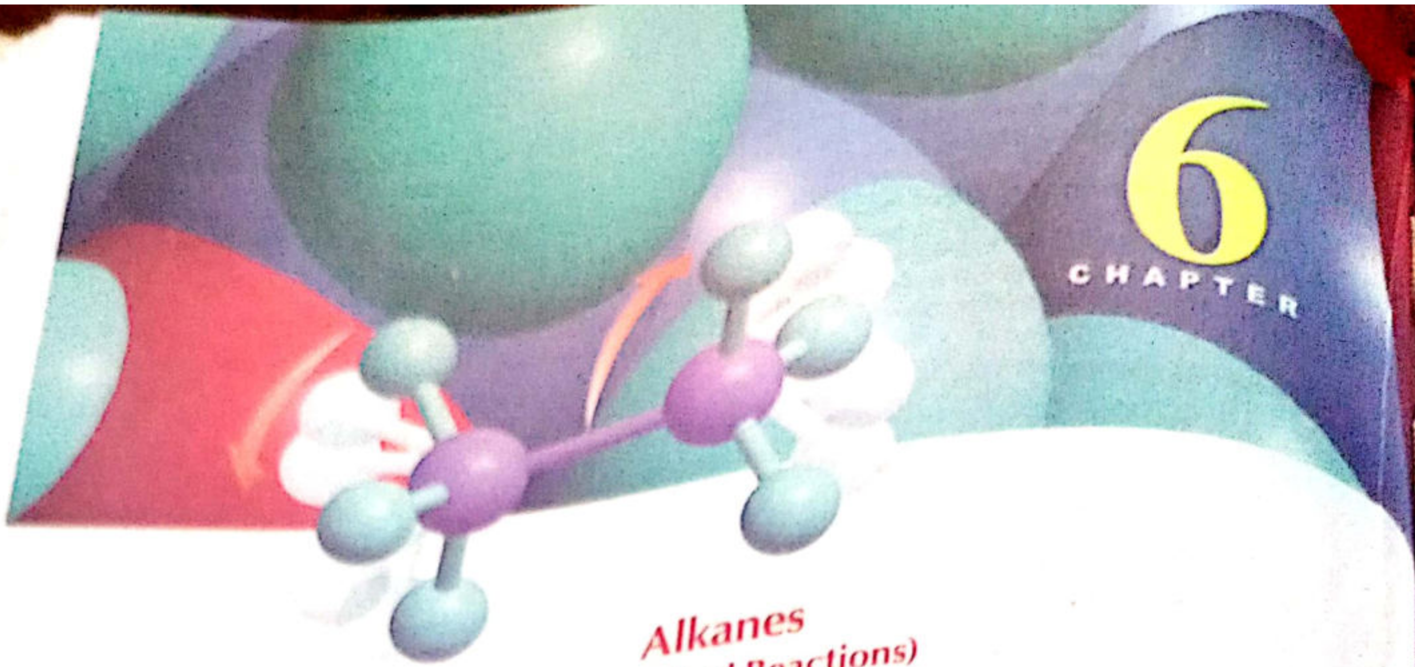
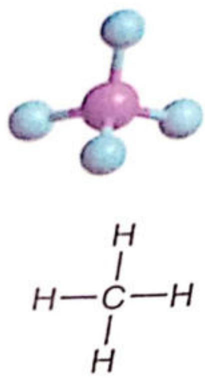
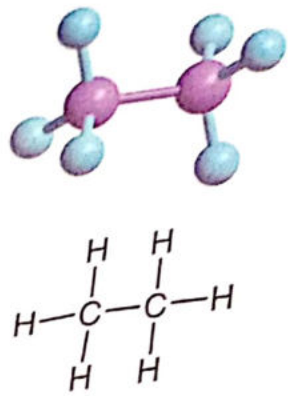


Alkanes
(Free-Radical Reactions)

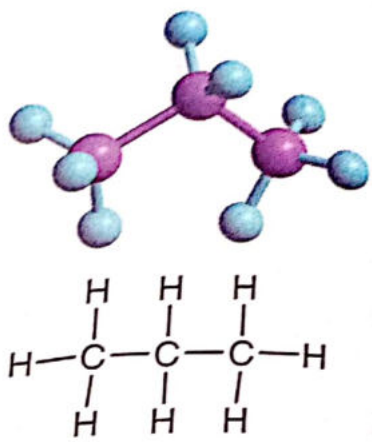
Alkanes are the simplest organic compounds made of carbon and hydrogen only. They have the general formula C_nH_{2n+2} where n = 1, 2, 3 etc. The first three members of this class can be represented as :



Methane



Ethane



Propane

The carbon atoms in their molecules are bonded to each other by single covalent bonds. Each carbon is again bonded to enough hydrogen atoms to give maximum covalence of 4. Since the carbon skeleton of alkanes is fully 'saturated' with hydrogens, they are also called **Saturated Hydrocarbons.**

Alkanes contain strong C–C and C–H covalent bonds. Therefore, this class of hydrocarbons are relatively chemically inert. Hence they are sometimes referred to as **Paraffins** (Latin, *parum affinis* = little affinity).

STRUCTURE

Let us consider methane (CH_4) and ethane (CH_3–CH_3) for illustrating the orbital make up of alkanes. In methane, carbon forms single bonds with four hydrogen atoms. Since the carbon atom is attached to four other atoms, it uses sp^3 hybrid orbitals to form these bonds. Each C–H bond is the result of the overlap of an sp^3 orbital from carbon and an s orbital from hydrogen (Fig. 6.1). All C–H bonds are σ bonds.

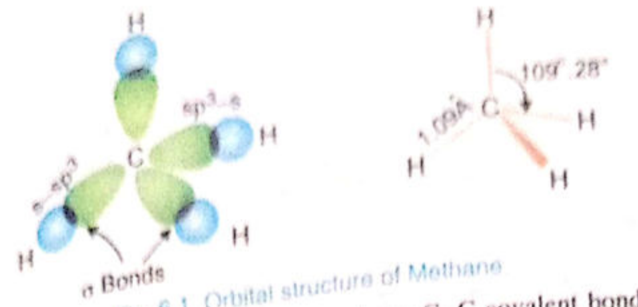


Fig 6.1. Orbital structure of Methane

In ethane, there are six C–H covalent bonds and one C–C covalent bond. As in the case of methane, each C–H bond is the result of overlap of an sp^3 hybrid orbital from carbon and an *s* orbital from hydrogen. The C–C bond arises from the overlap of the sp^3 orbitals, one from each carbon (Fig 6.2). All C–H bonds and the C–C bond are σ bonds.

