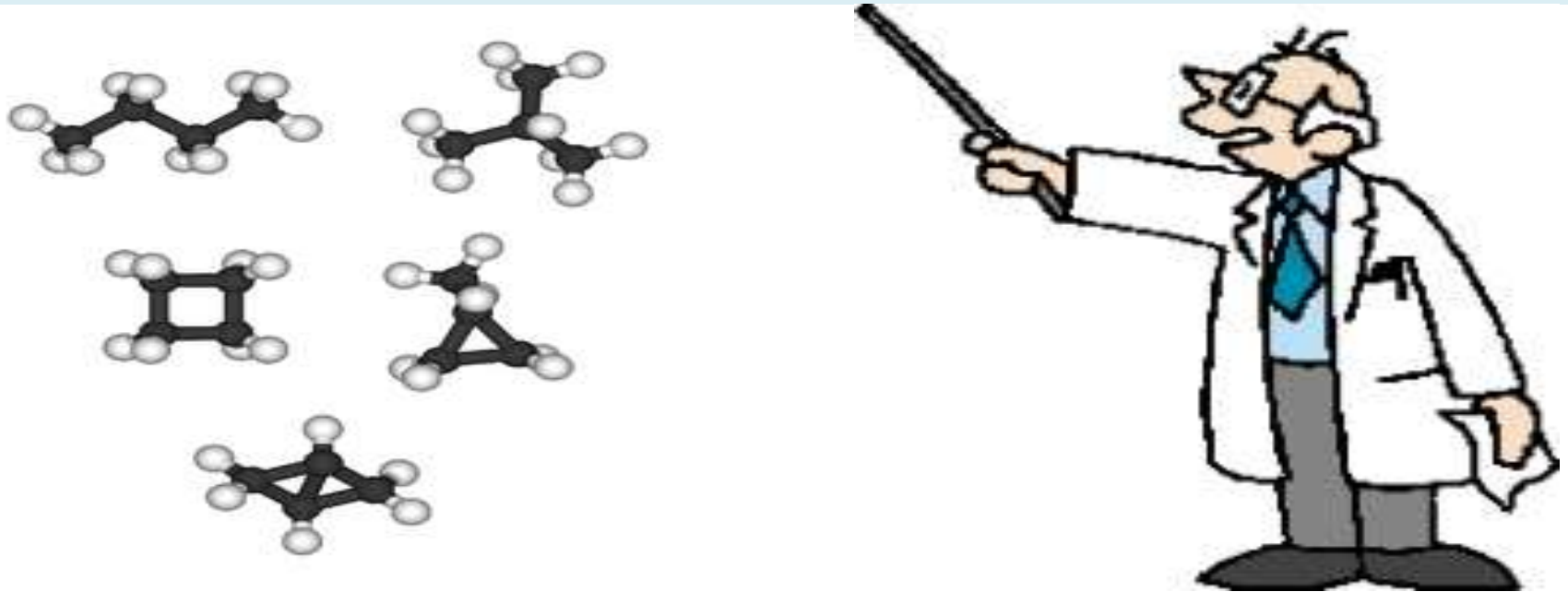


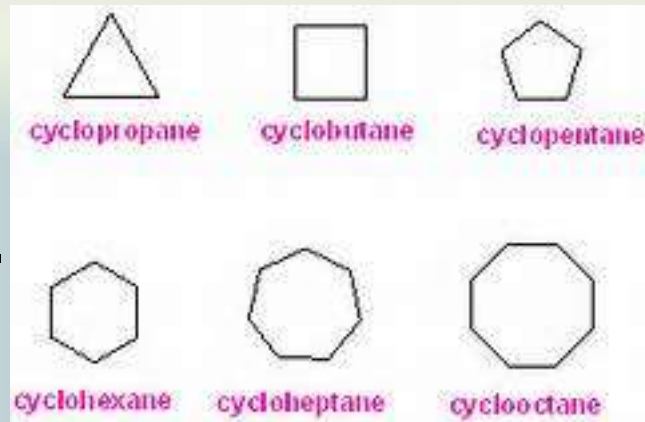
ALKANES AND THEIR PREPARATION



CLASSIFICATION OF ALKANES

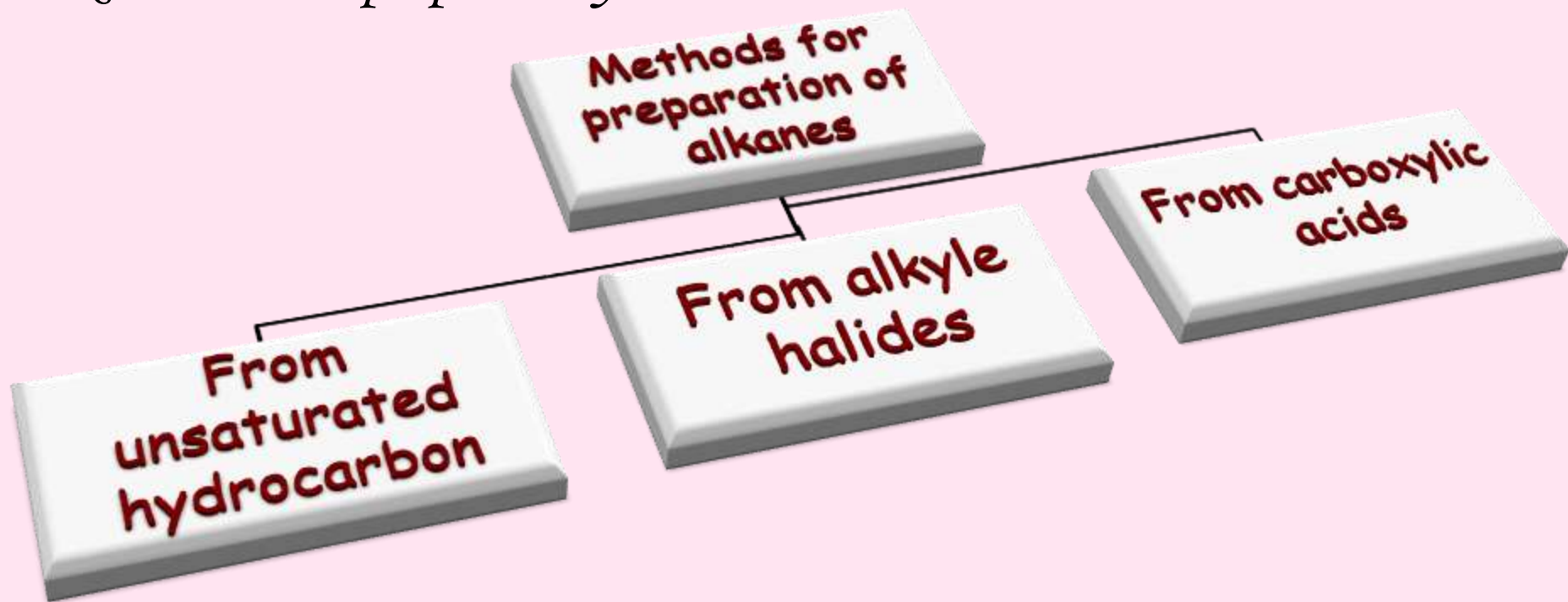
Alkanes are saturated hydrocarbon containing only carbon-carbon single bond in their molecule. They are also called Paraffins. At high temperatures and pressure do undergo some reaction. The alkanes may be divided as:

- 1) Open chain or Acyclic alkanes .
- 2) Cycloalkanes or cyclic alkanes.



Preparation of Alkanes

Petroleum and natural gas are the main source of alkanes. However, alkanes can be prepared by three methods.



