

Solubility. Solubility of a substance (solute) in a solvent depends on the relative attractive forces acting between the molecules of the solute themselves, the molecules of the solvent themselves, and the molecules of the solute and the solvent. If the attractive forces between the molecules of solute and solvent are greater than those between the molecules of either the solute alone or the solvent, the solute is expected to dissolve in the solvent readily.

An alkane molecule consists entirely of covalent bonds each joining two atoms of either the same kind or of very little electronegativity difference. These bonds are thus either nonpolar or only slightly polar. Moreover, since these bonds are directed in a symmetrical way, the slight individual bond polarities tend to cancel out. (The dipole moment of all alkanes, whether straight-chain or branched-chain, is zero). As a result, all alkanes are almost nonpolar.

There is a useful rule regarding the solubility that says "*like dissolves like*". Thus, the alkanes are soluble in nonpolar solvents such as ether, benzene, carbon tetrachloride, etc., and are insoluble in polar solvents such as water. The liquid alkanes can also be used as solvents that dissolve compounds of low polarity, and do not dissolve compounds of high polarity.

Density. The density of alkanes also increases with molecular weight till it reaches a maximum value of about 0.8. Thus, all alkanes are lighter than water. This is why petroleum which is mainly a mixture of alkanes, floats on the surface of water.

Branched-chain alkanes have different individual density. This criteria has sometimes been used for determining the composition of a mixture of two isomers because the density of such a mixture varies consistently with its composition.

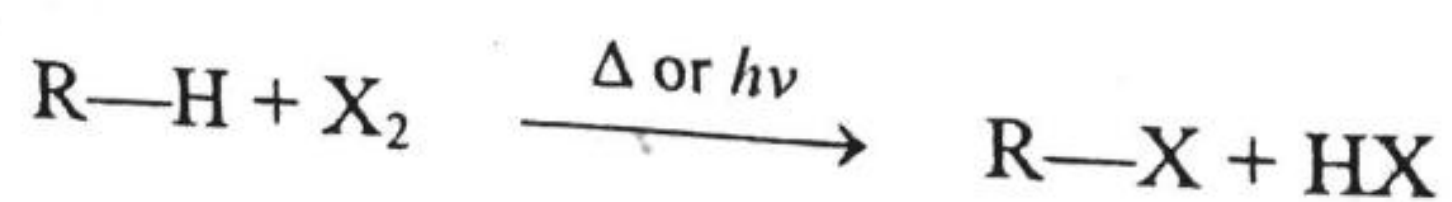
A mixture of volatile hydrocarbons (mostly pentanes and hexanes) is commonly known as '*petroleum ether*' because of the fact that it is obtained from petroleum and because of the similarity between these hydrocarbons and ethers in volatility, density and solvent action.

Reactions of Alkanes

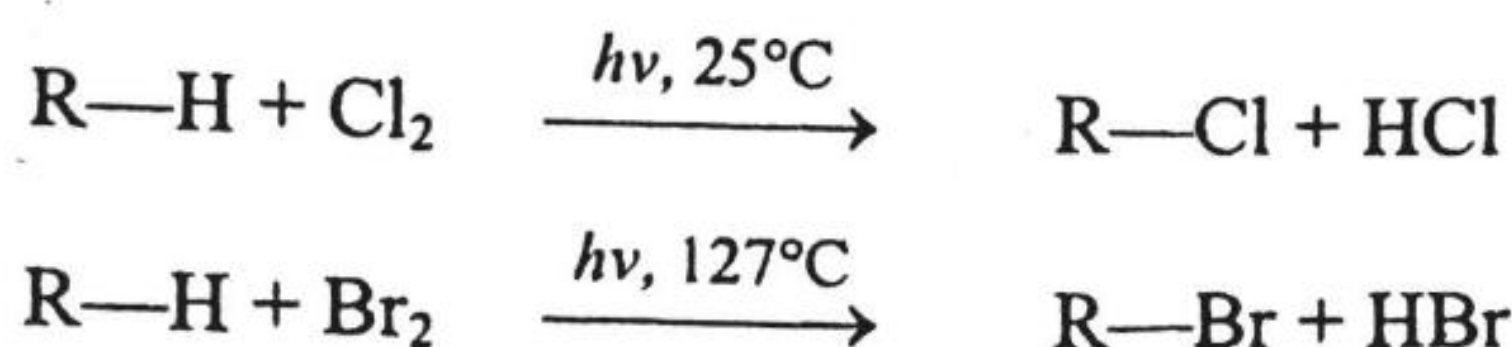
Characteristically, at ordinary temperature the alkanes are unreactive toward most reagents. This is why as a class they are also called '**paraffins**', the name derived from the Latin words *parum affinis* meaning 'little affinity'. The lack of reactivity of alkanes may be ascribed to the very strong C—H bond ($\Delta H = 415 \text{ kJ/mol}$). Thus, under ordinary conditions the alkanes do not react with acids, alkalis, oxidizing and reducing agents, etc. However, they may be made to react with certain reagents if the right conditions are used, as illustrated in the following reactions.

1. Halogenation. A reaction in which an atom or a group in a molecule is replaced by another atom or group is, in general, called a **substitution reaction**, and if the substituent is a halogen, the reaction is called **halogenation**.