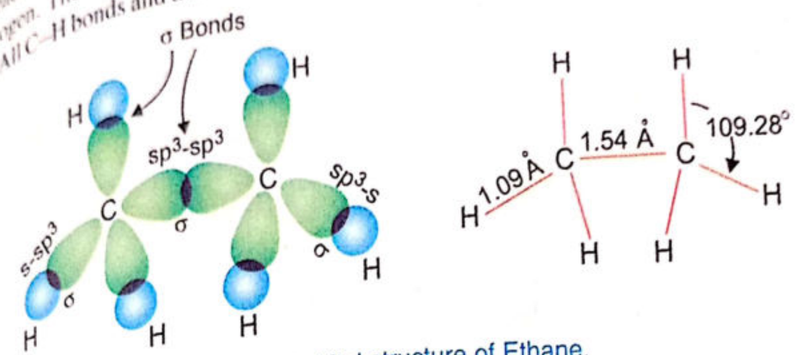


Fig. 6.2. Orbital structure of Ethane.

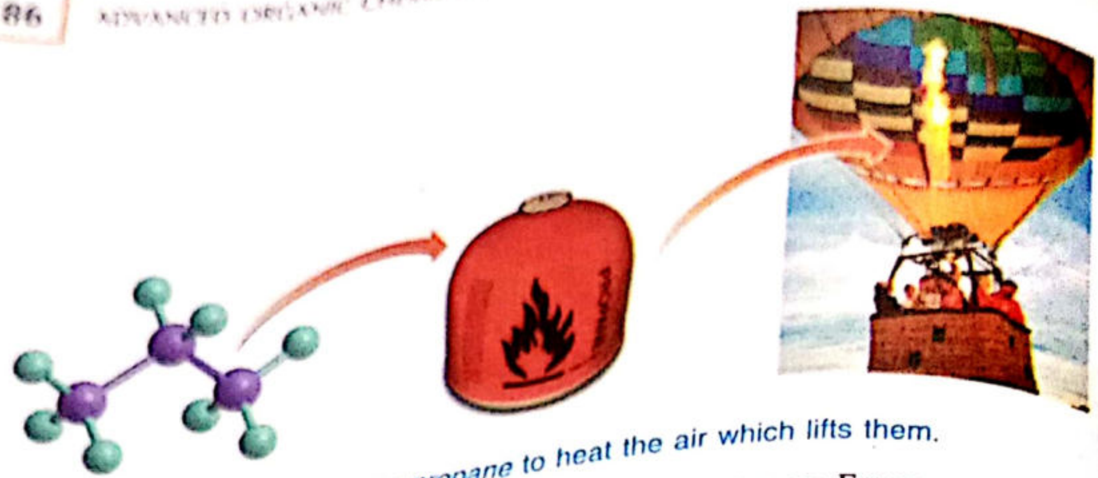
NOMENCLATURE

There are two systems of naming alkanes :

(1) **Common System**. The first four members of the series are called by their common names (trivial names) : *methane*, *ethane*, *propane*, and *butane*. The names of larger alkanes are derived from the Greek prefixes that indicate the number of carbon atoms in the molecule. Thus, *pentane* has *five* carbons, *hexane* has *six*, and so forth. See Table 6.1.

Table 6.1 NAMES OF ALKANES

Number of carbon atoms	Name	Molecular formula	Structure of the normal isomer
1	Methane	CH_4	CH_4
2	Ethane	C_2H_6	CH_3CH_3
3	Propane	C_3H_8	$CH_3CH_2CH_3$
4	Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$
5	Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$
6	Hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	Heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
8	Octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	Nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$



Hot air balloons use *propane* to heat the air which lifts them.

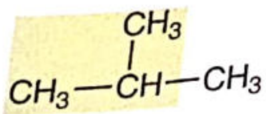
In the common system all isomeric alkanes have the same parent name. For example, two isomeric C_4H_{10} alkanes are known as butanes. The names of various isomers are distinguished by prefixes. The prefix indicates the type of branching present in the molecule.

(1) Prefix *n*- is used for those alkanes in which all carbons are in one continuous chain. The prefix *n*- stands for normal.

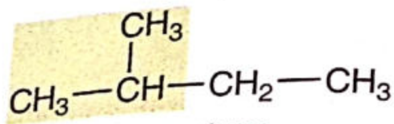
$CH_3CH_2CH_2CH_3$
n-Butane

$CH_3CH_2CH_2CH_2CH_3$
n-Pentane

(2) Prefix *iso*- is used for those alkanes which have a methyl group (CH_3-) attached to the second last carbon atom of the continuous chain.

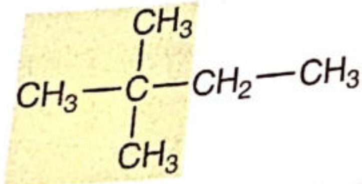


Isobutane



Isopentane

(3) Prefix *neo*- is used for those alkanes which have two methyl groups attached to the second last carbon atom of the continuous chain.



Neohexane

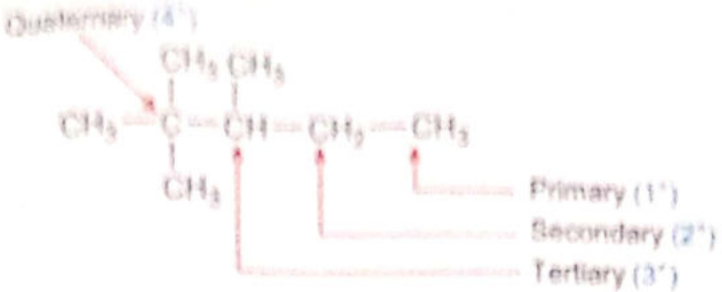
Primary, Secondary, and Tertiary Carbons. The structural formulas of alkanes contain four types of carbon atoms :

(1) A carbon atom attached to one other (or no other) carbon is called **primary carbon** (*1° carbon; 1° = primary*).

(2) A carbon atom attached to two other carbon atoms is called **secondary carbon** (*2° carbon; 2° = secondary*).

(3) A carbon atom attached to three other carbon atoms is called **tertiary carbon** (*3° carbon; 3° = tertiary*).

(4) A carbon atom attached to four other carbon atoms is called **quaternary carbon** (*4° carbon; 4° = quaternary*).



Hydrogen atoms attached to 1°, 2°, 3° carbon atoms are often referred to as primary, secondary, and tertiary hydrogen atoms.