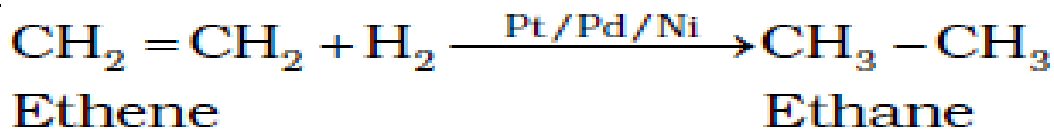
From Unsaturated Hydrocarbon

The unsaturated hydrocarbons (alkenes and alkynes) are converted into alkanes by catalytic hydrogenation. In this process dihydrogen is passed through alkenes or alkynes in the presence of finely divided catalysts such as Raney Ni, Pt or Pd.

These metals absorb dihydrogen gas on their surfaces and activate the hydrogen-hydrogen bond. Platinum and palladium catalyse the reaction at room temperature. However, higher temperature (523-573K) and pressure are required with nickel catalysts.

The hydrogenation reaction of unsaturated hydrocarbon using nickel at a temperature of 523-573K is commonly known as Sabatier and Sender's reaction or reduction.

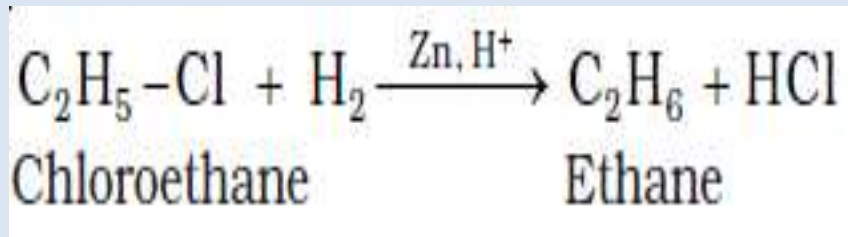
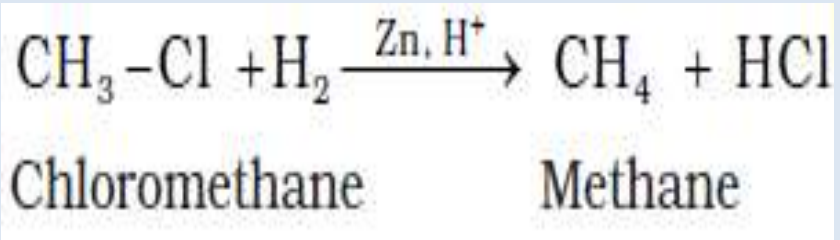
Methane cannot be prepared by this method because starting alkenes or alkynes must contain at least two carbon atoms.



From Unsaturated Hydrocarbon

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

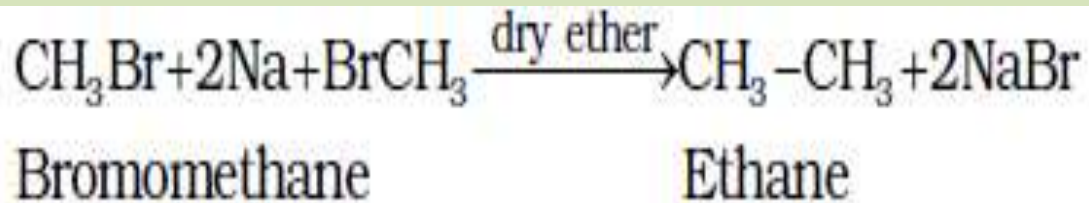
For eg:



Wurtz reaction of preparation of alkanes

Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes.

This reaction is known as Wurtz reaction and is used for the preparation of higher alkanes containing even number of carbon atom.



