By- Shailendra Shukla Sir

Hydrocarbons

The compounds consisting of only carbon and hydrogen are called hydrocarbons. Alkanes (saturated hydrocarbon), alkenes and alkynes (unsaturated hydrocarbons) are the common examples of hydrocarbons.

Saturated and Unsaturated Hydrocarbons

Such hydrocarbons in which all the four valencies of all the carbon atoms are satisfied only by single bonds but not by multiple bonds (double or triple bonds) are called saturated hydrocarbons. For example, alkanes.

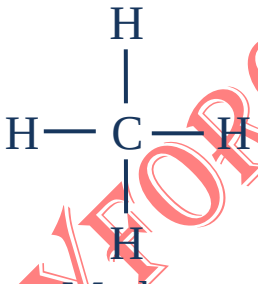
On the other hand, those hydrocarbons in which all the four valencies of all the carbon atoms are not satisfied by single bonds, but some of them are satisfied by multiple bonds (double or triple bonds) are called unsaturated hydrocarbons. For example, alkenes and alkynes.

Saturated Hydrocarbons (Alkanes)

Alkanes are the simplest saturated hydrocarbons consisting of only carbon and hydrogen. The general formula of alkanes is C_nH_{2n+2}.

- Here, if n = 1, then formula of alkane = $C_1H_{2\times1+2}$ = CH_4

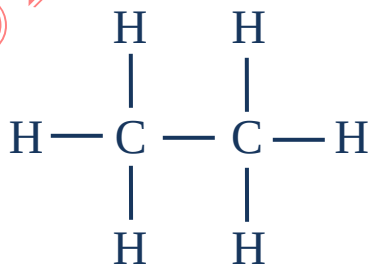
or



Methane

- Here, if n = 2, then formula of alkane = $C_2H_{2\times2+2}$ = C_2H_6

or

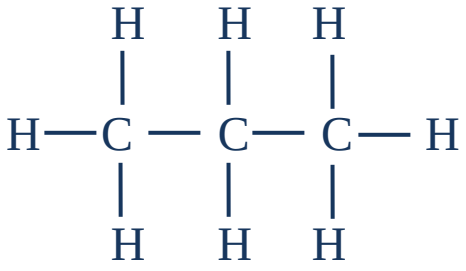


Ethane

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➢ Here, if n = 3, then formula of alkane = $C_3H_{2\times3+2}$ = C_3H_8

or



Propane

Because of their non-polar nature, alkanes are highly unreactive in nature and therefore, they are also called paraffins (Gk. parum = very less, affinis = reactivity).

Preparation Methods of Alkanes

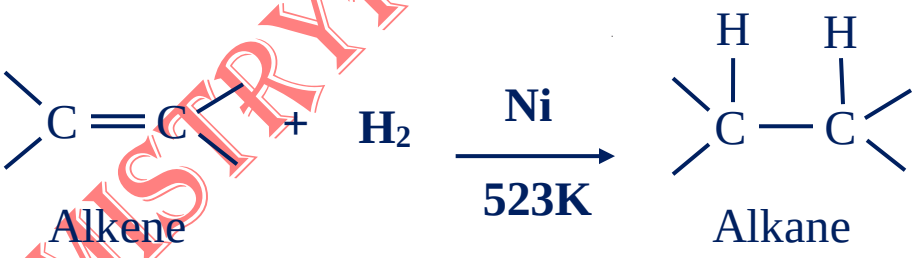
Petroleum and natural gases are the chief source of alkanes. However, alkanes can also be prepared by following general methods of preparation-

(1)From Unsaturated Hydrocarbons

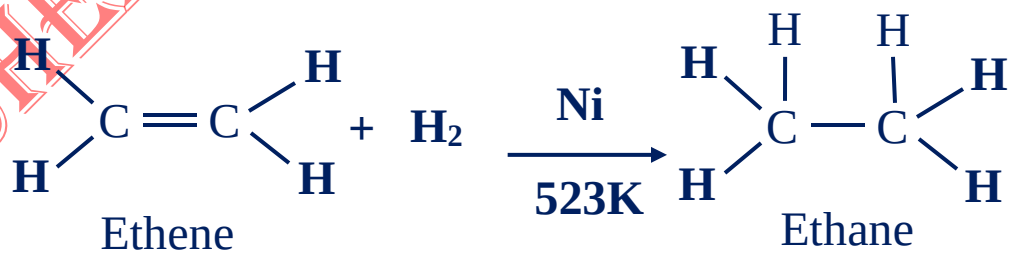
or

By hydrogenation of Alkenes and Alkynes

When hydrogen adds to the multiple bonds of unsaturated hydrocarbons (alkenes and alkynes) in the presence of finely divided nickel, platinum, or palladium, alkanes are obtained. This reaction is called **hydrogenation of alkenes and alkynes**. Platinum and palladium catalyze this reaction at room temperature, while, nickel catalyzes it at a relatively higher temperature (about 250^0C) and pressure.