Alkyl Groups. An alkyl group is formed by removing one hydrogen from an alkane. They are named simply by dropping *-ane* from the name of the corresponding alkane and replacing it by *-yl* (**alkane - ane + yl = alkyl**). For example,

$$\underset{\text{Alkane}}{RH} \xrightarrow{-H} \underset{\text{Alkyl group}}{R-}$$

$$\underset{\text{Methane}}{CH_4} \xrightarrow{-H} \underset{\text{Methyl group}}{CH_3-} \qquad \underset{\text{Ethane}}{CH_3CH_3} \xrightarrow{-H} \underset{\text{Ethyl group}}{CH_3CH_2-}$$

Table 6.2 shows the names of some important alkyl groups.

Table 6.2 NAMES OF COMMON ALKYL GROUPS

Parent alkane	Structure	Alkyl group	Name of alkyl group
Methane	CH_4	CH_3-	methyl
Ethane	CH_3CH_3	CH_3CH_2-	ethyl
Propane	$CH_3CH_2CH_3$	$CH_3CH_2CH_2-$	*n*-propyl
		$CH_3\overset{\vert}{C}HCH_3$	isopropyl
n-Butane	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2-$	*n*-butyl
		$CH_3CH_2\overset{\vert}{C}HCH_3$	*sec*-butyl (secondary-butyl)
Isobutane	$CH_3\overset{CH_3}{\overset{\vert}{C}}HCH_3$	$CH_3\overset{CH_3}{\overset{\vert}{C}}HCH_2-$	isobutyl
		$CH_3\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}CH_3$	*t*-butyl or *tert*-butyl (tertiary-butyl)

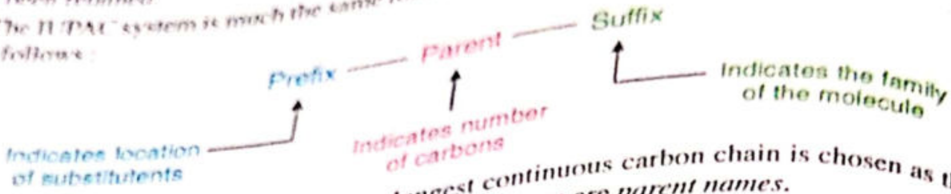
Nonalkyl Groups. A number of nonalkyl groups are used in naming organic compounds. For example,

Group	Name	Group	Name
–F	fluoro	$-NO_2$	nitro
–Cl	chloro	$-NH_2$	amino
–Br	bromo	–OH	hydroxy
–I	iodo		

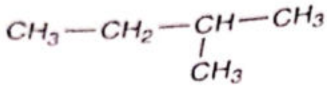
(2) **IUPAC System.** The common system has some limitations. Pentane has three isomers ; hexane has five. The more complicated the alkane, the greater the number of special prefixes needed to

name the isomers. In order to device a system of nomenclature that could be used for even the most complicated compounds, committees of chemists have met periodically since 1892. The system resulting from these meetings is called the IUPAC (International Union of Pure and Applied Chemistry) system. In this system, not all of the old common names have been discarded. Some common names have been retained.

The IUPAC system is much the same for all families of organic compounds. The steps for alkanes are as follows:

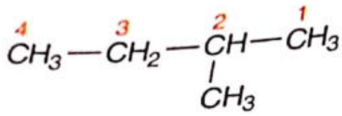


Step 1. Name the longest chain The longest continuous carbon chain is chosen as the basis for the name. The names are those given in Table 6.1. These are *parent names*.

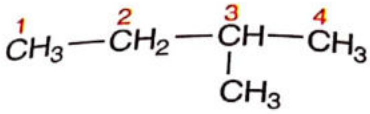


The longest continuous chain has four carbon atoms. Thus, the compound is named as a butane.

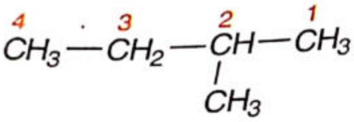
Step 2. Number the longest chain. The carbon atoms in the longest chain are numbered. The numbering is started from that end which will give numbers having the lowest value to carbons carrying substituents.



and not

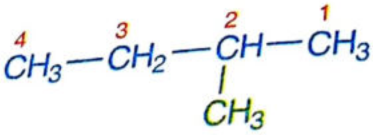


Step 3. Locate and name the substituents. Each substituent is named, and the position of each substituent is indicated by the number of the carbon atom to which it is attached.

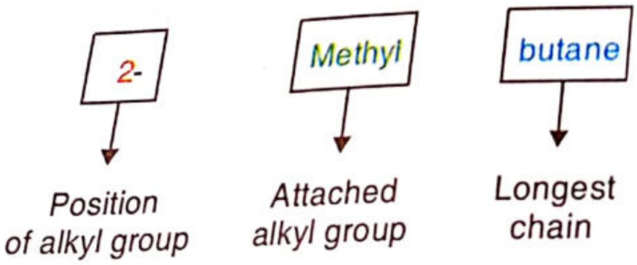


The attached group is located on carbon 2 of the chain, and it is a methyl group.

Step 4. Combine the longest chain and substituents into the name. The position and the name of the substituent are added to the name of the longest chain and written as one word.

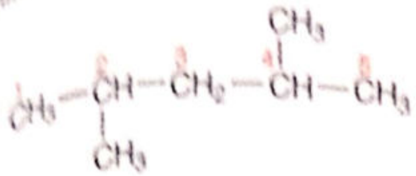


2-Methylbutane

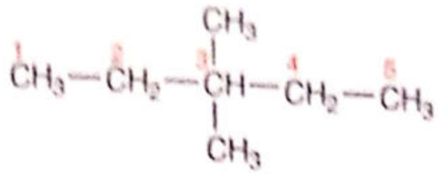


Additional steps are needed when more than one substituent is attached to the longest chain.

Step 3. Indicate the number and position of substituents. If the same substituent is present two or more times in the molecule, the number of this substituent is indicated by a prefix di-, tri-, tetra-, penta-, etc., and the location of each is indicated by a separate number. These position numbers, separated by commas, are put just before the name of the substituent, with hyphen before and after the numbers when necessary.

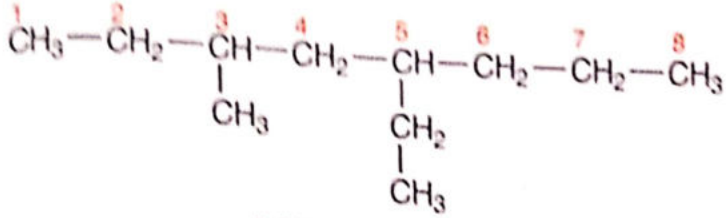


2,4-Dimethylpentane



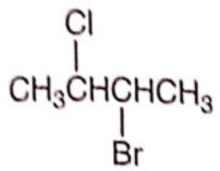
3,3-Dimethylpentane

If two or more substituents are present, their names are alphabetized and added to the name of the parent alkane, again as one word.