CHARLES ADOLPH
WURTZ

From carboxylic acids

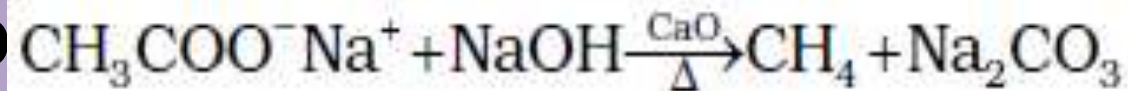
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graph TD; A[From carboxylic acids] --> B[Decarboxylation reaction]; A --> C[Kolbe's electrolytic method]
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Decarboxylation reaction

Kolbe's electrolytic method

DECARBOXYLATION REACTION

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



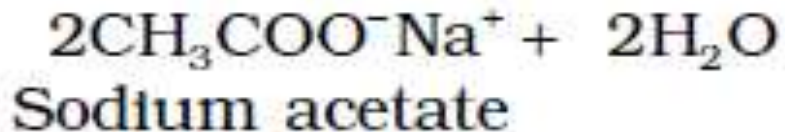
Sodium ethanoate

KOLBE'S ELECTROLYTIC METHOD

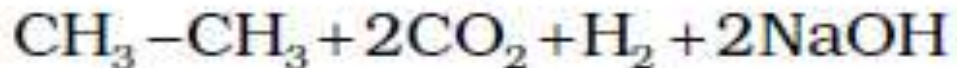
- This METHOD IS USED FOR THE REDUCTION OF CO_2 .

An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode.

AT THE CATHODE THERE IS REDUCTION OF WATER INTO HYDROGEN FREE RADICALS AND THAT IS CONVERTED INTO HYDROGEN AND GIVEN OFF.



↓ Electrolysis

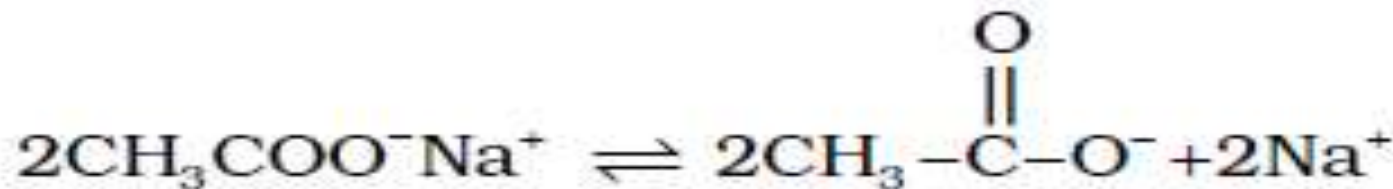


Reaction mechanism of Kolbe's electrolytic method

- In a mechanism there are three steps :-
Initiation , propagation and termination.

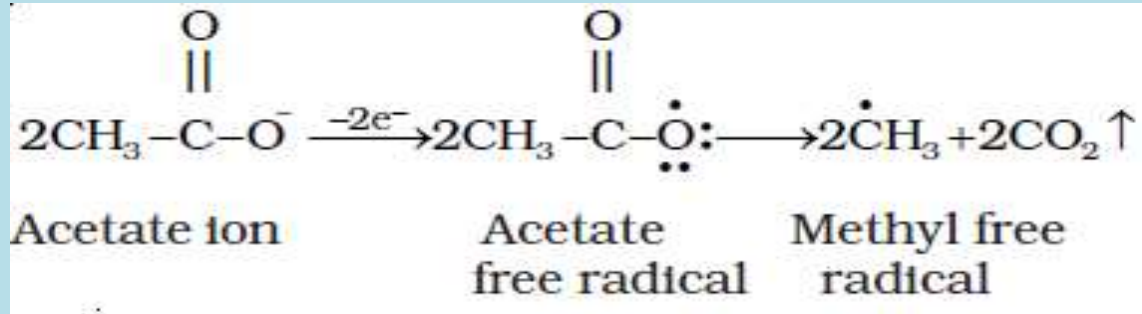
INITIATION

Here sodium acetate is converted into acetate and sodium ions.