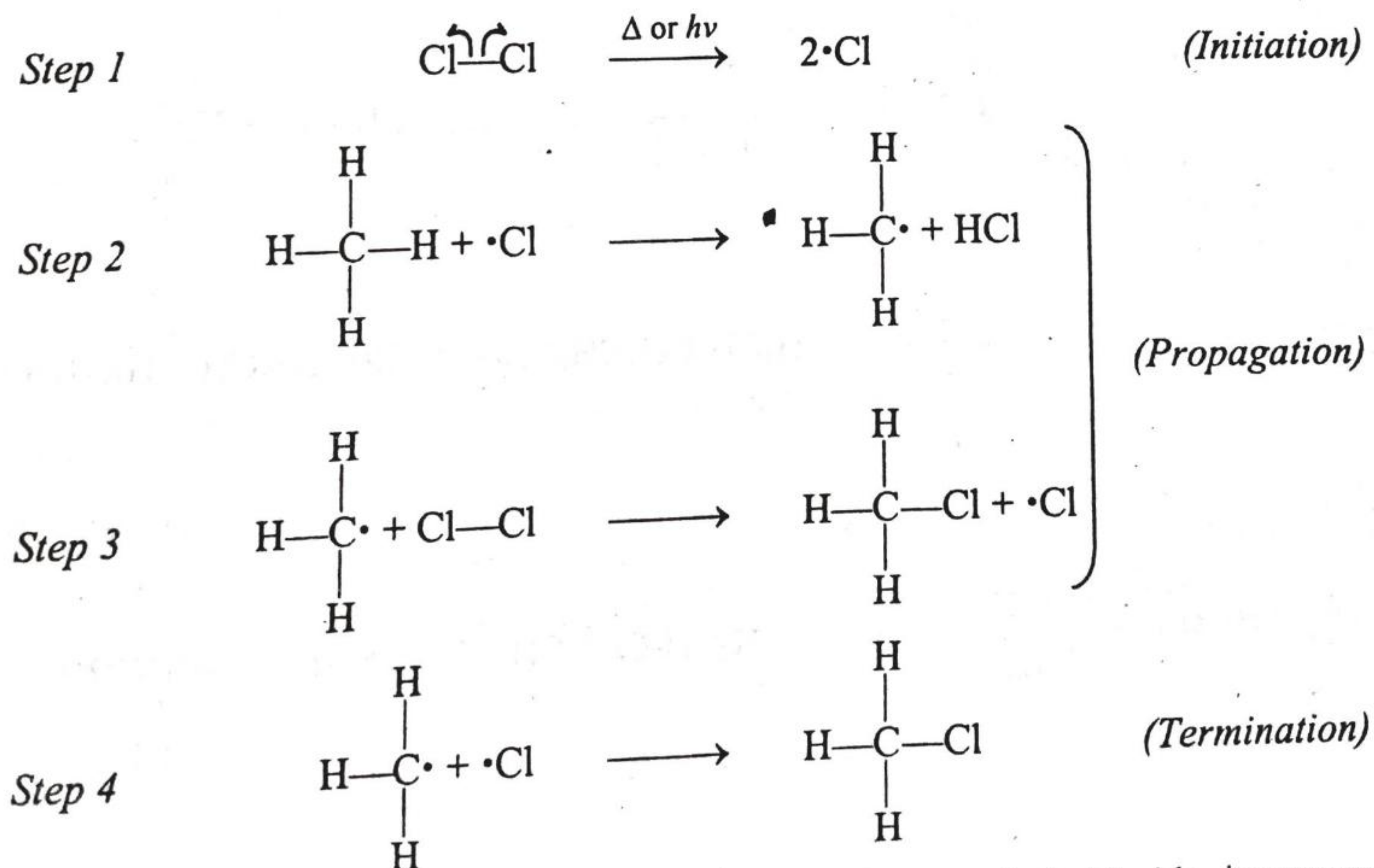
Halogenation of alkanes takes place when they react with halogens, usually chlorine and bromine, either on heating at $250\text{--}400^\circ\text{C}$, or under the influence of light, to form haloalkanes.



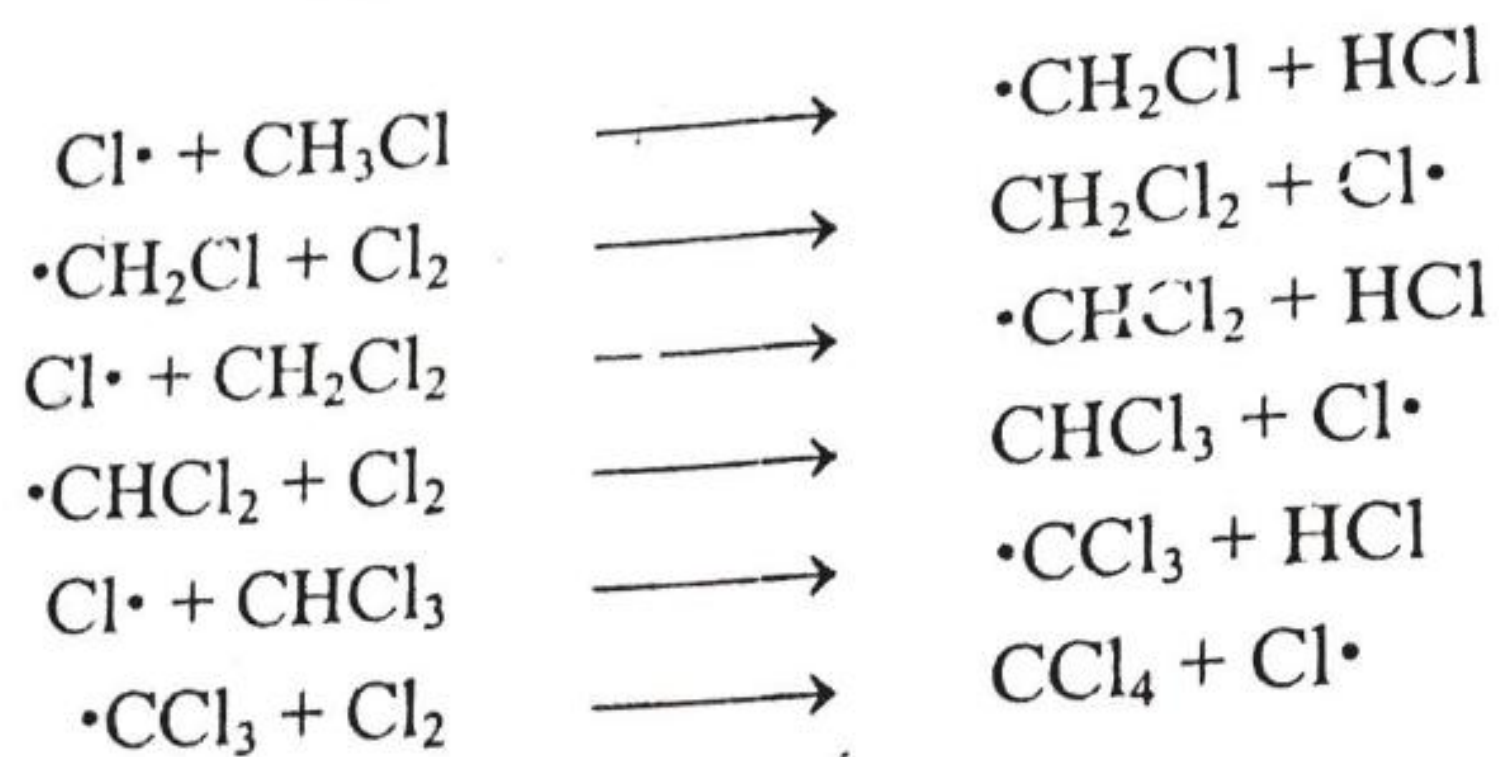
The symbol Δ is used for heat, and $h\nu$ for light. Halogenation of alkanes does not take place at a perceptible rate at room temperature in the absence of light. Chlorine is more reactive than bromine; chlorination of alkanes in the presence of light proceeds readily at room temperature, whereas bromination in the presence of light occurs only at higher temperature.