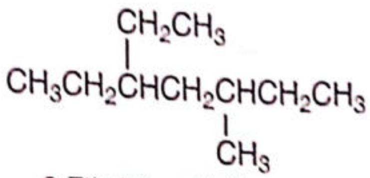


5-Ethyl-3-methyloctane

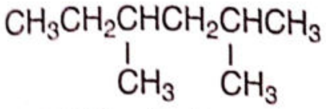
The following examples further illustrate the application of the above rules :



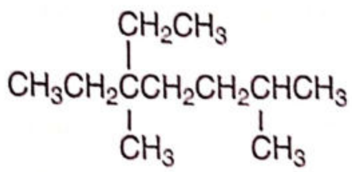
2-Bromo-3-chlorobutane



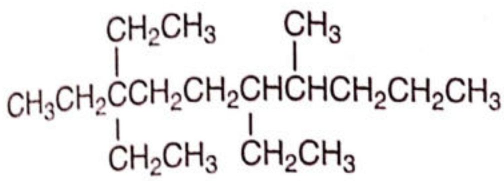
3-Ethyl-5-methylheptane



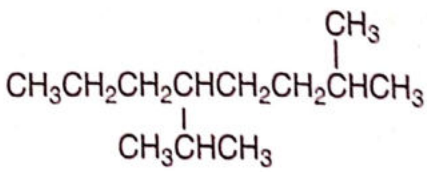
2,4-Dimethylhexane



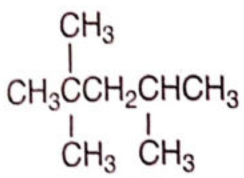
5-Ethyl-2,5-dimethylheptane



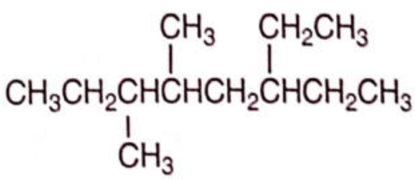
3,3,6-Triethyl-7-methyldecane



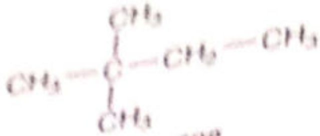
5-Isopropyl-2-methyloctane



2,2,4-Trimethylpentane



6-Ethyl-3,4-dimethyloctane



Neohexane
(2,2-Dimethylbutane)

As we go higher in the series C_nH_{2n+2}, with the increase in the number of carbons, the number of isomers increases very rapidly. For example, there are 9 heptanes, 18 octanes, and 75 decanes.

NATURAL SOURCES OF ALKANES

The two main sources of alkanes are *natural gas* and *petroleum*. Both of these substances are frequently found together in underground deposits. Natural gas contains about 80% methane and 10% ethane, the remaining 10% being a mixture of higher members. Petroleum is a chief source of alkanes containing up to 40 carbons.

METHODS OF PREPARATION

Alkanes are prepared by the following methods :

(1) **Hydrogenation of Alkenes or Alkynes.** Alkenes or alkynes react with hydrogen in the presence of nickel catalyst at 200-300°C to form alkanes. Other catalysts which can be used are platinum and palladium.

(a)

$$\underset{\text{Alkene}}{R{-}CH{=}CH_2} + H_2 \xrightarrow[\Delta]{Ni} \underset{\text{Alkane}}{R{-}CH_2{-}CH_3}$$

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2 \xrightarrow[\Delta]{Ni} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + H_2 \xrightarrow[\Delta]{Pt} \underset{\text{Propane}}{CH_3{-}CH_2{-}CH_3}$$

(b)

$$\underset{\text{Alkyne}}{R{-}C{\equiv}CH} + 2H_2 \xrightarrow[\Delta]{Ni} \underset{\text{Alkane}}{R{-}CH_2{-}CH_3}$$

$$\underset{\text{Acetylene}}{CH{\equiv}CH} + 2H_2 \xrightarrow[\Delta]{Ni} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

(2) **Reduction of Alkyl Halides.** Alkyl halides undergo reduction with nascent hydrogen to form alkanes.

$$\underset{\text{Alkyl halide}}{R{-}X} + 2[H] \longrightarrow \underset{\text{Alkane}}{R{-}H} + HX$$

$$\underset{\text{Methyl iodide}}{CH_3{-}I} + 2[H] \longrightarrow \underset{\text{Methane}}{CH_4} + HI$$

$$\underset{\text{Ethyl bromide}}{CH_3CH_2{-}Br} + 2[H] \longrightarrow \underset{\text{Ethane}}{CH_3{-}CH_3} + HBr$$

The hydrogen for reduction may be obtained by using any of the following reducing agents : $Zn + HCl$; $Zn + CH_3COOH$; Zn–Cu couple in ethanol ; or $LiAlH_4$; Hydrogen gas and Ni or Pt catalyst may also be used.

(3) **Decarboxylation of Carboxylic Acids.** When the sodium salt of a carboxylic acid is heated strongly with sodalime ($NaOH + CaO$), a molecule of carbon dioxide is split off as carbonate and an alkane is formed. Notice that the alkane so produced contains one carbon less than the original acid.

$$R{-}COONa + NaOH \xrightarrow{\Delta} \underset{\text{Alkane}}{RH} + Na_2CO_3$$

$$\underset{\text{Sodium acetate}}{CH_3{-}COONa} + NaOH \xrightarrow{\Delta} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

(4) **Hydrolysis of Grignard Reagents.** Alkyl magnesium halides (Grignard reagents) are obtained by treating alkyl halides with magnesium in anhydrous ether. These on treatment with water give alkanes.

$$RX + Mg \xrightarrow{\text{ether}} \underset{\text{Alkylmagnesium halide}}{RMgX}$$

$$RMgX + HOH \longrightarrow \underset{\text{Alkane}}{RH} + MgX(OH)$$

$$\underset{\text{Methylmagnesium iodide}}{CH_3MgI} + HOH \longrightarrow \underset{\text{Methane}}{CH_4} + MgI(OH)$$

(5) **Wurtz Synthesis.** Higher alkanes are produced by heating an alkyl halide (RX) with sodium metal in dry ether solution. Two molecules of the alkyl halide lose their halogen atoms as NaX. The net result is the joining of two alkyl groups to yield a symmetrical alkane (R—R type) having an even number of carbon atoms.

