CuI to give Dialkyl Lithium Cuprate known as Gilman reagent.

#### $2\mathbf{R}\text{-}\mathbf{L}\mathbf{i} + \mathbf{C}\mathbf{u}\mathbf{I} \twoheadrightarrow \mathbf{R}_{2}\mathbf{C}\mathbf{u}\mathbf{L}\mathbf{i} + \mathbf{L}\mathbf{i}\mathbf{I}$

**Step III:** This dialkyl lithium cuprate reacts with alkyl halide to give alkane and the reaction is known as Corey-House synthesis.

#### $R_2CuLi + R'-X \rightarrow R-R' + R-Cu + LiX$

In this reaction R'-X may be methyl halide, p-alkyl halide or sec alkyl halide. The alkyl group of dialkyl lithium cuprate may be methyl, primary, secondary or tertiary.

In this reaction dialkyl lithium cuprate also reacts with aryl halide, alkyl halide and vinyl halide.

$$\begin{array}{c} \operatorname{CH}_{3} - \operatorname{CH}_{2} - \operatorname{Cl} + 2\operatorname{Li} & \xrightarrow{\operatorname{Dry}}_{\operatorname{ether}} \operatorname{CH}_{3} - \operatorname{CH}_{2} - \operatorname{Li} \\ & + \operatorname{LiCl} \\ 2\operatorname{CH}_{3} - \operatorname{CH}_{2} - \operatorname{Li} + \operatorname{Cul} \longrightarrow \\ & (\operatorname{CH}_{3} - \operatorname{CH}_{2})_{2}\operatorname{CuLi} + \operatorname{LiI} \\ & \operatorname{Ethyl} \operatorname{lithium} \\ (\operatorname{CH}_{3} - \operatorname{CH}_{2})_{2}\operatorname{CuLi} + \operatorname{CH}_{3}\operatorname{CH}_{2} - \operatorname{CH}_{2} - \operatorname{Cl} \xrightarrow{\operatorname{Dry}}_{\operatorname{ether}} \\ & \operatorname{n-Propyl} \operatorname{chloride} \\ \end{array}$$

$$\begin{array}{c} \operatorname{CH}_{3} - \operatorname{CH}_{2} - \operatorname{CH}_{2} - \operatorname{CH}_{2} - \operatorname{Cl} \xrightarrow{\operatorname{Dry}}_{\operatorname{ether}} \\ & \operatorname{n-Propyl} \operatorname{chloride} \\ \end{array}$$

#### 03) By decarboxylation of carboxylic acids:

Decarboxylation refers to the process of removal of  $CO_2$  from the molecules having -COOH group. Saturated monocarboxylic acid salt of sodium potassium on dry distillation with soda lime gives alkane.

The alkane formed by decarboxylation process always contains one carbon atom less than the original acid. The yield is good in case of lower members but poor for higher members.

Soda lime is prepared by soaking quick lime CaO in caustic soda solution and then drying the products. It is generally written as NaOH + CaO. Its reaction is milder than caustic soda. Otherwise the reaction will occur violently. Also CaO used along with NaOH keeps it dry (NaOH is hygroscopic) to aid fusion.