Halogenation of alkanes proceeds by a **free-radical chain mechanism** that can be explained by the chlorination of methane. It involves four main steps. In the *first step* which is known as **Initiation**, fragmentation of a chlorine molecule into two chlorine atoms takes place by heat or light. The chlorine atom (a free-radical) abstracts hydrogen from the methane molecule in the *second step* to create a methyl radical which reacts with another molecule of chlorine in the *third step* to form methyl chloride and another chlorine atom that can attack another methane molecule to *repeat step 2*, followed again by *step 3*. In this way there is a chain of repetition of steps 2 and 3 producing a molecule of methyl chloride with each repetition. Thus, the steps 2 and 3 are called **propagation**. As the reaction continues, the amount of methane and molecular chlorine decreases and the possibility of the existing free-radicals, i.e., methyl and chlorine free-radicals, to collide with each other increases, which also results in the formation of the product, methyl chloride, in the *fourth step* without forming any new free-radical. This fourth step is therefore called **termination**.

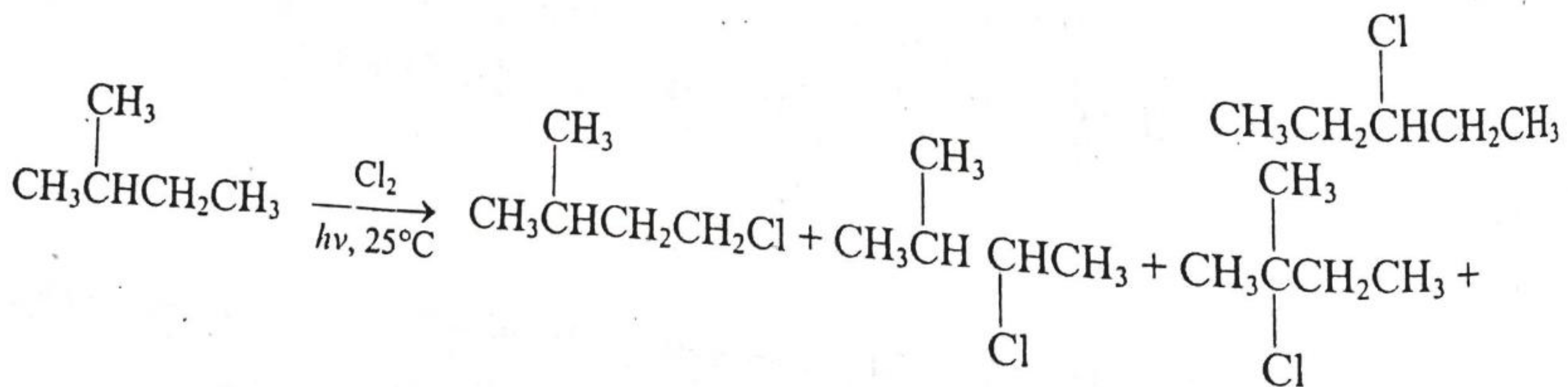
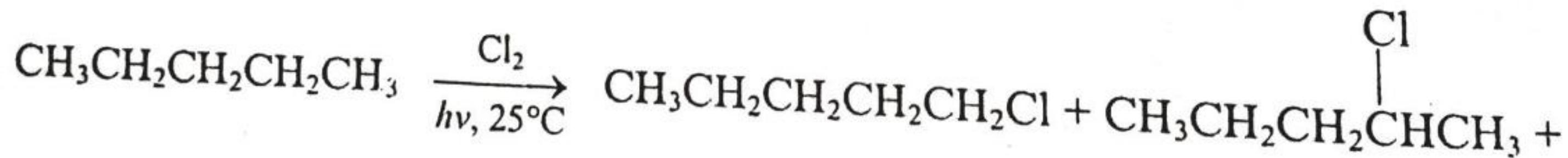
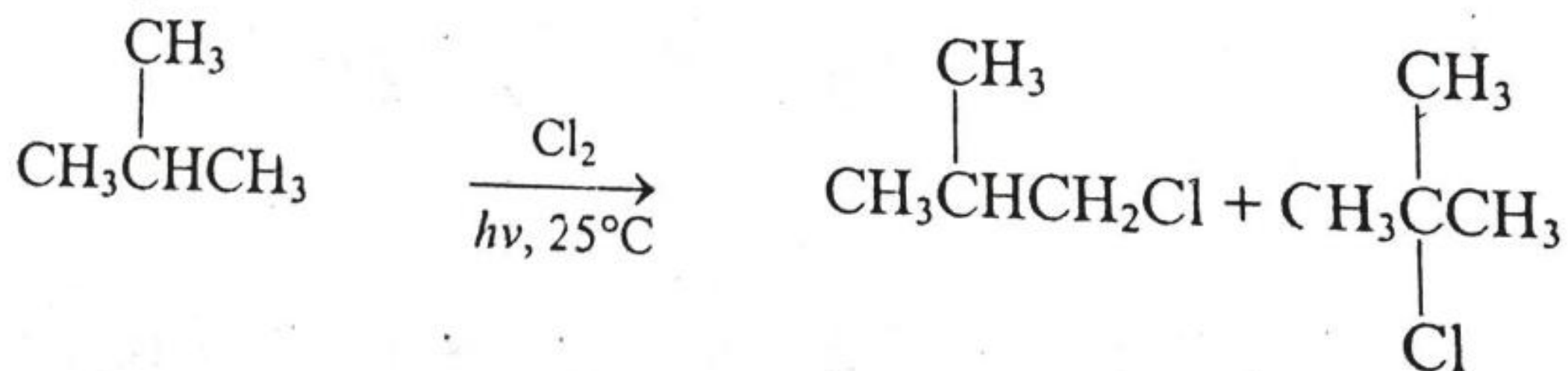
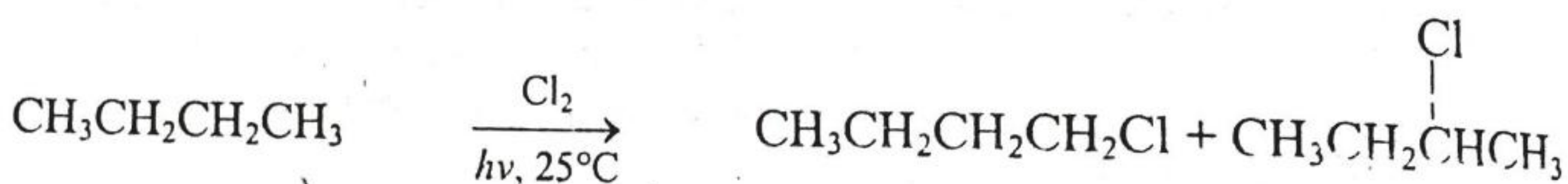
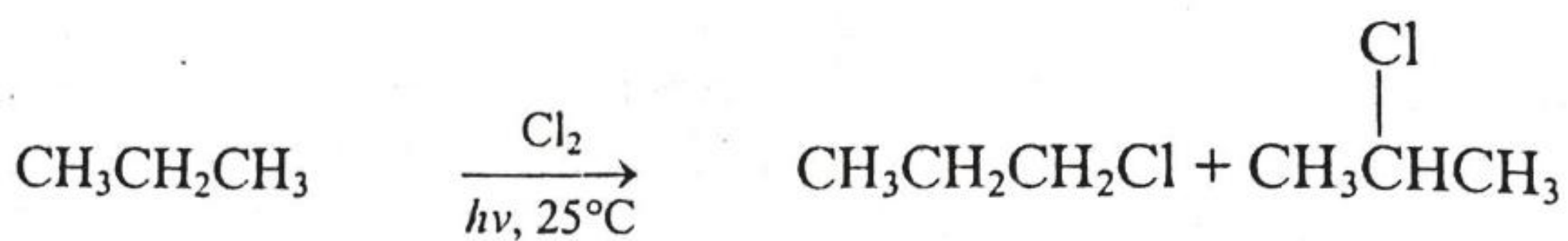