$$R{-}X + 2Na + X{-}R \xrightarrow{\text{ether}} \underset{\text{symmetrical alkane}}{R{-}R} + 2NaX$$

$$\underset{\text{Methyl bromide}}{CH_3{-}Br} + 2Na + Br{-}CH_3 \xrightarrow{\text{ether}} \underset{\text{Ethane}}{CH_3{-}CH_3} + 2NaBr$$

The mechanism involves the formation of an extremely reactive organosodium intermediate:

$$RX + 2Na \longrightarrow [RNa] + NaX$$

$$RX + [RNa] \longrightarrow R{-}R + NaX$$

The reaction between two different alkyl halides and sodium gives a mixture of products that are difficult to separate. For example, methyl chloride and ethyl chloride when treated with sodium give three products : propane from the combination of methyl chloride and ethyl chloride; ethane from the combination of two molecules of methyl chloride ; and *n*-butane from two molecules of ethyl chloride.

$$\underset{\text{Ethyl chloride}}{CH_3CH_2{-}Cl} + 2Na + \underset{\text{Methyl chloride}}{Cl{-}CH_3} \xrightarrow{\text{ether}} \underset{\text{Propane}}{CH_3CH_2{-}CH_3} + 2NaCl$$

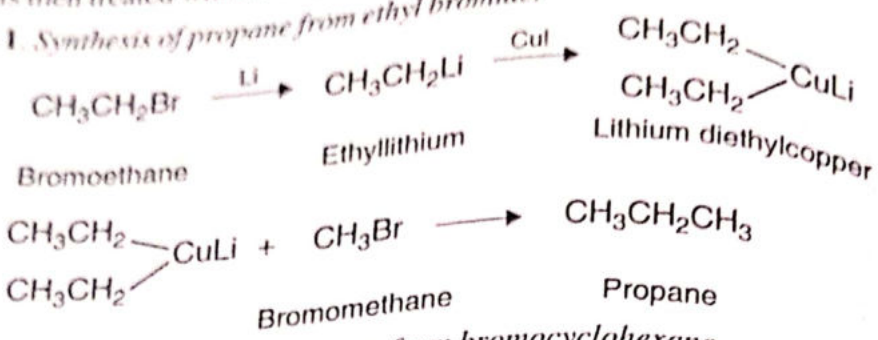
$$\underset{\text{Methyl chloride}}{CH_3{-}Cl} + 2Na + Cl{-}CH_3 \xrightarrow{\text{ether}} \underset{\text{Ethane}}{CH_3{-}CH_3} + 2NaCl$$

$$\underset{\text{Ethyl chloride}}{CH_3CH_2{-}Cl} + 2Na + Cl{-}CH_2CH_3 \xrightarrow{\text{ether}} \underset{n\text{-Butane}}{CH_3CH_2{-}CH_2CH_3} + 2NaCl$$

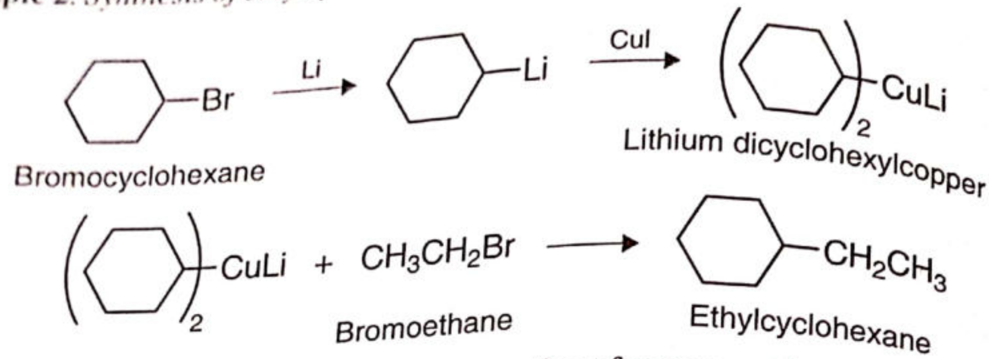
LIMITATION. As shown above, the use of two different alkyl halides in Wurtz reaction always leads to a mixture of alkanes. The separation of these alkanes is not always easy because of little difference in their boiling points. The problem of isolating the desired product limits the usefulness of this method to the preparation of only the symmetrical alkanes.

(6) **Corey-House Alkane Synthesis.** An alkyl halide is first converted to lithium dialkylcopper, LiR_2Cu. This is then treated with an alkyl halide to give an alkane.

Example 1. *Synthesis of propane from ethyl bromide.*



Example 2. *Synthesis of ethylcyclohexane from bromocyclohexane.*



This method is particularly suitable for the preparation of unsymmetrical alkanes, *i.e.*, those of the type R—R′.

(7) **Kolbe's Synthesis.** When a concentrated solution of sodium salt of a carboxylic acid is electrolysed, an alkane is formed.

$$2RCO\bar{O}\overset{+}{Na} + 2H_2O \longrightarrow \underset{\text{at anode}}{R{-}R + 2CO_2} + \underset{\text{at cathode}}{2NaOH + H_2}$$

Sodium carboxylate

$$2CH_3CO\bar{O}\overset{+}{Na} + 2H_2O \longrightarrow \underset{\text{at anode}}{CH_3{-}CH_3 + 2CO_2} + \underset{\text{at cathode}}{2NaOH + H_2}$$

Sodium acetate

This reaction is only suitable for the preparation of symmetrical alkanes, *i.e.*, those of the type, R–R.

PHYSICAL PROPERTIES

(1) First four alkanes *methane*, *ethane*, *propane* and *butane* are gases. Next fifteen members (C_5 to C_{19}) are colorless liquids. Higher alkanes are wax-like solids.

(2) **Solubilities of Alkanes.** Alkanes are nonpolar compounds. Their solubility characteristic may be predicted by what is commonly known as the 'like dissolves like' rule. What this rule means is that nonpolar compounds are soluble in other nonpolar solvents and that polar compounds are generally soluble in other polar solvents. Thus, alkanes are soluble in the nonpolar solvents like carbon tetrachloride and benzene, but they are insoluble in polar solvents such as water.

However, alkanes undergo two types of reactions :

(*a*) Substitution Reactions

(*b*) Thermal and Catalytic Reactions

These reactions take place at high temperatures or on absorption of light energy through the formation of highly reactive *free radicals*.

Some of the important reactions of alkanes are described below :

(1) **Halogenation.** This involves the substitution of hydrogen atoms of alkanes with halogen atoms.