$$\begin{array}{c} \mathbf{RCOONa} \\ \mathbf{Sodium \ salt \ of} \\ \mathrm{CaO} \\ \mathbf{Heat} \end{array} \xrightarrow{\mathbf{CaO}} \mathbf{RH} + \mathrm{Na}_{2}\mathrm{CO}_{3} \\ \mathbf{Heat} \xrightarrow{\mathbf{CaO}} \mathrm{Alkane} + \mathrm{Na}_{2}\mathrm{CO}_{3} \\ \mathbf{CH}_{3}\mathrm{COONa} + \mathrm{NaOH} \xrightarrow{\mathbf{CaO}} \mathrm{Heat} \xrightarrow{\mathbf{CaO}} \mathrm{CH}_{4} + \mathrm{Na}_{2}\mathrm{CO}_{3} \\ \mathbf{CaO} \\ \mathbf{Heat} \xrightarrow{\mathbf{CaO}} \mathrm{Heat} \xrightarrow{\mathbf{CH}_{4}} \mathrm{Heat} + \mathrm{Na}_{2}\mathrm{CO}_{3} \\ \mathbf{Methane} \xrightarrow{\mathbf{CaO}} \mathrm{Heat} \xrightarrow{\mathbf{CaO}} \mathrm{Heat} \xrightarrow{\mathbf{CH}_{4}} \mathrm{Heat} + \mathrm{Na}_{2}\mathrm{CO}_{3} \\ \mathbf{C}_{2}\mathrm{H}_{5}\mathrm{COONa} + \mathrm{NaOH} \xrightarrow{\mathbf{CaO}} \mathrm{Heat} \xrightarrow{\mathbf{CaO}} \mathrm{Heat} \xrightarrow{\mathbf{CH}_{4}} \mathrm{Heat} + \mathrm{Na}_{2}\mathrm{CO}_{3} \\ \mathbf{C}_{2}\mathrm{H}_{5}\mathrm{COONa} + \mathrm{NaOH} \xrightarrow{\mathbf{CaO}} \mathrm{Heat} \xrightarrow{\mathbf{CaO}} \mathrm{Heat} \xrightarrow{\mathbf{CH}_{4}} \mathrm{Heat} + \mathrm{Na}_{2}\mathrm{CO}_{3} \\ \mathbf{C}_{2}\mathrm{H}_{6} + \mathrm{Na}_{2}\mathrm{CO}_{3} \\ \mathbf{C}_{2}\mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} + \mathrm{Na}_{2}\mathrm{CO}_{3} \\ \mathbf{C}_{2}\mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} + \mathrm{Na}_{2}\mathrm{CO}_{3} \\ \mathbf{C}_{2}\mathrm{Heat} \xrightarrow{\mathbf{CO}} \mathrm{Heat} \xrightarrow{\mathbf{CO}} \operatorname{Heat} \operatorname{Heat} \operatorname{Heat} \xrightarrow{\mathbf{CO}} \operatorname{Heat} \xrightarrow{\mathbf{CO}} \operatorname{Heat} \xrightarrow{\mathbf{CO}} \operatorname{Hea$$

The decarboxylation of sodium formate yields H<sub>2</sub>.

 $\begin{array}{c} \text{HCOONa} + \text{NaOH} & \xrightarrow{\text{CaO}} & \text{H}_2 + \text{Na}_2\text{CO}_3 \\ \\ \text{CH}_3\text{COONa} + \text{NaOH} & \xrightarrow{\text{CaO}} & \text{CH}_4 + \text{Na}_2\text{CO}_3 \end{array}$ 

**04) Wurtz Reaction:** The Wurtz reaction is a very useful reaction in the fields of organic chemistry and organometallic chemistry for the formation of alkanes. In this reaction, two different alkyl halides are coupled to yield a longer alkane chain with the help of sodium and dry ether solution. Wurtz reaction is useful for the preparation of alkanes containing even number of carbon atoms. Methane cannot be prepared by this method.

$$2RX + 2Na \xrightarrow{Dry \text{ ether}} R-R + 2NaX$$

$$2R-X + Zn \xrightarrow{Dry \text{ ether}} R-R + ZnX_2 \quad \text{Where } X= Cl,Br \text{ or } I$$

$$2CH_3Cl + 2Na \xrightarrow{Dry \text{ ether}} CH_3-CH_3 + 2NaI$$

$$2C_2H_5Br + Zn \xrightarrow{Dry \text{ ether}} Heat \quad C_4H_{10} + ZnBr_2$$

If a mixture of two different alkyl halides e.g. methyl and ethyl iodide is reacted with sodium or zinc metal, Wurtz reaction takes place with the formation of alkanes containing even number of carbon atoms (ethane and n-butane) a major product and alkane containing odd number of carbon atoms (propane) as minor product.