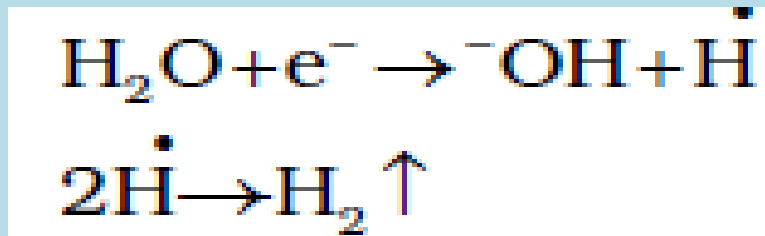
• PROPAGATION

At anode:-



TERMINATION

At cathode:-



Chemical properties of alkanes

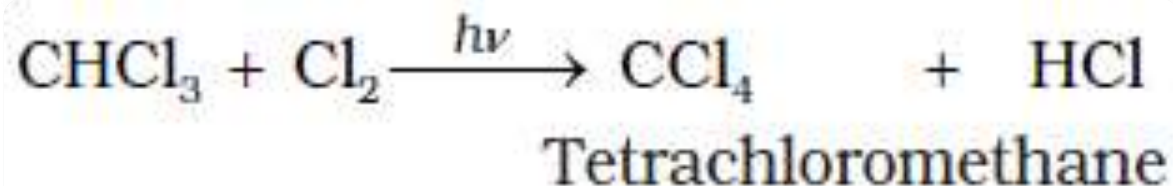
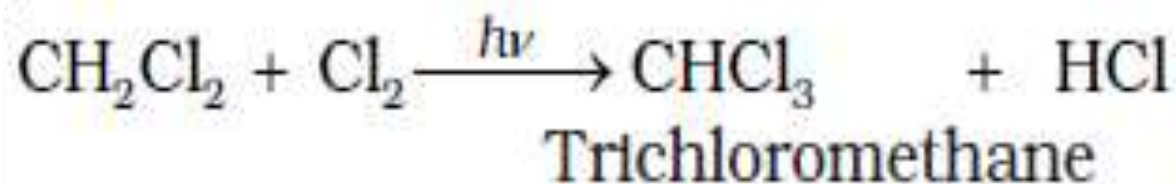
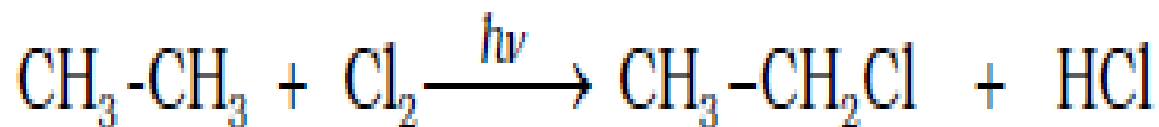
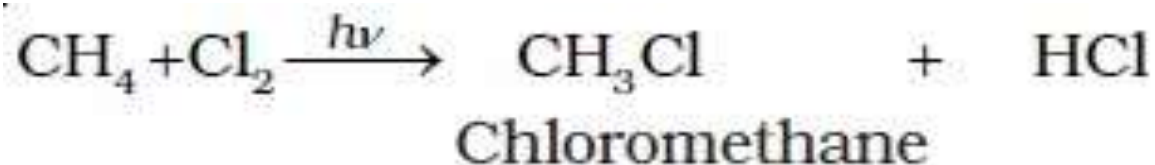
Substitution reactions

- The reaction in which an atom or a group of atoms in a molecule is replaced by some other atom or group of atom. Alkanes undergo substitution reaction in which one or more hydrogen atoms are replaced or substituted by different atoms or groups such as halogen atom (Cl, Br or I), nitro group ($-\text{NO}_2$) or sulphonic acid ($-\text{SO}_3\text{H}$) group.