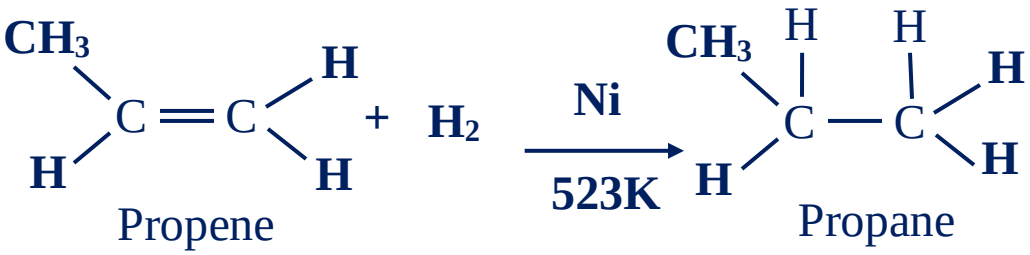


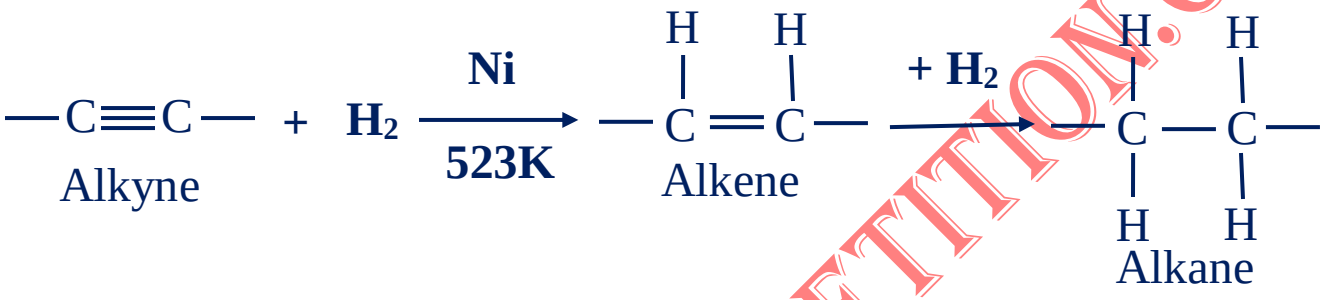
Alkene Alkane

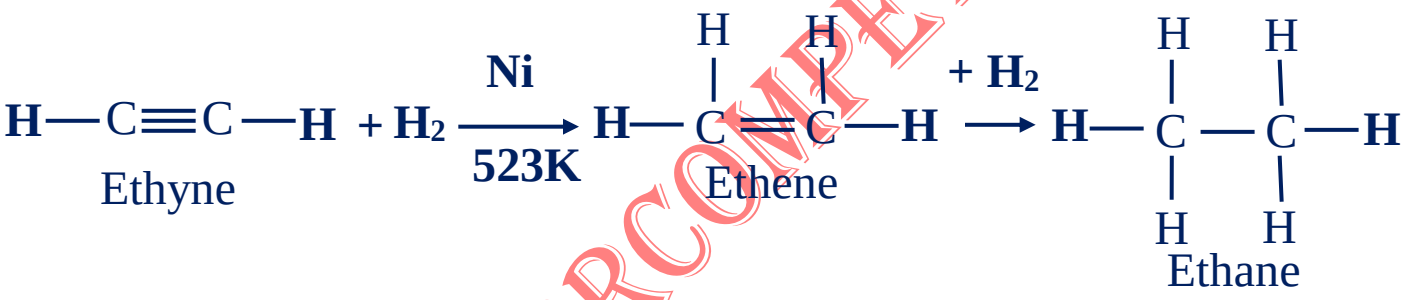


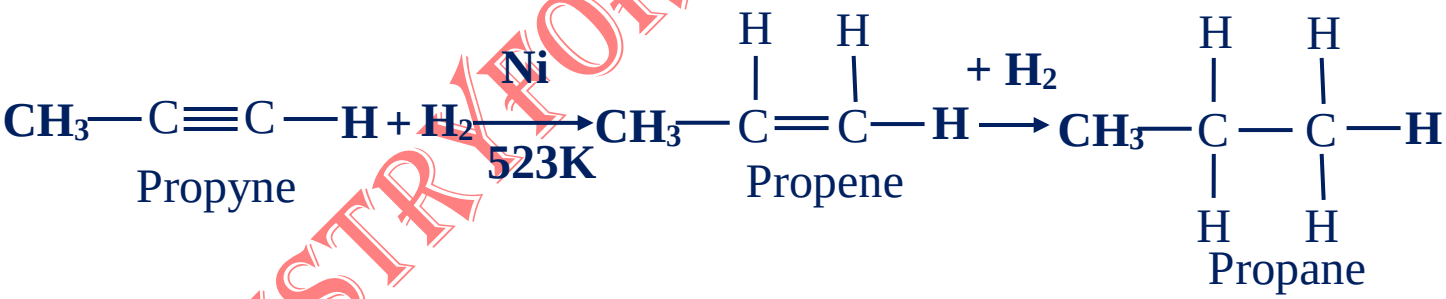
Ethene Ethane

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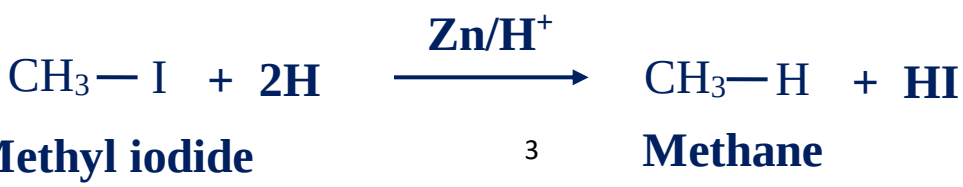