| CH <sub>3</sub> I + 2Na + 0 | $C_2H_5I = \frac{Dry \text{ ethe}}{Heat}$ | er >                                    | CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub> + 2NaI<br>Propane (Minor) |
|-----------------------------|---|---|---|
| 2CH <sub>3</sub> I + 2Na -  | Dry ether<br>Heat                         | CH <sub>3</sub> -(<br>etha              | CH <sub>3</sub> + 2NaI<br>ane   |
| $2C_2H_5I + 2Na$            | Dry ether<br>Heat                         | C <sub>4</sub> H <sub>1</sub><br>n-buta |   |

#### **Physical properties of Alkane:**

**1) Odor and color:** Alkanes containing carbon atoms 1 to 4 are colorless and odorless gases, alkanes containing carbon atoms 5 to 13 are colorless and odorless liquids.

Alkanes containing more than 13 carbon atoms i.e. higher alkanes are white solids.

2) **Solubility:** Due to very little difference of electronegativity between carbon and hydrogen and covalent nature of C-C bond or C-H bond, alkanes are generally non-polar molecules.

As we generally observe, polar molecules are soluble in polar solvents whereas non-polar molecules are soluble in non-polar solvents. Hence, alkanes are hydrophobic in nature that is, alkanes are insoluble in water.

However, they are soluble in organic solvents as the energy required to overcome the existing Van Der Waals forces and generate new Van Der Waals forces is quite comparable.

#### 3) Boiling Point of Alkanes:

As the intermolecular Van Der Waals forces increase with the increase of the molecular size or the surface area of the molecule we observe

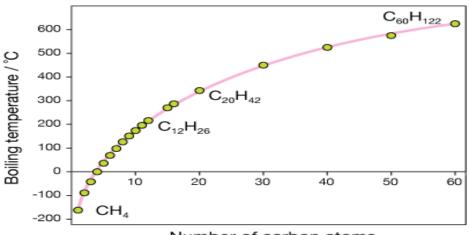
• The boiling point of alkanes increases with increasing molecular weight.

• The straight-chain alkanes are observed to have a higher boiling point in comparison to their structural isomers.

#### 4) Melting Point of Alkanes:

- The melting point of alkanes follows the same trend as their boiling point that is; it increases with an increase in molecular weight.
- This is attributed to the fact that higher alkanes are solids and it's difficult to overcome intermolecular forces of attraction between them.

• It is generally observed that even-numbered alkanes have higher trend in melting point in comparison to odd-numbered alkanes as the even-numbered alkanes pack well in the solid phase, forming a well-organized structure which is difficult to break.



Number of carbon atoms

Generally a branched chain isomer has lower M.P. and B.P. than corresponding straight chain isomer. Branching in n-alkanes decreases their M.P. and B.P.
5) Density: The density of alkanes increases with increase in molecular weight and becomes constant at 0.76 g/ml. Thus all alkanes are lighter than water.

**Reactivity of alkane:** Alkanes do not react with most reagents for two reasons. First, carbon-carbon and carbon-hydrogen single bonds are very strong due to good orbital overlap. Second, the carbon-hydrogen bonds make alkane molecules neither acidic nor basic because the electronegativity of both elements is very similar. This similarity gives the carbon hydrogen little is difficult. bond polarity, and without polarity, proton loss Thus, alkanes make poor acids. Likewise, a lack of non-bonded electron pairs on either the carbon or hydrogen atoms makes alkanes poor bases. However, under proper conditions, alkanes can react with halogens and oxygen.

**Chemical reactions of alkanes:** A) **Chlorination:** The reaction of a halogen with an alkane in the presence of ultraviolet (UV) light or heat leads to the formation of a haloalkane (alkyl halide). An example is the chlorination of methane.