(*a*) **Chlorination.** Alkanes react with chlorine in the presence of ultraviolet light, or diffused sunlight, or at a temperature of 300–400°C, yielding a mixture of products. For example, methane reacts with chlorine to give methyl chloride and HCl.

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow[\text{or } \Delta]{h\nu} \underset{\substack{\text{Methyl chloride} \\ \text{(Chloromethane)}}}{CH_3Cl} + HCl$$

The reaction does not stop at this stage. The remaining three hydrogen atoms of methyl chloride can be successively replaced by chlorine atoms.

$$CH_3Cl + Cl_2 \longrightarrow \underset{\substack{\text{Methylene chloride} \\ \text{(Dichloromethane)}}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \longrightarrow \underset{\substack{\text{Chloroform} \\ \text{(Trichloromethane)}}}{CHCl_3} + HCl$$

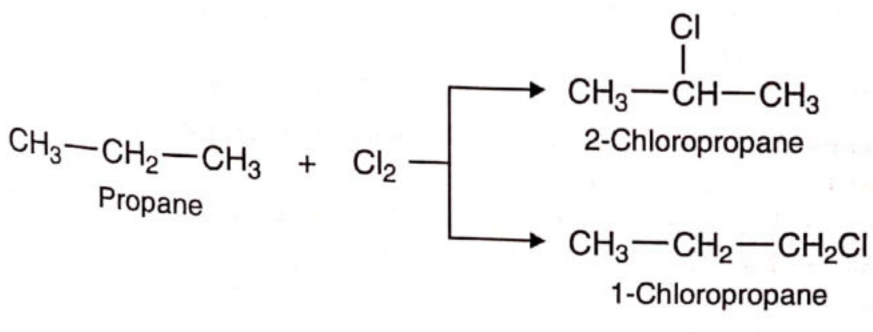
$$CHCl_3 + Cl_2 \longrightarrow \underset{\substack{\text{Carbon tetrachloride} \\ \text{(Tetrachloromethane)}}}{CCl_4} + HCl$$

In actual practice, all the four substitution products (CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4) are obtained. The extent to which each product is formed depends upon the initial chlorine to methane ratio. Carbon tetrachloride is the major product if an excess of chlorine is used. Methyl chloride is the major product if an excess of methane is used.

Ethane and higher alkanes react with chlorine in a similar way and all possible substitution products are obtained. For example, ethane reacts with chlorine to give chloroethane as the monosubstitution product.

$$\underset{\text{Ethane}}{CH_3CH_3} + Cl_2 \xrightarrow[\text{or heat}]{h\nu} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + HCl$$

Propane contains two types (primary and secondary) of hydrogens. Therefore, it gives two monosubstitution products. Generally speaking, a tertiary hydrogen is more readily replaced than a secondary hydrogen. A secondary hydrogen is more readily replaced than a primary hydrogen.

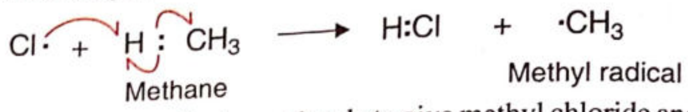


MECHANISM. The chlorination of alkanes takes place through the formation of free radicals. For example, chlorination of methane involves the following steps.

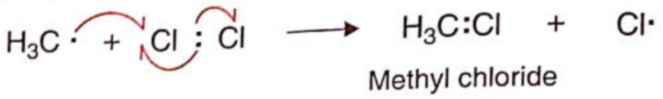
(1) **Chain-Initiation Step.** Chlorine molecule undergoes homolytic fission to give chlorine free radicals.

$$Cl : Cl \xrightarrow[\text{or } \Delta]{h\nu} Cl\cdot + Cl\cdot$$

(2) **Chain-Propagation Steps.** (*a*) Chlorine free radical attacks methane to produce HCl and methyl free radical. *Notice that fishhook arrows are used to indicate the movement of single electrons.*



(*b*) Methyl free radical attacks chlorine molecule to give methyl chloride and chlorine free radical.



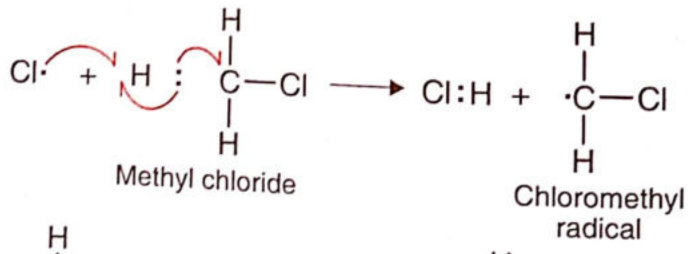
Steps (*a*) and (*b*) are repeated over and over again.

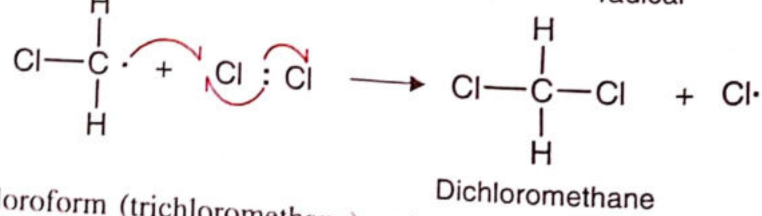
(3) **Chain-Termination Steps.** The above chain reaction comes to halt when any two free radicals combine. For example,

$$Cl\cdot + \cdot Cl \longrightarrow Cl{-}Cl$$
$$CH_3\cdot + \cdot Cl \longrightarrow CH_3{-}Cl$$
$$CH_3\cdot + \cdot CH_3 \longrightarrow CH_3{-}CH_3$$

Free-Radical Reactions Yield Mixtures of Products. Free-radical reactions are often characterized by a multitude of products. The chlorination of methane can yield four organic products. The reason for the formation of these mixtures is that the high-energy chlorine free radical is not particularly selective about which hydrogen it abstracts during the propagation step.

While chlorine is undergoing reaction with methane, methyl chloride is being formed. In time, the chlorine free radicals are more likely to collide with methyl chloride molecules than with methane molecules, and a new propagation cycle is started. In this new cycle, chloromethyl free radicals ($\cdot CH_2Cl$) are formed. These undergo reaction with chlorine molecules to yield methylene chloride (CH_2Cl_2). As in the previous cycle leading to CH_3Cl, another chlorine free radical is regenerated in the process.