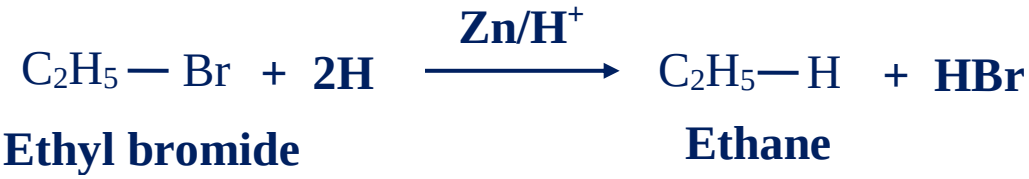
(2)From Haloalkanes (Alkyl halides)

(a)By reduction of Haloalkanes- When alkyl halides (except fluorides) are reduced by zinc and dilute hydrochloric acid, alkanes are obtained.





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(b)By reaction of Haloalkanes with sodium (Wurtz Reaction)- When alkyl halides are treated with sodium in presence of dry ether, higher alkanes are obtained. This reaction is called **Wurtz reaction.**

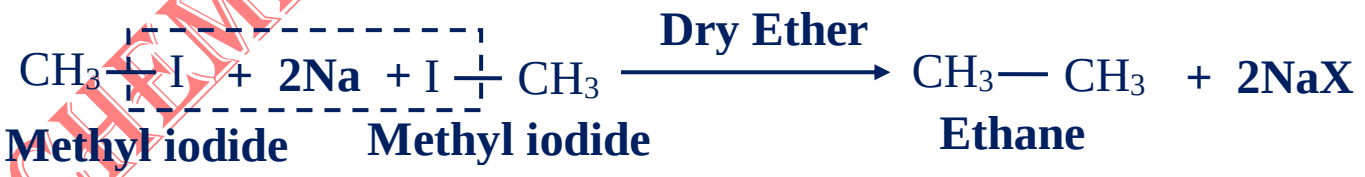




This reaction is used in preparation of higher alkanes containing even number of carbon atoms.

In this reaction, if a mixture of two different alkyl halides is used, then a mixture of three different alkanes is obtained. For example, if a mixture of methyl iodide and ethyl iodide is used in Wurtz reaction, then a mixture of ethane, propane and butane is obtained.







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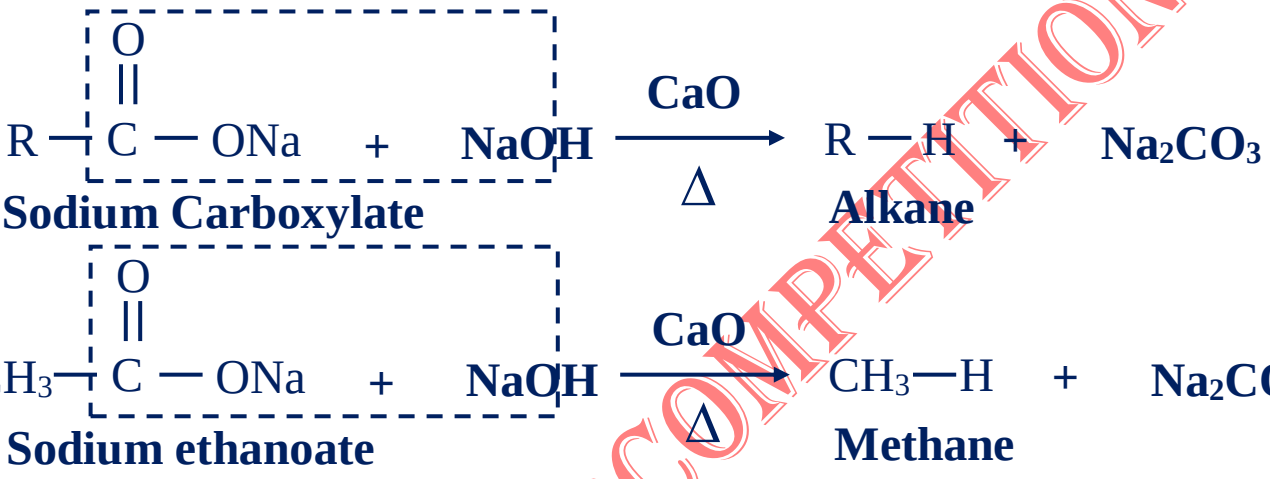
These alkanes have very close boiling point and therefore, they cannot be separated easily by simple distillation process. It is the reason why the use of Wurtz reaction is limited to the preparation of only symmetrical alkanes i.e. a mixture of two different alkyl halides is never used in this reaction.