In halogenation of an alkane, the alkane is said to undergo fluorination, chlorination, bromination or iodination depending on the identity of the halogen reactant. Chlorination and bromination are the two widely used alkane halogenation reactions. Fluorination reactions generally proceed too quickly to be useful and iodination reactions go too slowly.

Halogenations usually result in the formation of a mixture of products rather than a single product. More than one product results because more than one hydrogen atom on an alkane can be replaced with halogen atoms.

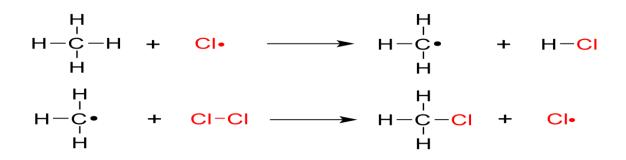
Methane and chlorine when heated to a high temperature in the presence of light react as follows,

 $CH_4 + Cl_2 + energy \rightarrow CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$ 

**1. Initiation Step:** The Cl-Cl bond of elemental chlorine undergoes hemolysis when irradiated with UV light, and this process yields two chlorine atoms, also called chlorine radicals.

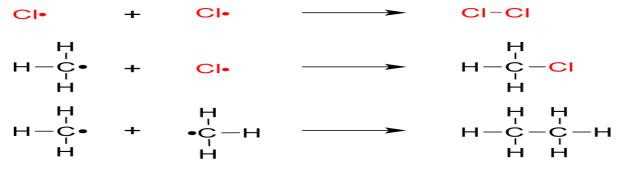


**2. Propagation Step:** Chlorine radical abstracts a hydrogen atom from methane to produce the methyl radical. The methyl radical in turn abstracts a chlorine atom from a chlorine molecule and chloromethane is formed. The second step of propagation also regenerates a chlorine atom. These steps repeat many times until termination occurs.



**3. Termination Step:** Termination takes place when a chlorine atom reacts with another chlorine atom to generate Cl<sub>2</sub>, or chlorine atom can react with a methyl radical to form chloromethane which constitutes a minor pathway by which the product is made. Two methyl radicals can also combine to produce ethane, a very minor by product of this reaction.

The reaction does not stop at this step, however because the chlorinated methane product can react with additional chlorine to produce polychlorinated products.



#### **Summary:**

- When treated with Br<sub>2</sub> or Cl<sub>2</sub>, radical substitution of R-H generates the alkyl halide and HX.
- Alkane R-H relative reactivity order: tertiary > secondary > primary > methyl.
- Halogen reactivity  $F_2 > Cl_2 > Br_2 > I_2$
- Only chlorination and bromination are useful in the laboratory.
- Bromination is selective for the R-H that gives the most stable radical.
- Chlorination is less selective.
- Reaction proceeds via a radical chain mechanism which involves radical intermediates.
- The termination steps are of low probability due to the low concentration of the radical species meaning that the chances of them colliding are very low.
- If light is used to initiate halogenation, thousands of molecules react for each photon of light absorbed.
- Halogenation reactions may be conducted in either the gaseous or liquid phase.
- In gas phase chlorination's the presence of oxygen (a radical trap) inhibits the reaction.
- In liquid phase halogenations radical initiators such as peroxides facilitate the reaction.

**B)** Nitration of alkanes: The process which involves the replacement of hydrogen atom of alkanes by nitro group (-NO<sub>2</sub>) is known nitration of an alkane, the nitration of alkanes to give nitro paraffins, Such reactions usually are carried out in the vapor phase at elevated temperatures using nitric acid (HNO<sub>3</sub>) or nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>) as the nitrating agent.