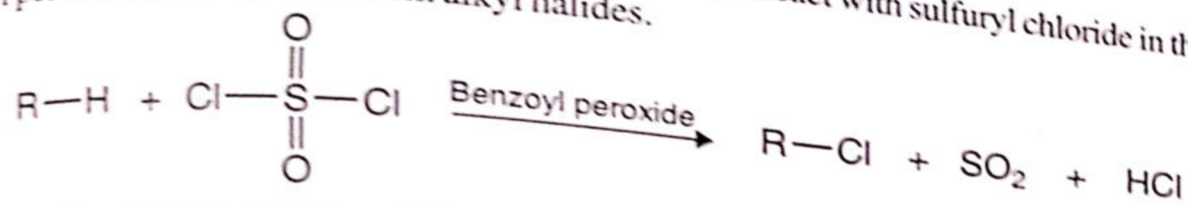


Similarly, chloroform (trichloromethane) and carbon tetrachloride (tetrachloromethane) are obtained by further chain reaction.

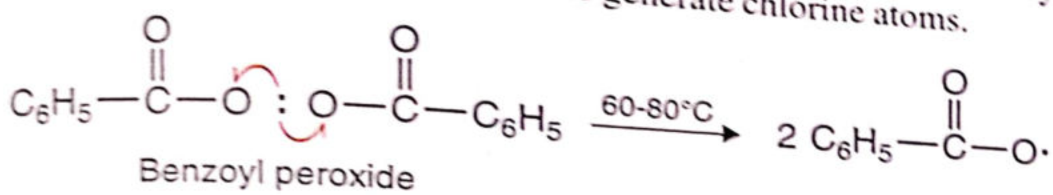
The free-radical chlorination of methane yields four organic products. Higher alkanes can produce even larger numbers of products because there are more hydrogens available that can enter into propagation reactions.

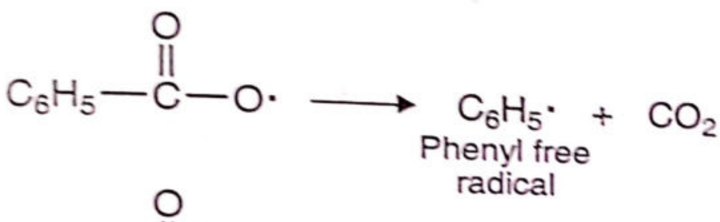
Less reactive

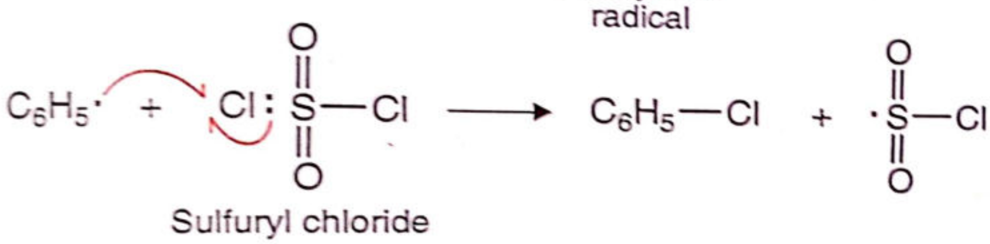
(2) Reaction with Sulfuryl Chloride ($SOCl_2$). Alkanes react with sulfuryl chloride in the presence of benzoyl peroxide at 60-80°C to form alkyl halides.

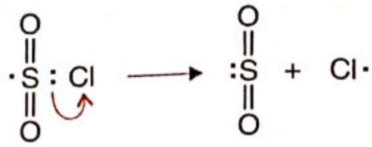


This is a free-radical reaction. It is initiated by the decomposition of benzoyl peroxide into radicals, which in turn react with sulfuryl chloride to generate chlorine atoms.

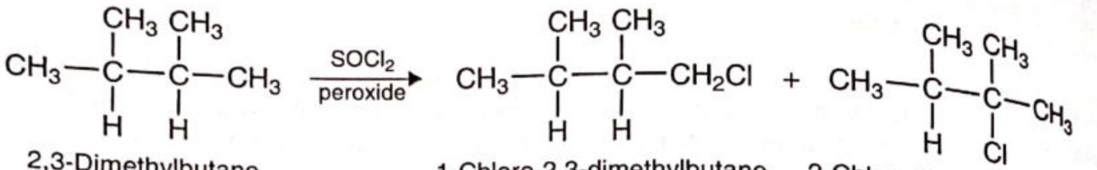








For example,



2,3-Dimethylbutane → 1-Chloro-2,3-dimethylbutane 38% + 2-Chloro-2,3-dimethylbutane 62%

(3) **Nitration of Alkanes.** Another reaction of alkanes is **nitration,** in which a nitro group, $-NO_2$, is substituted for a hydrogen. This reaction requires exceptionally vigorous conditions and provides very small yields of product. With methane, the only product is nitromethane, CH_3-NO_2; this reaction is carried out with methane and concentrated nitric acid at 400 to 500°C and under high pressure:

$$\underset{\text{Methane}}{CH_4} + \underset{(HNO_3)}{HO-NO_2} \xrightarrow[\text{pressure}]{400\text{–}500°C} \underset{\text{Nitromethane}}{CH_3-NO_2} + H_2O$$

With higher alkanes, a mixture of products is obtained, some of which result from rupturing carbon-carbon bonds. For example, the nitration of ethane results in a mixture of nitromethane and nitroethane:

$$\underset{\text{Ethane}}{CH_3-CH_3} + HO-NO_2 \xrightarrow[\text{pressure}]{400\text{–}500°C} \underset{\text{Nitroethane}}{CH_3-CH_2-NO_2} + \underset{\text{Nitromethane}}{CH_3-NO_2} + H_2O$$

MECHANISM. Free-radical mechanism is involved. The reaction is *initiated* by thermal splitting of alkane molecules into free radicals.

$$\underset{\text{Ethane}}{CH_3CH_2 : H} \xrightarrow{400\text{–}500°C} \underset{\text{Ethyl free radical}}{CH_3CH_2\cdot} + H\cdot$$

and

$$\underset{\text{Ethane}}{CH_3 : CH_3} \xrightarrow{400\text{–}500°C} \underset{\text{Methyl free radical}}{2\ CH_3\cdot}$$

Chain *propagation* occurs as follows :

$$\underset{\text{Ethyl free radical}}{CH_3CH_2\cdot} + HO : NO_2 \longrightarrow \underset{\text{Nitroethane}}{CH_3CH_2-NO_2} + \underset{\text{Hydroxyl radical}}{HO\cdot}$$

$$CH_3CH_2 : H + HO\cdot \longrightarrow CH_3CH_2\cdot + H_2O$$

Chain termination involves the recombination of any two free radicals.

$$CH_3\cdot + CH_3\cdot \longrightarrow \underset{\text{Ethane}}{CH_3 : CH_3}$$

$$CH_3CH_2\cdot + CH_3CH_2\cdot \longrightarrow \underset{\text{Butane}}{CH_3CH_2 : CH_2CH_3}$$

Nitration of alkanes is exclusively a *commercial* process. As a result of the low yields and the mixture of isomers formed, aliphatic nitro compounds are seldom encountered. On the other hand aromatic nitro compounds are easily prepared and widely used.