(3) From Carboxylic Acids

Or

By Decarboxylation of Sodium salts of Carboxylic Acids

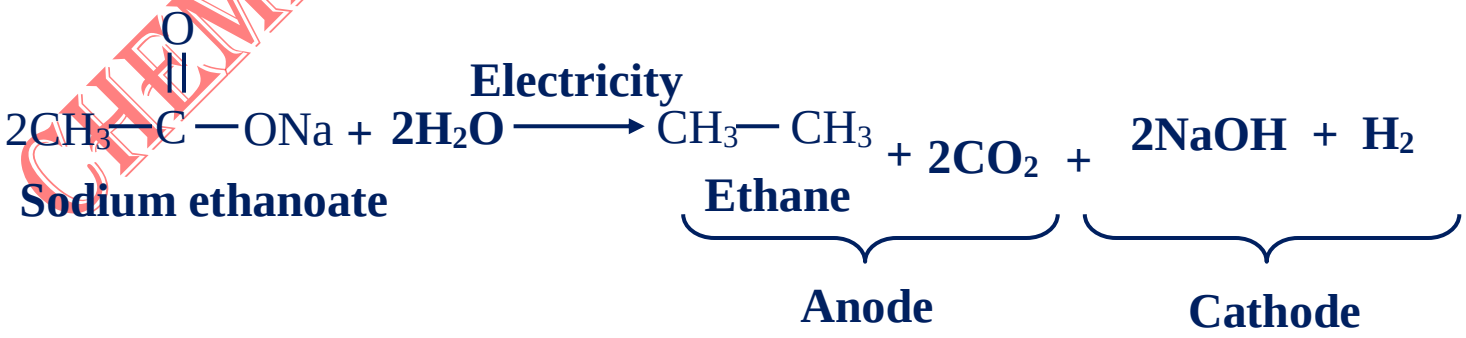
When Sodium salts of Carboxylic Acids are heated with soda lime (a mixture of NaOH and CaO), they undergo decarboxylation to form alkanes.



In this reaction, carboxylic group of original carboxylic acid gets removed. Hence, this reaction is called decarboxylation reaction.

Here, the alkane formed contains one carbon atom lesser than the parent carboxylic acid. Hence, this reaction is used for stepping down in a series i.e. to get lower member of an organic family.

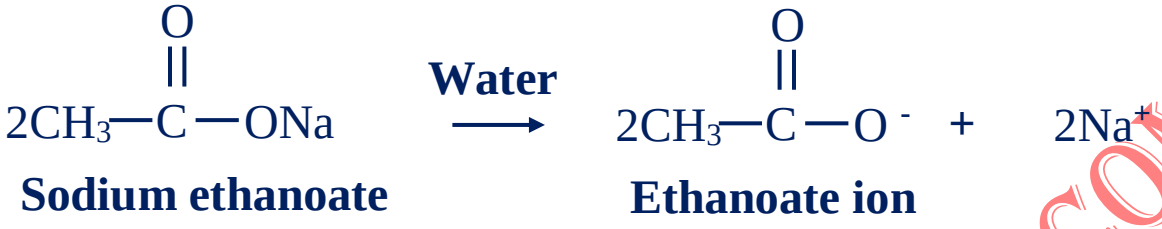
(4) By Kolbe's Electrolysis- When aqueous solution of sodium or potassium salt of carboxylic acids are electrolyzed, then alkanes are obtained at anode. This process is called Kolbe's electrolysis.



Here, alkane obtained contains even number of carbon atoms.

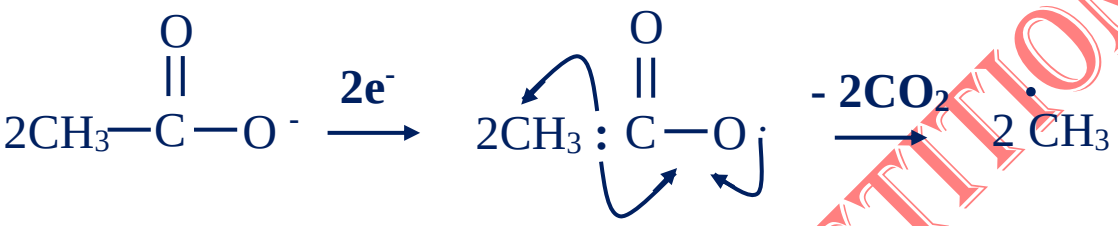
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Mechanism- This reaction involves the formation of free radicals as reaction intermediate and supposed to follow following mechanism-



Sodium ethanoate **Ethanoate ion**

At anode-



Ethanoate ion **Ethanoate free radical** **Methyl free radical**



Methyl free radicals **Ethane**

At cathode-



Hydrogen free radicals





Hydrogen free radicals

Methane cannot be prepared by this method.

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Properties of Alkanes

(a)Physical Properties

(1) Alkanes are almost non-polar and involve a very weak van-der Waal's force amongst the molecules.