As the reaction proceeds, the concentration of the product, methyl chloride, increases and the possibility of the chlorine atom to collide with methyl chloride instead of methane, also increases. This results in the creation of a different free-radical, i.e., $\cdot\text{CH}_2\text{Cl}$, which on reacting with chlorine molecule forms dichloromethane. Dichloromethane then in a similar fashion leads to more highly chlorinated products in the propagation steps as follows:

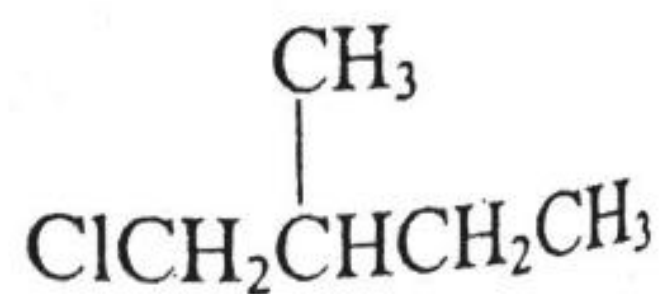


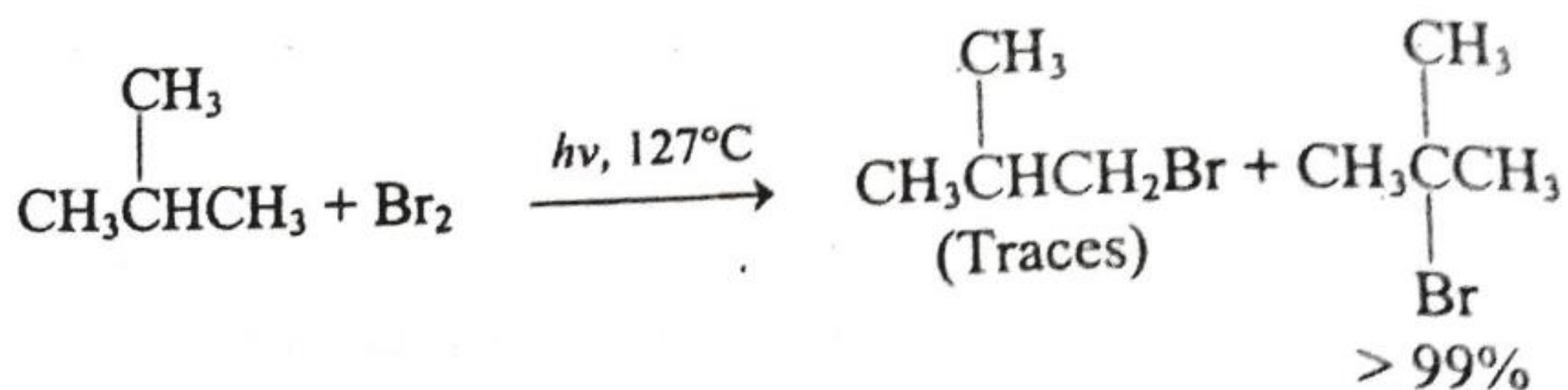
However, polychlorination can be minimized by using a large excess of methane.

Chlorination of a single alkane, except methane and ethane which give only one product each, can yield a variety of products depending on which hydrogen atom is replaced. In fact, a mixture of all possible isomeric monochloroalkanes is obtained, indicating that all hydrogen atoms are susceptible to replacement. Thus, propane, *n*-butane and isobutane can yield two isomeric monochloro-derivatives each; *n*-pentane can yield three isomers, and isopentane can yield four isomers, as shown below:



However, different isomeric monochloroalkanes are obtained in different amounts because the different types of hydrogen atoms have different reactivity for substitution which is in the order: tertiary > secondary > primary hydrogen. This is because the dissociation energy of C—H bond increases in the order: tertiary < secondary < primary. For example, the C—H bond dissociation energy (ΔH) of:



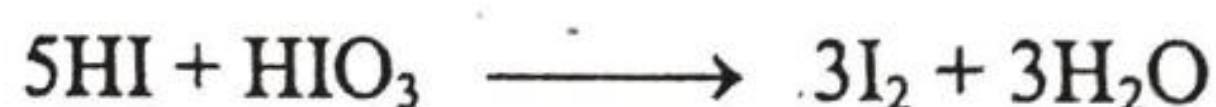


The ratio of the relative reactivity of a tertiary, secondary and primary hydrogen atom toward bromination at 127°C is 1600 : 80 : 1.