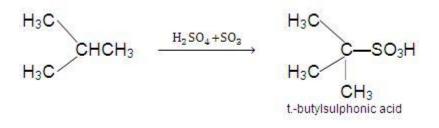
$$RH + HNO_3 \xrightarrow{\sim 425^{\circ}} RNO_2 + H_2O$$

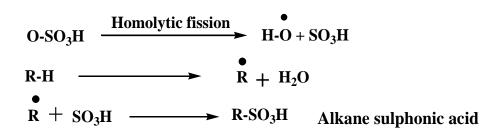
All available evidence points to a radical mechanism for nitration, but many aspects of the reaction are not fully understood. Mixtures are obtained; nitration of propane gives not only 1- and 2-nitropropanes but nitroethane and nitromethane.

$$CH_{3}CH_{2}CH_{3} + HNO_{3} \longrightarrow \begin{cases} CH_{3}CH_{2}CH_{2}NO_{2} & CH_{3}CHCH_{3} \\ 1-nitropropane (25\%) & & | \\ & & NO_{2} \\ & & 2-nitropropane (40\%) \\ CH_{3}CH_{2}NO_{2} & CH_{3}NO_{2} \\ nitroethane (10\%) & nitromethane (25\%) \end{cases}$$

In commercial practice, the yield and product distribution in nitration of alkanes is controlled as far as possible by the judicious addition of catalysts (e.g., oxygen and halogens), which are believed to raise the concentration of alkyl radicals. The products are separated from the mixtures by fractional distillation.

C) Sulphonation of alkanes: The process which involves the replacement of hydrogen atom of alkanes with a sulphonic acid group (-SO<sub>3</sub>H) is known as sulphonation of alkane. It is carried out by heating higher alkanes (hexane or higher members) with fuming sulphuric acid. Lower members are sulphonated in vapour phase sulphonation. The reactivity order for sulphonation is T.H. > S.H. > P.H. Thus isobutene is easily sulphonated as it contains tertiary hydrogen atom. Sulphonation of alkanes also follows free radical mechanism





**D)** Catalytic oxidation of alkanes: catalytic oxidation of alkanes having from 3 to 20 carbon atoms in the molecule utilizing an organic hydro peroxide, such as tertiary butyl hydro peroxide in the presence of a chromium catalyst to produce alcohols and ketones as the primary products. Common applications involve oxidation of organic compounds by the oxygen in air. Such processes are conducted on a large scale for the remediation of pollutants, production of valuable chemicals, and the production of energy.

The oxidation can be done by using catalyst Cu or molybdenum oxide. A mixture of methane group and oxygen in the ratio of 9:1 is compressed to 100 atm. and passed through copper tubes at 200<sup>o</sup>C, methane is oxidized to methanol.

```
2CH_4 + O_2 \xrightarrow{\text{Oxidation}} 2CH_3OH
```



### **Question Bank**

Class: B.Sc. Semester -I

### Name of Paper: Organic Chemistry (Paper -II) CHE-102

### Title of Chapter: Alkanes

## Questions

1. What are paraffin's? Write structural formulae for the following

1)2-mthyl heptanes 2) 3-ethyl -2, 4-dimethyl octane

2.Describe general methods of preparation of alkanes?

3. Discuss free radical mechanism of halogenations of alkanes. Also comment on its reactivity and selectivity.

4. Explain the chemical reactions of alkanes?

5.Write notes on following

A) Wurtz reaction

B) Corey-House reaction

C) Kolbe reaction

D) Decarboxylation of carboxylic acid

E) Free radical halogenations (Chlorination) of alkane

F) Nitration of alkane

G) Sulphonation of alkane

H) Catalytic oxidation of alkane.