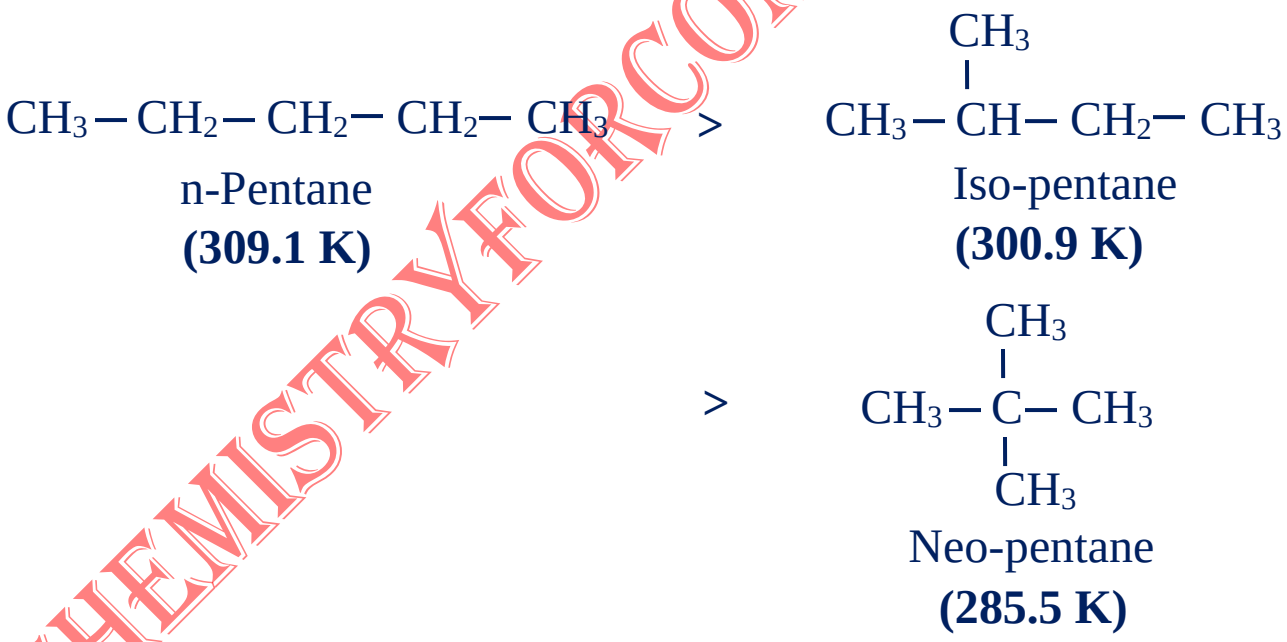
(2) Due to very weak van-der Waal's force amongst the molecules, the first four members of alkanes ($C_1 - C_4$) are gases, next 13 members ($C_5 - C_{17}$) are colourless liquids while, higher members are colourless solid at room temperature.

(3) Being non-polar in nature, alkanes are insoluble in water but they are fairly soluble in organic solvents like, carbon tetrachloride, ether, benzene etc. (Like dissolves like).

(4) Being insoluble and lighter than water, liquid alkanes float over water.

(5) Liquid alkanes have relatively lower boiling point but their boiling point in general increases with increase of their molecular mass. In fact, with increase of molecular mass, the molecular size and surface area increases and therefore, van-der Waal's force increases amongst the molecules.

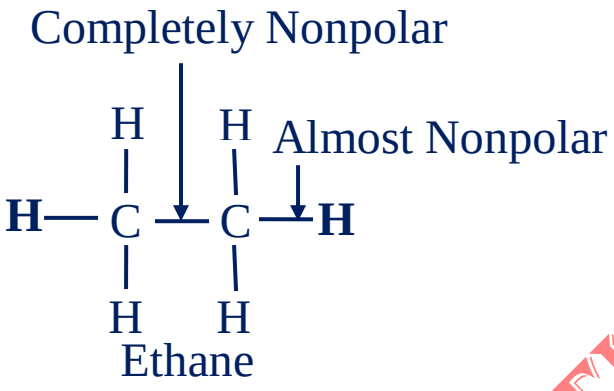
The boiling point of isomeric alkanes, decreases with branching. For example, isomeric pentanes have following order of their boiling point.



In fact, with increase of branching, the molecule becomes more and more compact, so that, the molecular size and surface area of molecule decreases and therefore, van-der Waal's force decreases amongst the molecules.

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(b) Chemical Properties-In alkanes, C-C bond is completely nonpolar and due to almost same electronegativity of carbon and hydrogen atoms, C-H bonds are almost nonpolar in nature.

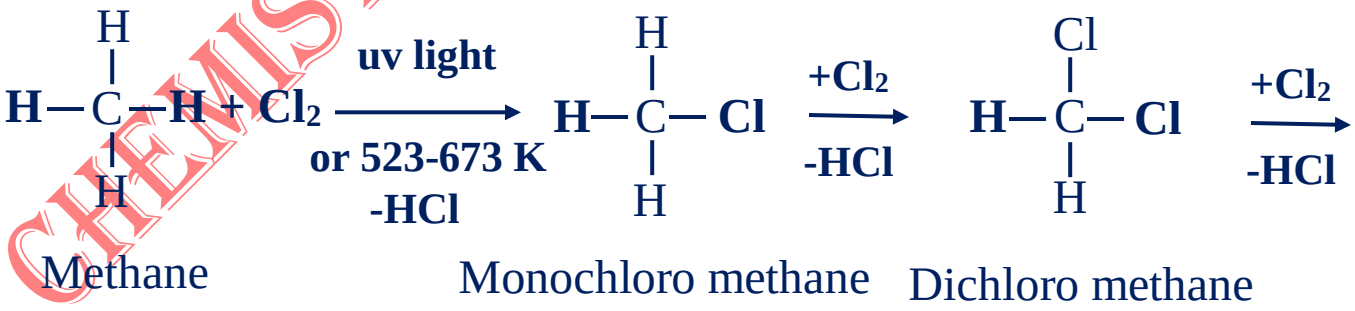


Thus, attacking reagents find no attacking site in alkanes. It is the reason why alkanes are highly unreactive in nature. They generally inert towards acids, bases, oxidizing and reducing agents in ordinary conditions and are called paraffins (Gk. parum = very less, affinis = reactivity). However, in drastic conditions they give following reactions.