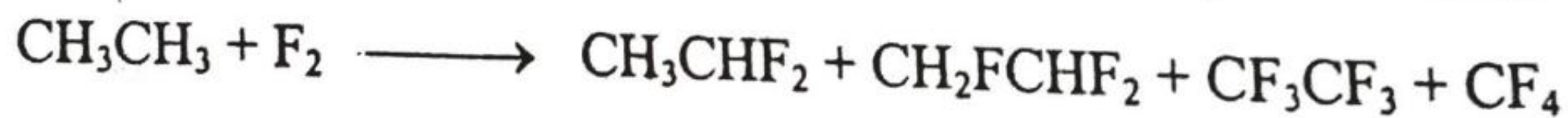
Iodine is the least reactive of the halogens toward alkanes. The general order of reactivity of halogens is: fluorine \gg chlorine $>$ bromine $>$ iodine. In fact, iodination of alkanes is a reversible process and the iodoalkanes which are formed in the reaction, are reduced back to alkanes by hydrogen iodide, the other product of the reaction.



However, if hydrogen iodide is destroyed as soon as it is formed, by an oxidizing agent such as HIO_3 , HNO_3 , HgO , etc., the reaction can be driven to the right.

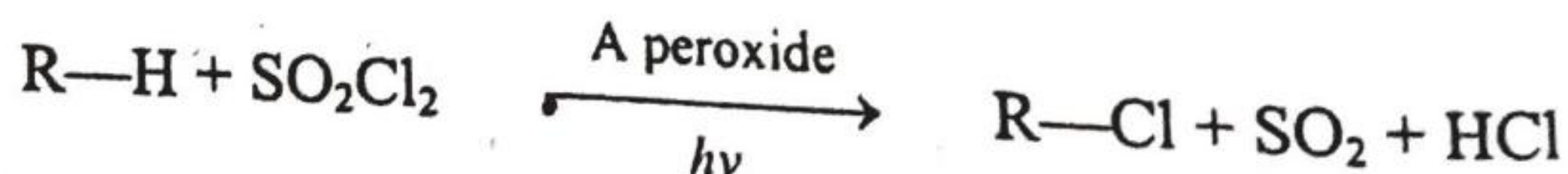


Fluorine is the most reactive halogen and reacts with most organic compounds with explosion. It is therefore very difficult to control the reaction, and special conditions are required for the fluorination of organic compounds. Fluorination of alkanes may be carried out by diluting fluorine with nitrogen (an inert gas) and carrying out the reaction in an apparatus specially designed to remove the heat produced in the reaction because the reaction is highly exothermic. If the heat produced in the reaction is not removed, the temperature may get so high as to induce cracking, resulting in the formation of fluoroalkanes with fewer carbons. The product is usually a complex mixture.