# Multiple choice questions

| 1. Alkanes undergo halogenation. It is an example of  |   |                             |                               |  |  |
|---|---|-----------------------------|-------------------------------|--|--|
| a) Nucleophilic su  | bstitution  | b) Elimination              | b) Elimination                |  |  |
| c) Free-radical sub   | ostitution  | d) Electrophilic            | d) Electrophilic substitution |  |  |
| 2. Which of the fo  | llowing is the most   | t volatile compound?        |                               |  |  |
| a) n-pentane  | b) Isobutane  | c) 2-methyl butane          | d) 2, 2-dimethyl propane      |  |  |
| 3. Paraffin wax is  |   |                             |                               |  |  |
| a) Saturated hydro  | ocarbons  | b) Unsaturated h            | ydrocarbons                   |  |  |
| c) Alcohol  | d) Ester  |                             |                               |  |  |
| 4. Find the correct   | order for the ease  | of formation of free radica | ls                            |  |  |
| a) $1^{\circ} > 2^{\circ} > 3^{\circ}$  | a) $1^{\circ} > 2^{\circ} > 3^{\circ}$ b) $3^{\circ} > 2^{\circ} > 1^{\circ}$ c) $2^{\circ} > 1^{\circ} > 3^{\circ}$ d) $2^{\circ} > 3^{\circ} > 1^{\circ}$ |                             |                               |  |  |
| 5. Formation of an  | alkane from the re  | eduction of an alkyl halide | with Zn is known as           |  |  |
| a) Cannizzaro read  | ction b) Frankland  | l reaction c) Kolbe react   | tion d) Wurtz reaction        |  |  |
| 6. Find the compo   | und with the highe  | st boiling point among the  | following                     |  |  |
| a) n-Butane   | b) n-Octane   | c) Iso-octane               | d) 2,2,3,3-Tetramethylbutane  |  |  |
| 7. Propane contain  | ns how many carbo   | n atoms?                    |                               |  |  |
| a) One  | b) Two  | c) Three                    | d) Four                       |  |  |
| 8. Which one of th  | ne following statem   | ents regarding alkanes is f | alse?                         |  |  |
| a) Alkanes are non-polar molecules b) Alkanes are soluble in water                          |   |                             |                               |  |  |
| c) Alkanes experience dispersion forces d) Alkanes have low boiling points                  |   |                             |                               |  |  |
| 9. Select the incorrect statement regarding alkanes.  |   |                             |                               |  |  |
| a) It is otherwise known as Paraffin b) It is an acyclic saturated hydrocarbon              |   |                             |                               |  |  |
| c) In alkanes, C-C bonds are single d) Alkanes have the general formula $C_nH_{2n}$         |   |                             |                               |  |  |
| 10. Identify the simplest alkane.   |   |                             |                               |  |  |
| a) Methane  | b) Methene  | c) Ethane                   | d) Ethene                     |  |  |
| 11. Select the minimum number of carbon atoms, a molecule must possess so as to be regarded |   |                             |                               |  |  |
| as a higher alkane.   |   |                             |                               |  |  |
| a) 15   | b) 16   | c) 17                       | d) 18                         |  |  |

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**Explanation:** A molecule with more than 17 carbon atoms are regarded as higher alkanes such as waxes and solids.

12. Identify the incorrect statement.

a) Alkanes with repeated -CH<sub>2</sub>- units constitute a homologus series

b) They are very reactive

c) They have very less biological activity

d) Petroleum and natural gas are the main sources of alkanes

Explanation: Alkanes in general are not very reactive, but they are associated with functional groups which are reactive.

13. The other name for branched chain alkanes is \_\_\_\_\_

a) Paraffins b) Isoparaffins c) Neoparaffins d) Naphthene

Explanation; Ans. (b) Linear and branched chain alkanes have difference in their physical

properties and hence they are given different prefix like n- and iso-respectively.

14. Select the incorrect statement regarding the boiling points of alkanes.

a) Boiling point increases with stronger Vander Waal's forces

b) Surface area is the only factor which determines the boiling point of alkane

c) Boiling point of straight chain alkanes is greater than that of branched chain alkanes

d) The boiling point of cycloalkanes is always higher than that of linear alkanes

15. Choose the correct statement.

a) Alkanes have poor conductivity

b) They form hydrogen bonds

c) They have good solubility in non polar solvents than polar solvents

d) Alkanes have less density than that of water

Answer: b Explanation: They undergo polarization and hence they do not form hydrogen bonds.

16. Liquefied petroleum gas is mainly composed of \_\_\_\_\_

a) Methane and ethane

b) Ethane and propane

c) Propane and butane

d) Butane and hexane

Answer: c

Explanation: At low pressure both propane and butane gets liquefied, hence they form the main components of LPG.