(4) **Sulfonation** This involves the substitution of a hydrogen atom of alkane with $-SO_3H$ group. At ordinary temperatures neither concentrated nor fuming sulfuric acid reacts with alkanes. However, when alkanes are subjected to a prolonged reaction with fuming H_2SO_4, one hydrogen atom on the alkane is replaced by the sulfonic acid group ($-SO_3H$).

$$\underset{\text{Alkane}}{R{-}H} + \underset{(\textit{fuming})}{HO{-}SO_3H} \xrightarrow{\Delta} \underset{\text{Alkanesulfonic acid}}{R{-}SO_3H} + H_2O$$

where $R = C_6H_{13}-$ or larger alkyl group. Lower alkanes like methane and ethane do not give this reaction.

(5) **Combustion (Oxidation).** The general equation for the combustion of a hydrocarbon is given below. This is one of the most important chemical reactions of modern society. It is the major route by which we provide energy for a wide range of purposes.

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow x\,CO_2 + \frac{y}{2} H_2O + \text{heat}$$

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

Energy input needed to break bonds (Endothermic process)

Energy released on forming bonds (Exothermic process)

The heat liberated during combustion is substantial. We make use of it in our homes and factories when we burn natural gas, kerosene, and other hydrocarbons.

We can make important deductions about the relative stabilities of hydrocarbons by comparing their heats of combustion. The **heat of combustion is the energy liberated when a compound is burned completely**. Compare the heats of combustion of the two isomers, pentane and 2-methylbutane (or isopentane), which are, respectively, 845.2 kcal/mole and 843.5 kcal/mole. The mass balance equations for the combustion of these two isomers are the same, as shown below.

$$C_5H_{12}(g) + 8\,O_2(g) \longrightarrow 5\,CO_2(g) + 6\,H_2O(g) + \text{heat}$$

$$\Delta H^\circ = -845.2 \text{ kcal/mole for Pentane}$$

$$\Delta H^\circ = -843.5 \text{ kcal/mole for 2-Methylbutane}$$

The combustion of pentane releases 1.7 kcal/mole more heat than does 2-methylbutane. Since the products of both combustion reactions are the same, we infer that pentane has a higher energy content than does 2-methylbutane (by 1.7 kcal/mole), and we conclude that 2-methylbutane is thermodynamically more stable than pentane by 1.7 kcal/mole. This comparison is illustrated in Figure 6.8.

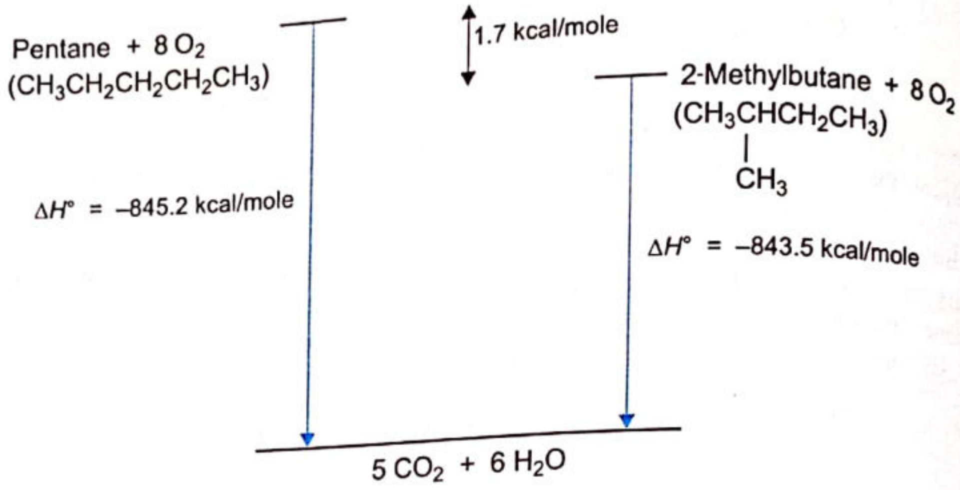


Fig.6.8. Energy changes on combustion of pentane and 2-methylbutane. Pentane has a more exothermic heat of combustion than does 2-methylbutane. We infer that pentane has a higher energy content than does 2-methylbutane, that is, pentane is thermodynamically less stable than 2-methylbutane.

We interpret this result as indicating that 2-methylbutane has stronger bonds than does pentane. Stronger bonds correlate with greater stability. An important general point to keep in mind throughout our discussion is that energy content and thermodynamic stability correlate *inversely*. **The higher the energy content, the lower the thermodynamic stability. Thermodynamically *less* stable compounds react *more* exothermically in the combustion reaction than do their more stable isomers.**

Differences in energy content between isomers of ordinary open-chain alkanes are usually quite small, as in the comparison above. The principal theme that emerges from many comparisons is that branching generally leads to an increase in stability.

(6) **Isomerization.** Normal alkanes are converted to their branched-chain isomers in the presence of aluminium chloride and HCl at 25°C. For example,

$$\underset{n\text{-Butane}}{CH_3-CH_2-CH_2-CH_3} \xrightarrow[HCl]{AlCl_3} \underset{\substack{\text{Isobutane}\\\text{(2-Methylpropane)}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3}$$

(7) **Pyrolysis (Cracking).** The decomposition of a compound by heat is called pyrolysis (Greek : *pyro*, fire + *lysis*, loosening). This process when applied to alkanes is known as *cracking*. When alkanes are heated to a high temperature in the absence of air, a thermal decomposition occurs. Large alkane molecules are broken down into a mixture of smaller, lower molecular weight *alkanes, alkenes*, and *hydrogen*. Pyrolysis generally requires temperatures in the range 500-800°C. However, in the presence of a catalyst (finely divided silica-alumina) reactions can be carried at less high temperatures. This is called **Catalytic Cracking.**

Ethane when heated to 500°C in the *absence of air*, gives a mixture of methane, ethylene, and hydrogen.

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow[\text{absence of air}]{500^\circ C} \underset{\text{Ethylene}}{CH_2{=}CH_2} + \underset{\text{Methane}}{CH_4} + H_2$$