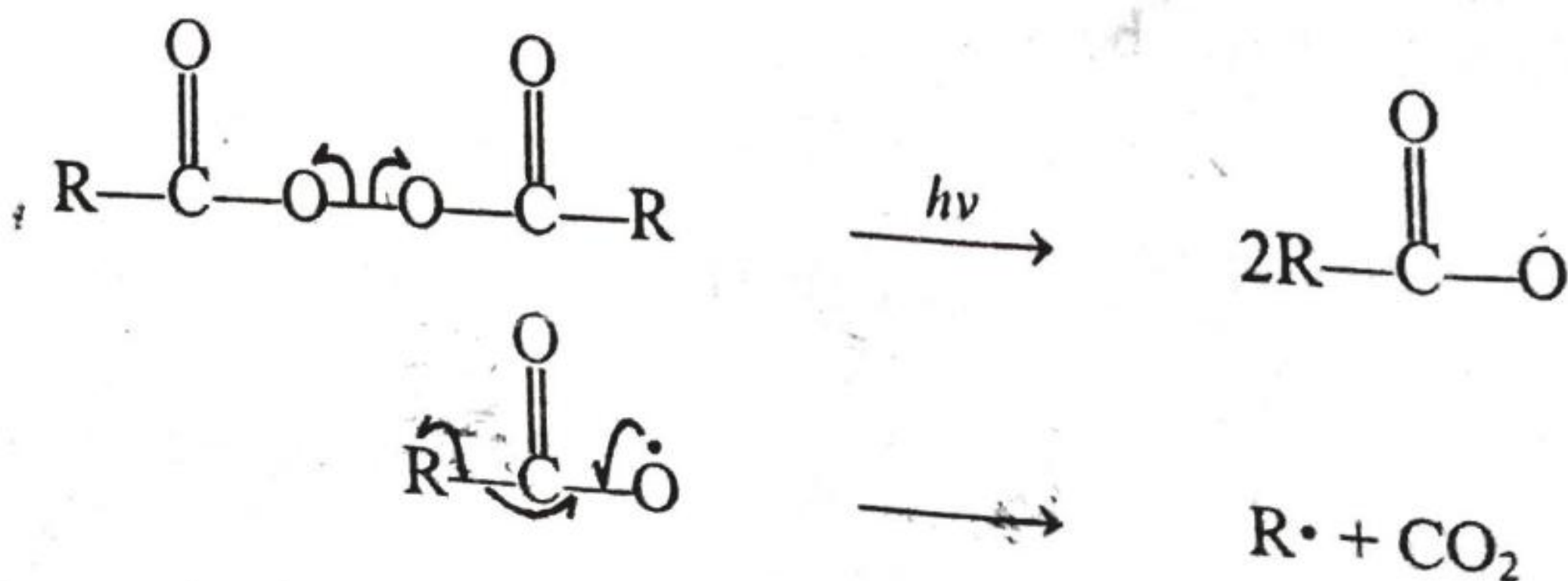


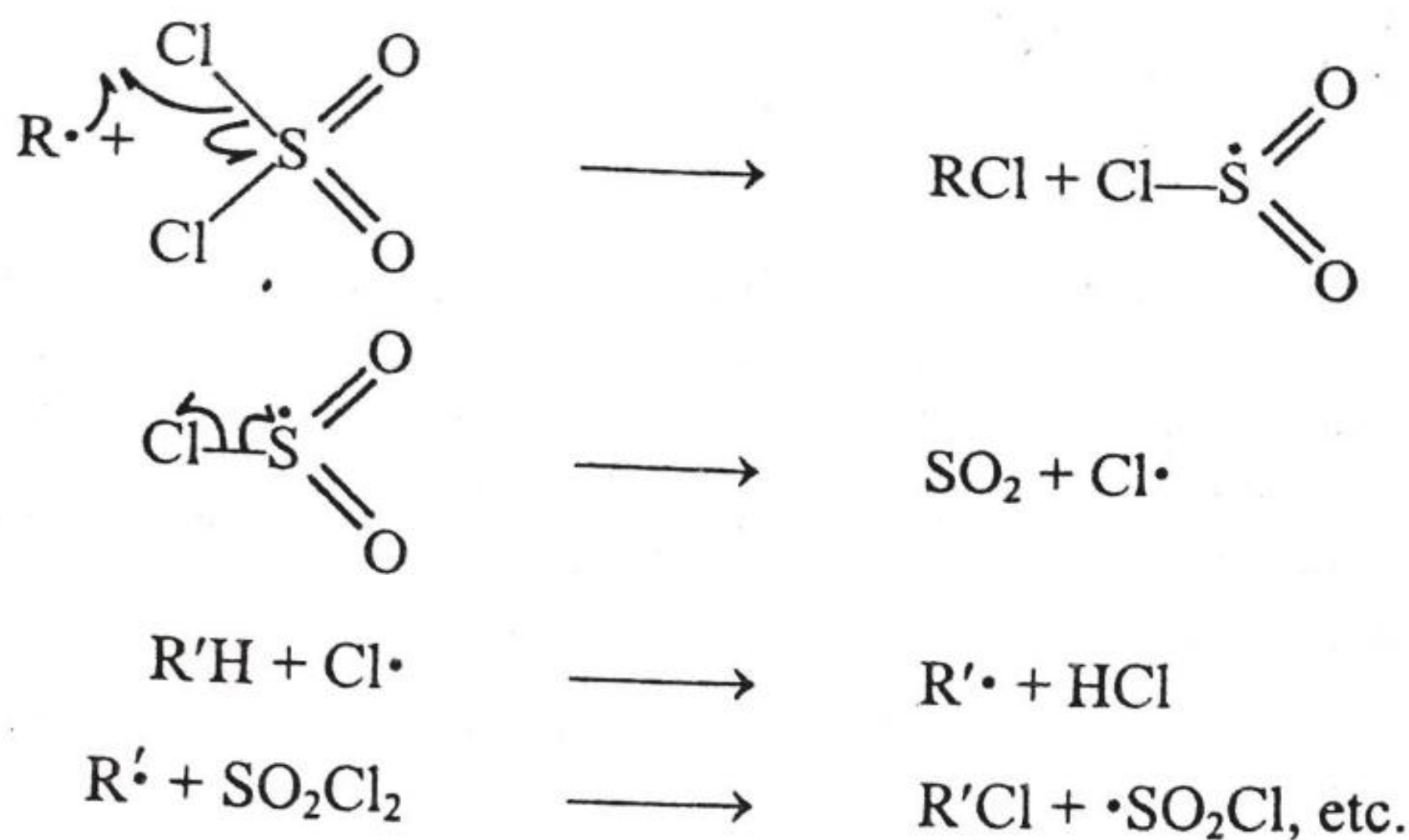
Monofluoroethane and symmetrical difluoroethane are not formed.

Direct chlorination of alkanes may also be effected by means of sulfuryl chloride (SO_2Cl_2) in the presence of light and a trace of an organic peroxide.



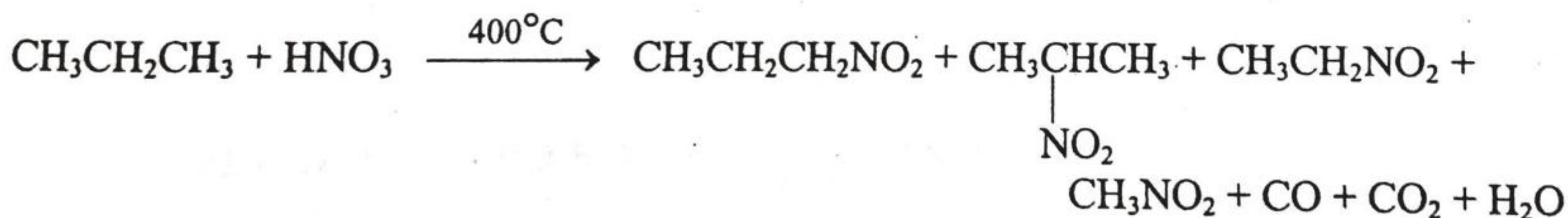
The mechanism of the reaction is:





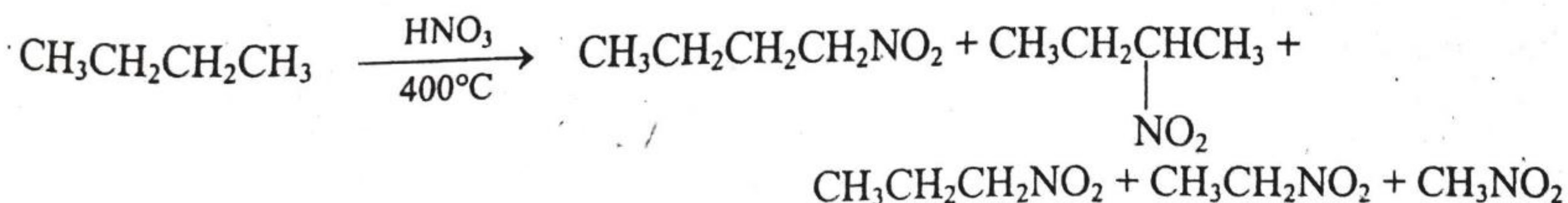
Sulfuryl chloride is more reactive, and therefore less selective, than chlorine.

2. Nitration. Nitration is another substitution reaction of alkanes in which a hydrogen atom of an alkane is replaced by nitro group (NO_2). The reaction is usually carried out in vapour phase. A gaseous mixture of alkane and a large excess of 60% nitric acid is passed rapidly through a narrow tube at elevated temperature (400°C), where upon a complex mixture of mononitroalkanes is obtained. Under the reaction conditions, the alkane molecules also undergo fragmentation. The mixture therefore consists of all the possible mononitro-derivatives of the alkane and the mononitro-derivative of its every possible fragment, together with the oxidation products of the alkane such as carbon monoxide, carbon dioxide, and water. In fact, 70 to 80% of nitric acid is consumed in the formation of oxidation products. Thus, propane yields a mixture containing 1-nitropropane, 2-nitropropane, nitroethane, nitromethane, and the oxidation products.