17. Which of the following is an alkane?

| a) C <sub>4</sub> H <sub>10</sub>   | b) C <sub>3</sub> H <sub>6</sub>  | c) C <sub>2</sub> H <sub>2</sub>                       | d) C <sub>6</sub> H <sub>8</sub>  |  |
|---|-----------------------------------|--|-----------------------------------|--|
|   |                                   |  |                                   |  |
| -   |                                   | e of these compounds, which is an                      |                                   |  |
| a) $C_3H_8$   | b) C <sub>2</sub> H <sub>4</sub>  | c) $C_5 H_{10}$  | $dC_{3}H_{7}$                     |  |
|   |                                   | which has the formula C <sub>4</sub> H <sub>10</sub> ? |                                   |  |
| a) Butane   | b) Isopentan                      | ,  | d)Neo-petane                      |  |
|   | •                                 | ons. What does this mean?                              |                                   |  |
| a) There are some C=  | =C double bond                    | s present in the molecule.                             |                                   |  |
| b) All C atoms are be   | onded by single                   | covalent bonds.  |                                   |  |
| c) They are very read   | ctive.                            |  |                                   |  |
| d)There are C≡C trip  | ole bond present                  | in the molecule.                                       |                                   |  |
| 21. What is needed in   | n order for chlo                  | rine to react with ethane in a substi                  | tution reaction?                  |  |
| a) High temperature   | e b) Cata                         | lyst c) UV light                                       | d) High pressure                  |  |
| 22. Find the alkane   | $(C_5H_{12})$ , which             | will give only one type of monohal                     | ogenated compound                 |  |
| a) 2,2-dimethylprop   | ane                               | b) 2-methylbutane                                      |                                   |  |
| c) cyclopentane   |                                   | d) n-pentane   |                                   |  |
| 23. Akanes undergo  | halogenation. It                  | is an example of                                       |                                   |  |
| a) nucleophilic subst   | itution                           | b) elimination   |                                   |  |
| c) free-radical substi-   | tution                            | d) electrophilic substitution                          |                                   |  |
| 24. Paraffin wax is   |                                   |  |                                   |  |
| a) saturated hydrocarbons b) Unsaturated hydrocarbons                         |                                   |  |                                   |  |
| c) Alcohol d) Ester   |                                   |  |                                   |  |
| 25. Formation of an alkane from reduction of alkyl halide with Zn is known as |                                   |  |                                   |  |
| a) Cannizzaro reaction b) Frackland reaction                                  |                                   |  |                                   |  |
| c) Kolbe reaction d) Wurtz reaction   |                                   |  |                                   |  |
| 26. Find the compound with the highest boiling point among the following      |                                   |  |                                   |  |
| a) n-Butane b) n-Octane   |                                   |  |                                   |  |
| c) Iso-octane d) 2,2,3,3-Tetramethylbutane                                    |                                   |  |                                   |  |
| 27. Which one of the following compounds is unsaturated?                      |                                   |  |                                   |  |
| a) C <sub>3</sub> H <sub>6</sub>  | b) C <sub>4</sub> H <sub>10</sub> | c) CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>     | d) C <sub>5</sub> H <sub>12</sub> |  |
| 28. The boiling points of hydrocarbons  |                                   |  |                                   |  |