Types of substitution reactions

Halogenation

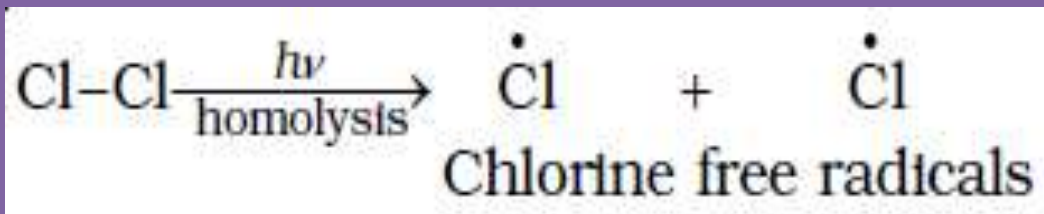
- This involves the replacement of one or more atoms of alkanes by the corresponding number of halogens atoms.
- It is found that the rate of reaction of alkanes with halogen is $F_2 > Cl_2 > Br_2 > I_2$. Rate of replacement of hydrogen of alkanes is: $3^\circ > 2^\circ > 1^\circ$.



Mechanism of halogenation reaction

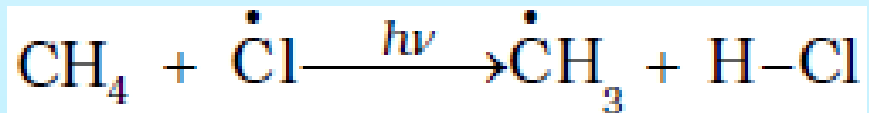
Initiation

The reaction is initiated by homolysis of chlorine molecule in the presence of light or heat, the Cl-Cl bond is weaker than the C-C and C-H bond and hence, is easiest to break

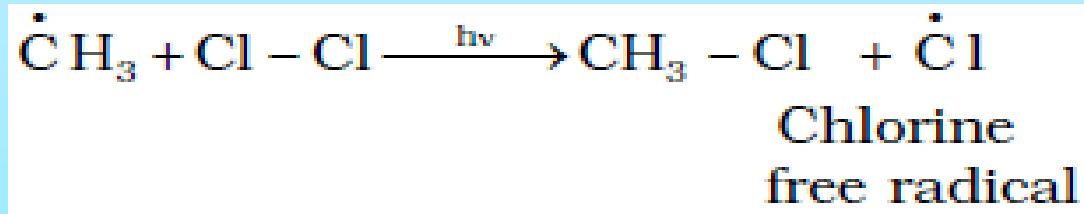


Propagation

Chlorine free radicals attacks the methane molecule and takes the reaction in the forward direction by breaking the C-H bond to generate methyl free radical with the formation of H-Cl.



The methyl radical thus obtained attacks the second molecule of chlorine to form $\text{CH}_3\text{-Cl}$ with the liberation of another chlorine free radical by homolysis of chlorine molecule.



Termination

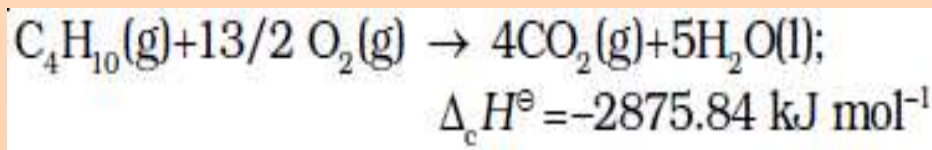
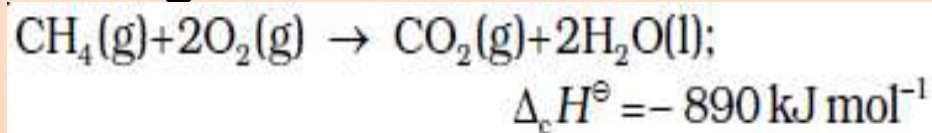
The reaction stops after some time due to consumption of reactants and/or due to following side reaction: The possible chain terminating steps are:



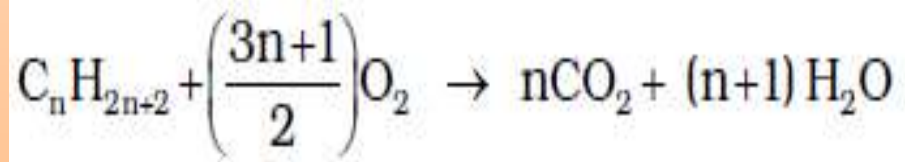
Though in (c) $\text{CH}_3\text{-Cl}$, the one of the product is formed but free radicals are consumed and the chain is terminated.