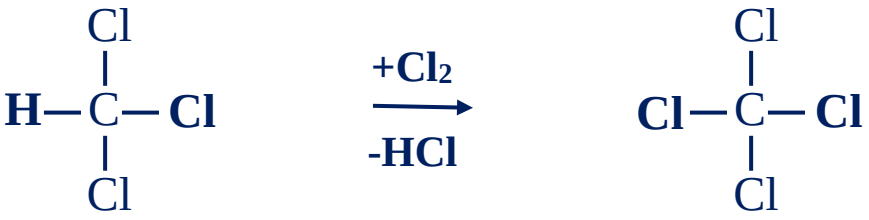
(1) Substitution Reactions

(a) Halogenation-When lower alkanes (methane and Ethane) are reacted with halogens (Cl_2 or Br_2) at 523-673 K temperature or in presence of uv light, their all the hydrogen atoms get successively replaced by halogen atoms and a mixture of all the possible halogen derivatives is obtained.

For example, chlorination of methane gives a mixture of mono, di, tri and tetra chloromethane.



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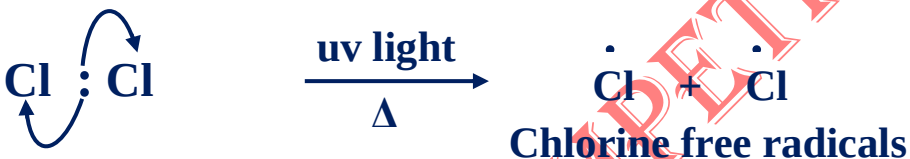


Trichloro methane Tetrachloro methane

Mechanism-

This reaction is the example of free radical substitution and involves following steps-

(i) Chain initiation-First halogen molecule undergoes homolytic bond fission by action of heat or energetic sun light to form halogen free radicals.

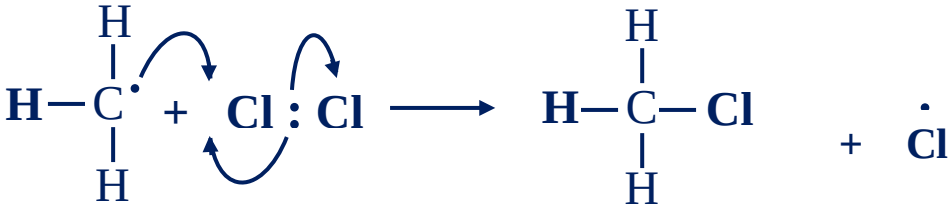


Chlorine free radicals

(ii) Chain propagation-In this step, the halogen free radicals formed in first step, attacks on one of the C-H bonds of alkanes to form alkyl free radical. The alkyl free radical thus formed attacks on another halogen molecule to form monohalogen derivative of alkane and a new halogen free radical.



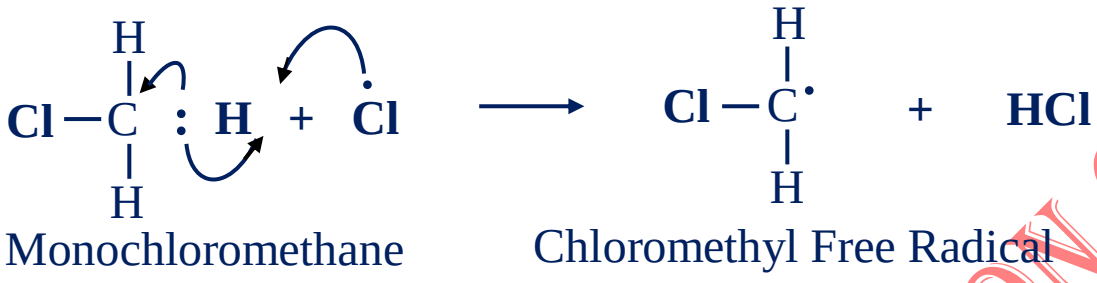
Methane Methyl Free Radical



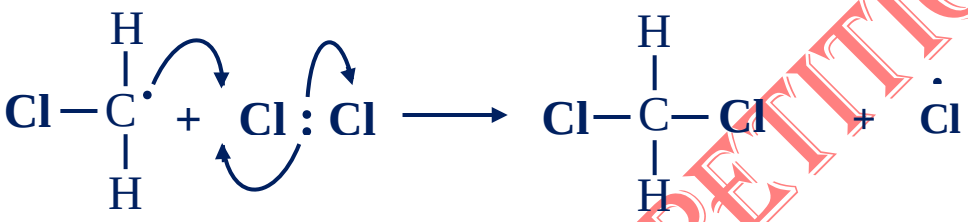
Monochloro methane

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These two steps are repeated again and over again until all the hydrogen atoms of alkane get replaced by halogen atoms. For example, second chlorine atom is replaced as under-