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a) Depends upon the number of double and triple bonds in the hydrocarbon. b) Increase with decreasing molecular mass. c) Increase with increasing molecular mass. d) Decrease with increasing numbers of carbon atoms. 29. The general name for the group of compounds that contain carbon and hydrogen only is a) alkynes. b) carbohydrates. c) alcohols. d) hydrocarbons. 30. What is the physical state of the first four alkanes? b) liquid d) plasma a) Solid c) gas 31. In which hydrocarbon all the four valencies of carbon are linked together with single bond? b) Alkenes c) Alkynes d) None of the above a) Alkanes 32. Name a hydrocarbon which is a main component of natural gas? a) Methyl b) Methane c) Ethyl alcohol d) Methanol 33. What is the general formula of alkenes? a)  $C_n H_{2n}$ b)  $C_n H_{2n-2}$ c) $C_nH_{2n+2}$ d)C<sub>n</sub>H<sub>2n</sub>+OH 34. As the number of carbon atoms in a formula <u>\_\_\_</u>, the number of possible isomers <u>\_\_\_</u>. a) Increases, decreases b) Increases, increases c) decreases, increases d) decreases, decreases 35. Hydrocarbons with double or triple bonds are said to be... a) Saturated b) Unsaturated c) Supersaturated d) Concentrated 36.Alkanes are not attacked by Nucleophiles and electrophile because they are.... a) Polar b) Non polar c) Volatile d) Unstable 37. As the number of carbons increases in an homologous series the melting point generally... a) Increases b) Decreases c) Remains the same d) Varies. 38. Which of the following has the highest viscosity... a) Petrol b) Diesel c) Petroleum gas d) superliquid 39. Which one of the following is saturated? a) Water b)  $C_4H_8$ c)  $C_4H_{10}$ d)  $C_5H_8$ 40. Which of the followings is giving substitution reaction with alkanes d) Acids a) Halogen b) Alkali c) Water 41. Alkanes react with aqueous bromine with UV light. a) True b) False

42. Kolbe electrolytic method can be applied on.....

|   | СН <sub>2</sub> СООК   | CHCOOK               | CH <sub>2</sub> COOK |  |  |  |
|---|--|----------------------|----------------------|--|--|--|
| a) CH <sub>3</sub> CH <sub>2</sub> COOK   | ы) сн₂соок   | <sub>с)</sub> снсоок | l<br>d) CH₂COONa     |  |  |  |
| 43.The halogen which  | 43. The halogen which is most reactive in the halogenations of alkanes under sunlight is |                      |                      |  |  |  |
| a) Chlorine   | b) Bromine   | c) Iodine            | d) Fluorine          |  |  |  |
| 44. Catalytic oxidation   | 44. Catalytic oxidation of alkanes usually carried out by using                          |                      |                      |  |  |  |
| a) Cu or molybdenum oxide b) Iron and peroxide c) Lead and acid d) Zn and Alkali                |  |                      |                      |  |  |  |
| 45. Sulphonation of alkanes is carried out by using   |  |                      |                      |  |  |  |
| a) Nitric acid  | b) Phosphoric acid   | c) Sulphuric acid    | d) Peracids          |  |  |  |
| 46. In which of the process involves the replacement of hydrogen atom of alkanes by nitro group |  |                      |                      |  |  |  |
| (-NO <sub>2</sub> ) group   | (-NO <sub>2</sub> ) group  |                      |                      |  |  |  |
| a) Halogenation   | b) Hydrolysis  | c) Acylation         | d) Nitration         |  |  |  |
| 47. Which one of the following is suitable reagent for preparation of alkane by decarboxylation |  |                      |                      |  |  |  |
| a) NaOH   | b) NaOH+ CaO   | c) HCl               | d) CuCl <sub>2</sub> |  |  |  |
| 48. Which of the following pair is suitable for synthesis of alkane by Corey-House reaction.    |  |                      |                      |  |  |  |
| a) R-Li and CuI   | b) R <sub>2</sub> -Zn and ether  | c) R-Cd and DMF      | d) R-Na and alcohol  |  |  |  |
| 49. The density of alkanes increases with increase in   |  |                      |                      |  |  |  |
| a) No. of bonds   | b) Volume  | c) Molecular weig    | ght d) Pressure      |  |  |  |
| 50. In liquid phase halogenations radical initiators such as facilitate the reaction.           |  |                      |                      |  |  |  |
| a) Peroxides  | b) Mineral acids   | c) Propagators       | d) radicals          |  |  |  |

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