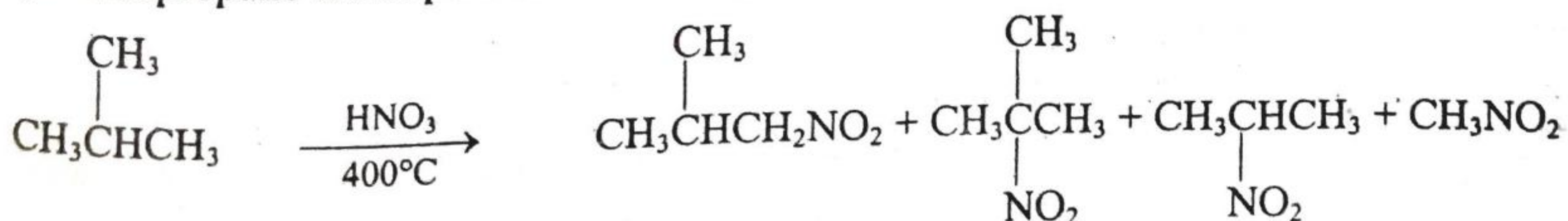


The product mixture may be separated by fractional distillation.

The components of the product mixture obtained by the high temperature vapour phase nitration of a particular alkane can be predicted by a very simple rule. 'All those mononitroalkanes are produced that would result from the replacement of any hydrogen atom or any alkyl group of the starting alkane'. This rule is illustrated by the nitration of *n*-butane and isobutane.



(2-Nitropropane is not possible according to the rule).

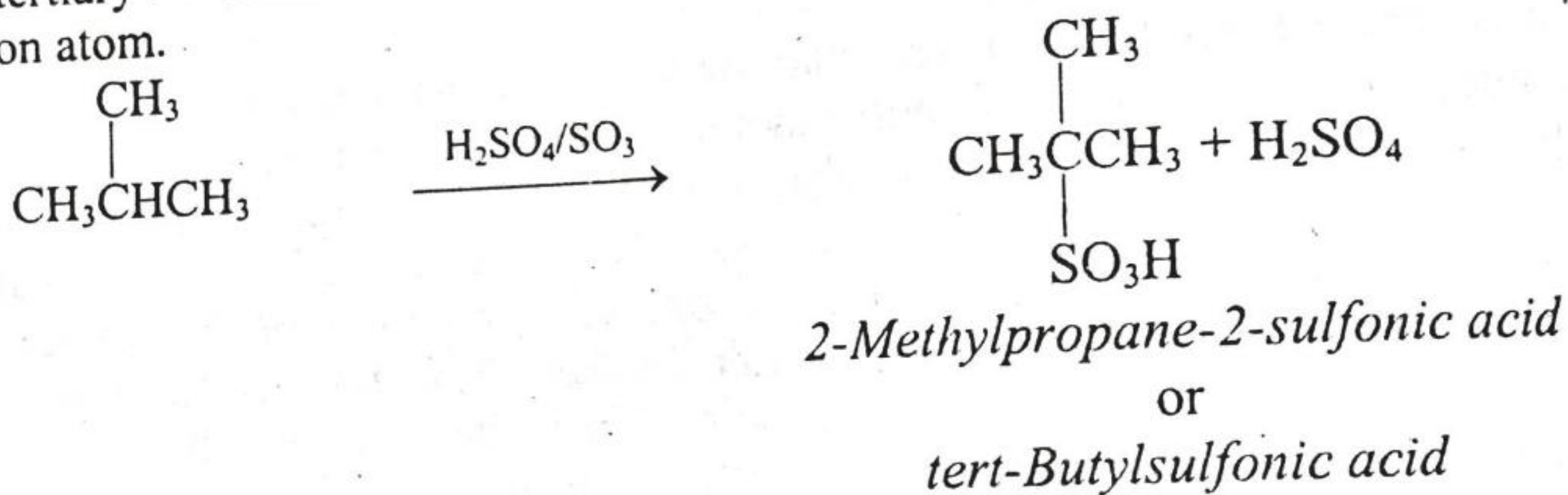


(No other products are formed).

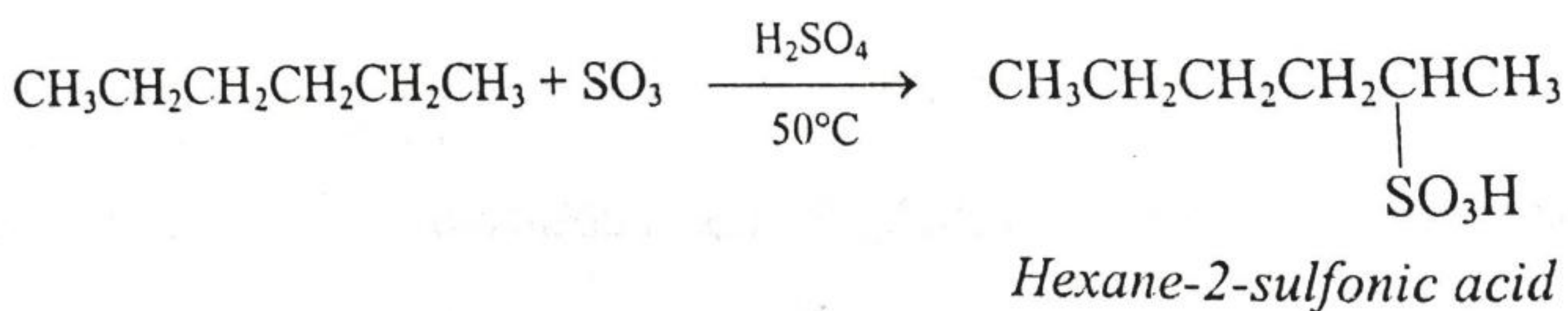
All available evidences suggest that the nitration of alkanes proceeds by a free-radical mechanism and, like halogenation, the various types of hydrogen atoms are not replaced with equal ease.

Nitration of alkanes has also been carried out in liquid phase at low temperature, e.g., by heating a mixture of alkane and nitric acid at 100–150°C for several hours. Only a mixture of isobutane and nitric acid is replaced in this way, and that too in a poor yield. For example, when isobutane is volatile, only 2-methyl-2-nitropropane is obtained. So this method is not applicable to all alkanes and therefore has little practical utility.

3. Sulfonation. Replacement of a hydrogen atom by the sulfonic acid group (SO₃H) is known as **sulfonation**. Sulfonation of alkanes may be carried out by treating them with oleum (fuming sulfuric acid or sulfuric acid containing sulfur trioxide). The product is named as either alkylsulfonic acid or alkanesulfonic acid, e.g., CH₃SO₃H is called either methylsulfonic acid or methanesulfonic acid. The ease of replacement of hydrogen atoms is in the order: tertiary >> secondary > primary. Thus, isobutane is readily sulfonated at the tertiary carbon atom.



n-Alkanes with six or more carbon atoms are sulfonated when heated with oleum at about 50°C. The sulfonic acid group probably enters the chain at the second carbon atom.