Combustion

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



The general combustion equation for any alkane is:

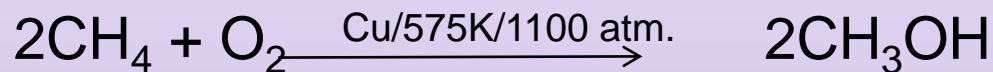


Due to the evolution of large amount of heat during combustion, alkanes are used as fuels cells.

Controlled Oxidation

Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalyst give a variety of oxidation product:

- i) When a mixture of methane and oxygen in the molar ratio of 9:1 is compressed to about 1100 atmospheres and passed through copper tubes at 575 K, methane is oxidised to methanol.

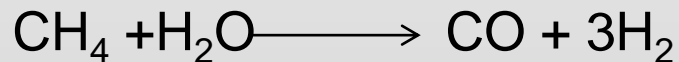


- ii) When methane is mixed with oxygen and passed through heated molybdenum oxide (Mo_2O_3), under pressure it is oxidised to methanal.



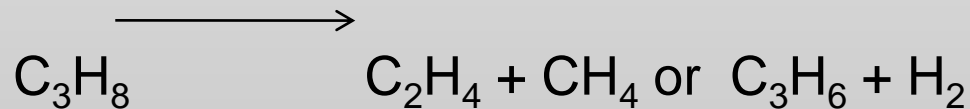
Reaction of steam

On passing a mixture of steam and methane over heated nickle (supported over alumina, Al_2O_3) catalyst at 1273 K, methane is oxidised to carbon monoxide and hydrogen is evolved.

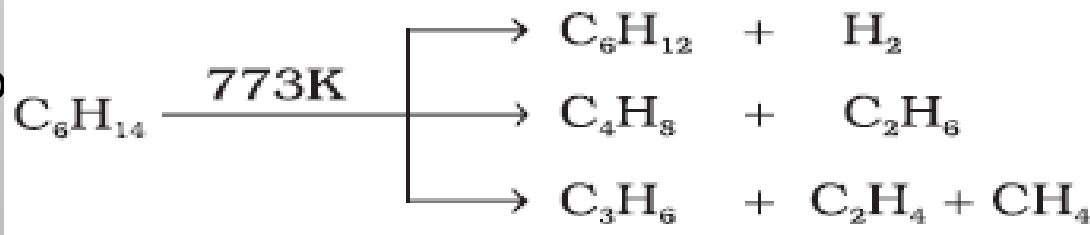


Pyrolysis

When higher alkanes are heated to high temperture in the presence of alumina or silica catalysts, the alkanes break down to lower alkanes and alkenes. For eg:



This reaction is called Fragmentation or Cracking or Pyrolysis. Pyrolysis of hexane gives following products



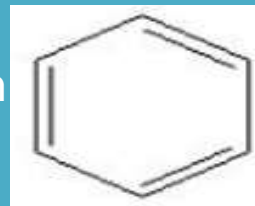
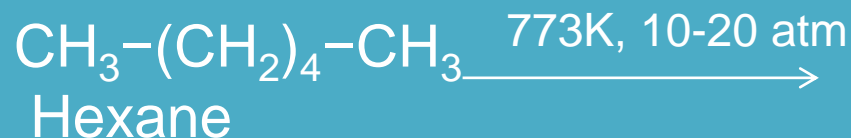
Isomerisation

Alkane isomerise to branched chain alkanes when heated with anhydrous aluminium chloride (AlCl_3) and hydrogen chloride at 573 K under a pressure of about 30-35 atmosphere.



Aromatization

The alkanes containing six or more carbon atoms when heated at about 773K under high pressure of 10-20 atm in the presence of catalyst on alumina gel get converted to aromatic compounds. This process is called aromatization.