Monochloromethane Chloromethyl Free Radical

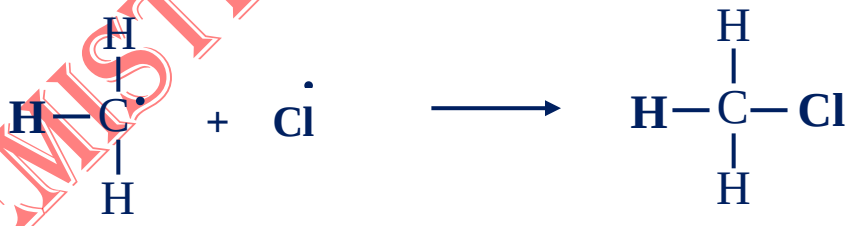


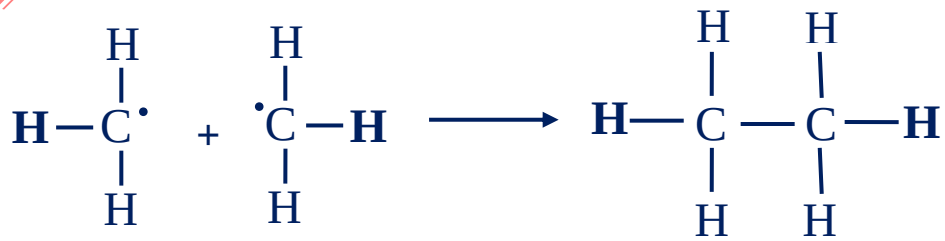
Dichloro methane

(iii) Chain termination-In this step two free radicals combine together to form a neutral molecule, so that the chain gets terminated.



Chlorine free radicals





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The formation of a trace amount of ethane in chlorination of methane is an evidence about free radical mechanism of this reaction.

Bromination is similar to chlorination, but it occurs at relatively slower rate.

Iodination of alkanes is found to be reversible. In fact, HI formed in Iodination being a strong reducing agent reduces the alkyl halide formed in the reaction back to alkane and therefore, makes the reaction reversible.

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

Hence, iodination is carried out in presence of a strong oxidizing agent, such as concentrated nitric acid or iodic acid.

$$CH_4 + I_2 \xrightarrow{HIO_3} CH_3I + HI$$

Here, concentrated nitric acid and iodic acid decompose the HI formed back to iodine and therefore, prevent the reversibility of the reactions.

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

Higher alkanes on halogenation give a mixture of all the possible mono substitution products. For example, propane on chlorination gives a mixture of 1-chloropropane and 2-chloropropane where, 2-chloropropane is measure product.

$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow[\Delta]{Cl_2} \underset{\text{2-Chloropropane (Major)}}{CH_3-\overset{\overset{Cl}{|}}{CH}-CH_3} + \underset{\text{1-Chloropropane (Minor)}}{CH_3-CH_2-CH_2-Cl}$$

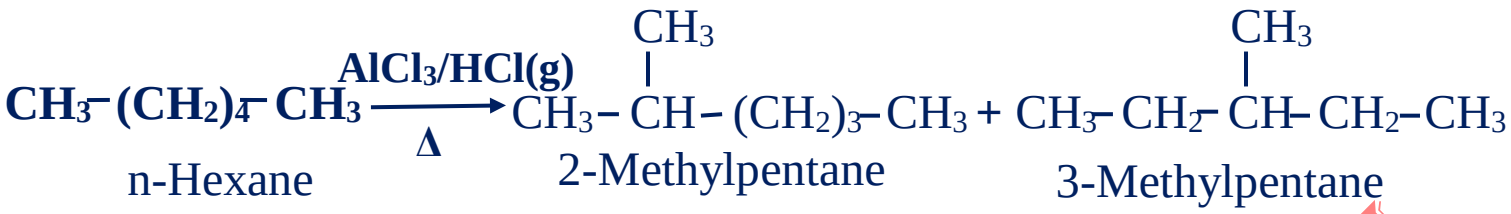
Here, the order of ease of replacement for different types of hydrogen atoms is as under-

$$3^0 > 2^0 > 1^0$$

This order corresponds to the order of stability of different types of alkyl free radicals formed as reaction intermediates during the reaction.

(2)Isomerisation-When straight chain alkanes are heated in the presence of anhydrous $AlCl_3$ and HCl(g), they isomerise to form branched chain alkanes. This reaction is called isomerisation. For example,