Benzene

CONFORMATIONS

Types of conformations

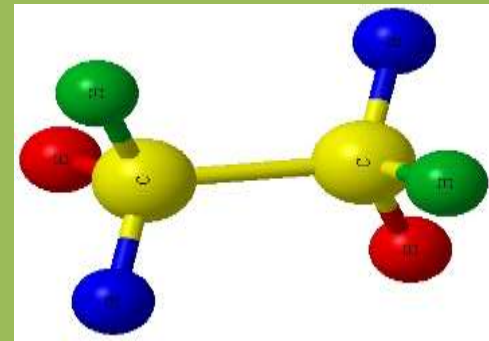
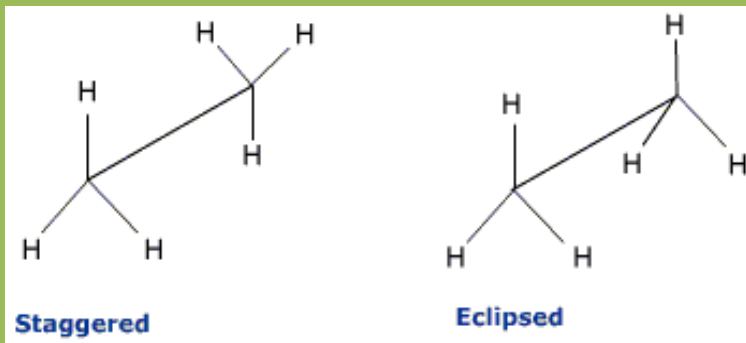
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graph TD; A[Types of conformations] --> B[Saw horse projections]; A --> C[Newman's projections]
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Saw horse projections

Newman's projections

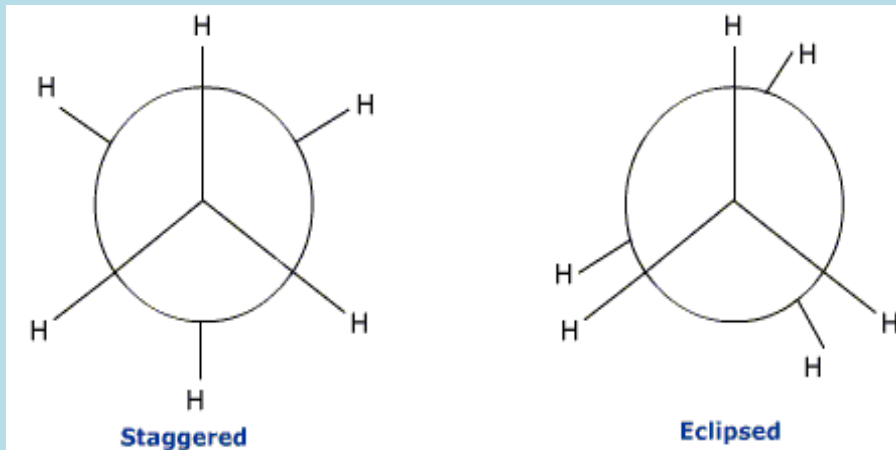
Saw horse's projections

- In this projection, the molecule is viewed along the axis of the model from an oblique angle.
- The central carbon-carbon bond (C-C) is drawn as a straight line slightly tilted to right for the sake of clarity.
- The front carbon is shown as the lower left hand carbon and the back carbon is shown as the upper right hand carbon.



Newman's projections

- In this method, the molecule is viewed from the front along the carbon-carbon bond axis.
- The two carbon atoms forming the σ bond are represented by two circle; one behind the other so that only the front carbon is seen.
- The front carbon atom is shown by a point whereas the carbon further from the eye is represented by the circle.
- Therefore, the C-H bonds of the front carbon are depicted from the centre of the circle while C-H bonds of the back carbon are drawn from the circumference of the circle at an angle of 120° at each other.



PAUL NEW MAN