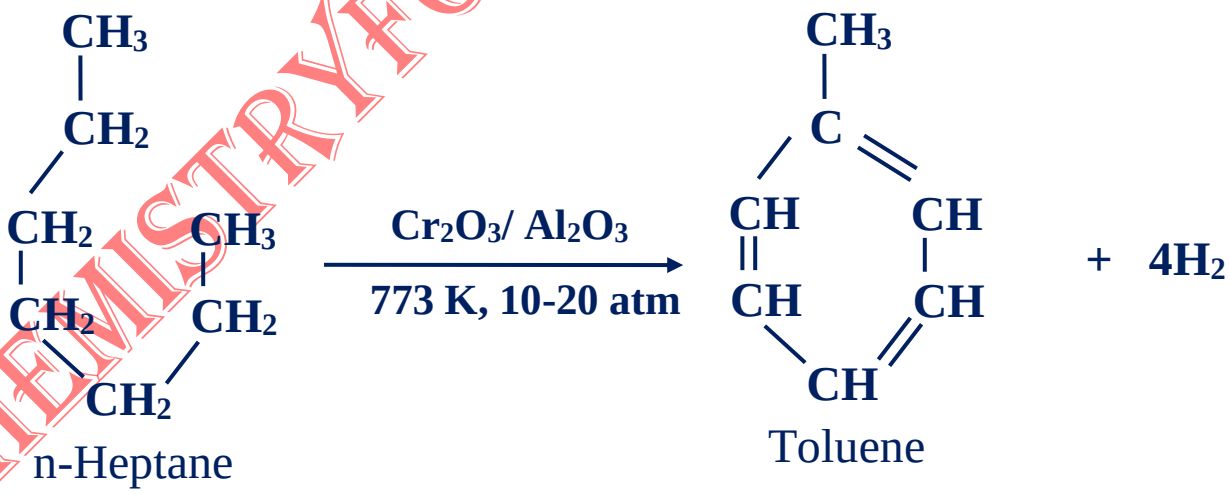
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This reaction is used in preparation of petrol of higher octane number.

(3)Aromatization- When *n*-alkanes having six or more carbon atoms are heated at about 773K temperature and at 10-20 atm pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina, they get dehydrogenated and cyclised to form benzene and its homologues. This reaction is known as aromatization or reforming. For example,

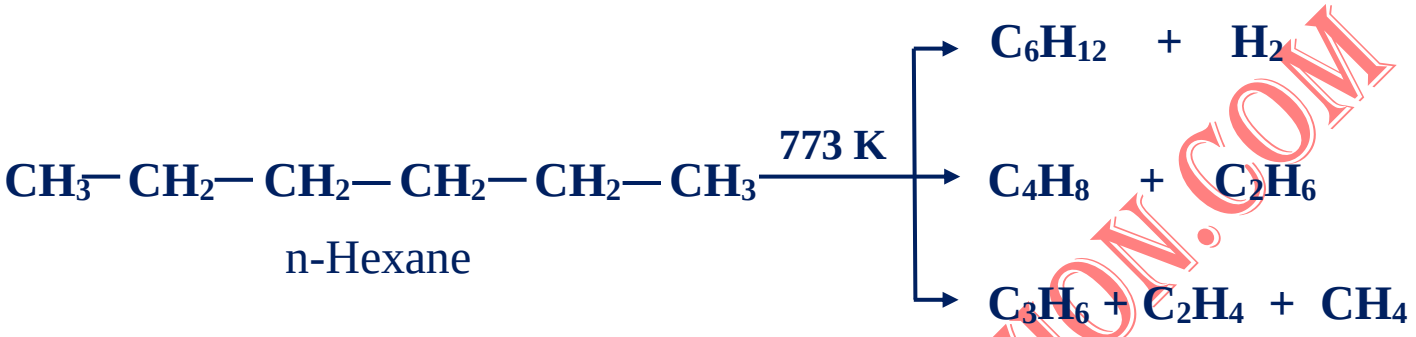




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Now a days, platinium is being used in this reaction and therefore, this reaction is also called platforming.

(4) Pyrolysis or Cracking- When higher alkanes are heated at a higher temperature in absence of air, they get decomposed to give a mixture of lower alkanes, alkenes and hydrogen. This reaction is called pyrolysis (Pyro = fire, lysis = bracking) or cracking.



Pyrolysis is considered to be a free radical reaction. Preparation of oil gas or petrol gas from kerosene oil or petrol is based on 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.



(5) Combustion-

(a) Complete Combustion- When alkanes are heated in presence of excess of air or oxygen they undergo complete combustion to form carbon dioxide and water with evolution of a large amount of heat.



This reaction is highly exothermic. Hence, alkanes are used as fuel.

(b) Incomplete combustion- When alkanes are heated in presence of insufficient amount of air or oxygen, they undergo incomplete combustion to form carbon black which is used in making ink, black pigments and filters.



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(6) Controlled oxidation- Alkanes on controlled oxidation using regulated supply of oxygen at high temperature, high pressure and suitable catalyst give a number of valuable compounds. For example,

(i) $2CH_4 + O_2 \xrightarrow[523\ K,\ 100\ atm]{Cu} CH_3OH$

(ii) $CH_4 + O_2 \xrightarrow[\Delta]{Mn_2O_3} HCHO + H_2O$

Methanal

(iii) $C_2H_6 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} CH_3COOH$

(iv) In general, alkanes are very resistant to oxidation. However, alkanes containing tertiary hydrogen on oxidation with $KMnO_4$ give corresponding alcohol.



Isobutane **Isobutyl alcohol**

(7) Reaction with Steam- Methane reacts with steam at 1273 K temperature in the presence of nickel catalyst to form carbon monoxide and hydrogen.

$$CH_4 + H_2O(g) \xrightarrow[1273\ K]{Ni} CO + 3H_2$$

This method is used for the industrial preparation of hydrogen gas.

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