The sulfonic acid group is often introduced into long-chain alkanes to increase their solubility in water so that they can be used as detergents.

4. Combustion. Although alkanes as a class are considered to be unreactive, they readily burn if ignited in the presence of air or oxygen, and are oxidized to carbon dioxide and water, with the evolution of a large amount of heat. For example, combustion (burning) of methane is accompanied by the evolution of heat equal to 891 kJ/mol, which is called the heat of combustion of methane.



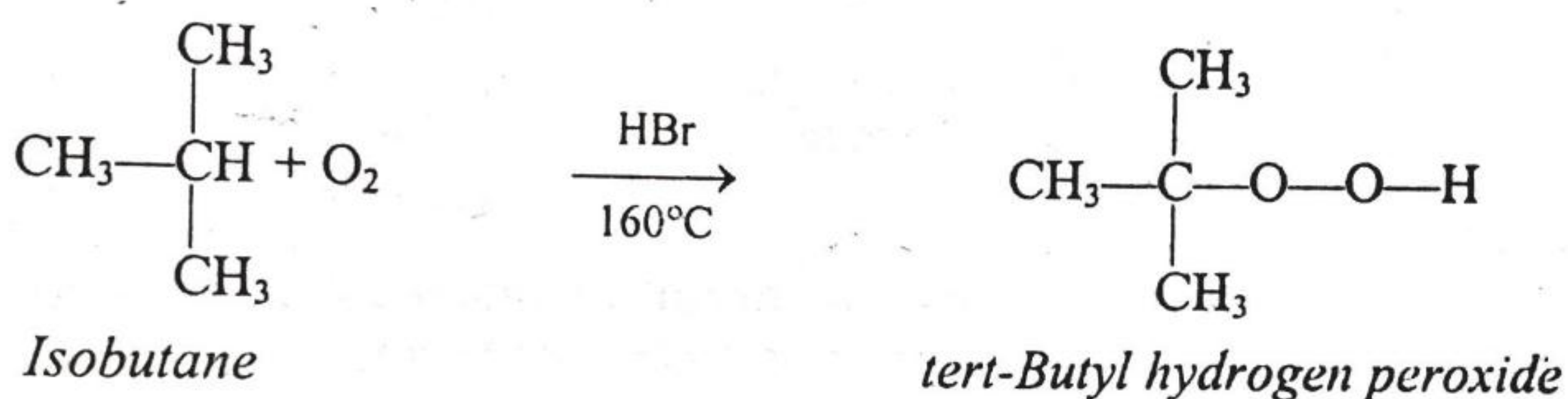
The amount of heat evolved when one mole of a hydrocarbon is burnt to carbon dioxide and water, is called the **heat of combustion**. Although the reaction is highly exothermic, it requires a very high temperature to initiate the reaction and once the reaction has been started by a flame or a spark, it produces sufficient heat to continue itself. In fact, the important product of this reaction is heat which is used as a source of energy. It is therefore of practical interest to determine the amount of heat liberated in the combustion

of various alkanes. Whereas the heat of combustion of methane is 891 kJ/mol, its value for ethane is 1559 kJ/mol, for propane is 2220 kJ/mol, for *n*-butane is 2877 kJ/mol and for octane (a component of gasoline), it is as high as 5.57×10^4 kJ/mol. These values of heats of combustion are also used for the estimation of individual bond energies.

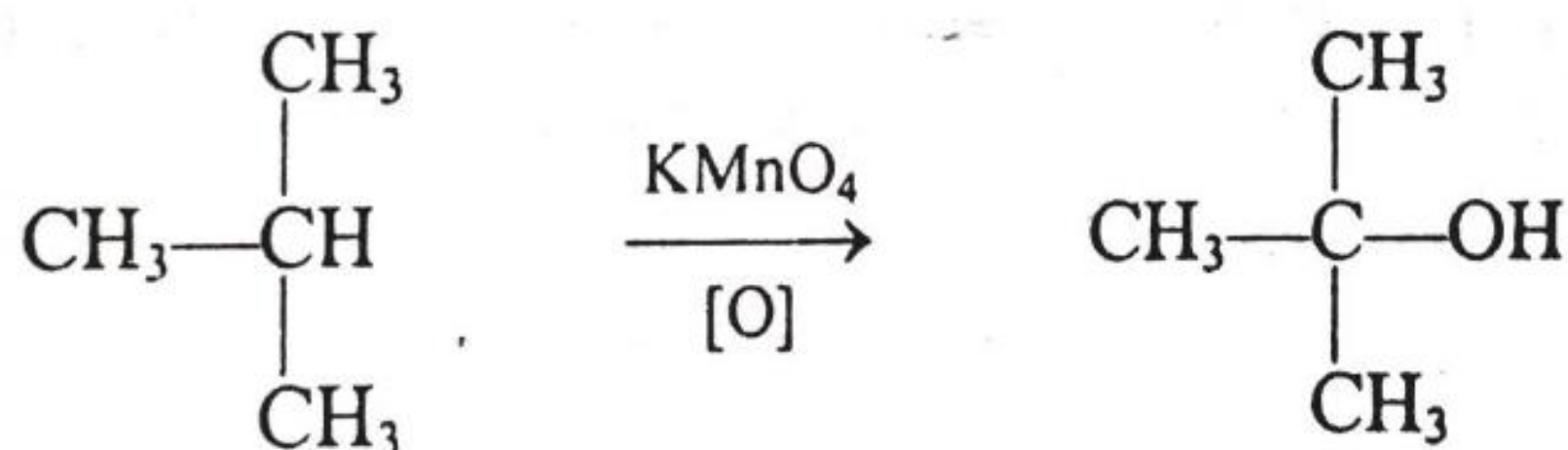
The mechanism of the combustion reaction is not fully understood but probably it also involves a free-radical chain mechanism.

Alkanes, particularly those present in natural gas (methane, ethane, propane and *n*-butane), on partial oxidation that can be effected either by insufficient supply of oxygen or by controlling the temperature to about 400°C, yield valuable oxygen-containing organic compounds such as methyl alcohol (CH₃OH), ethyl alcohol (CH₃CH₂OH), formaldehyde (HCHO) and acetic acid (CH₃COOH), on commercial scale.

Oxidation of alkanes at low temperature (100 to 200°C) can be induced by light or by certain radical initiators such as HBr. This process is particularly useful for the preparation of peroxides which are unstable at high temperatures.



A tertiary hydrogen atom of an alkane is also oxidized to a hydroxyl group by an oxidizing agent such as potassium permanganate.

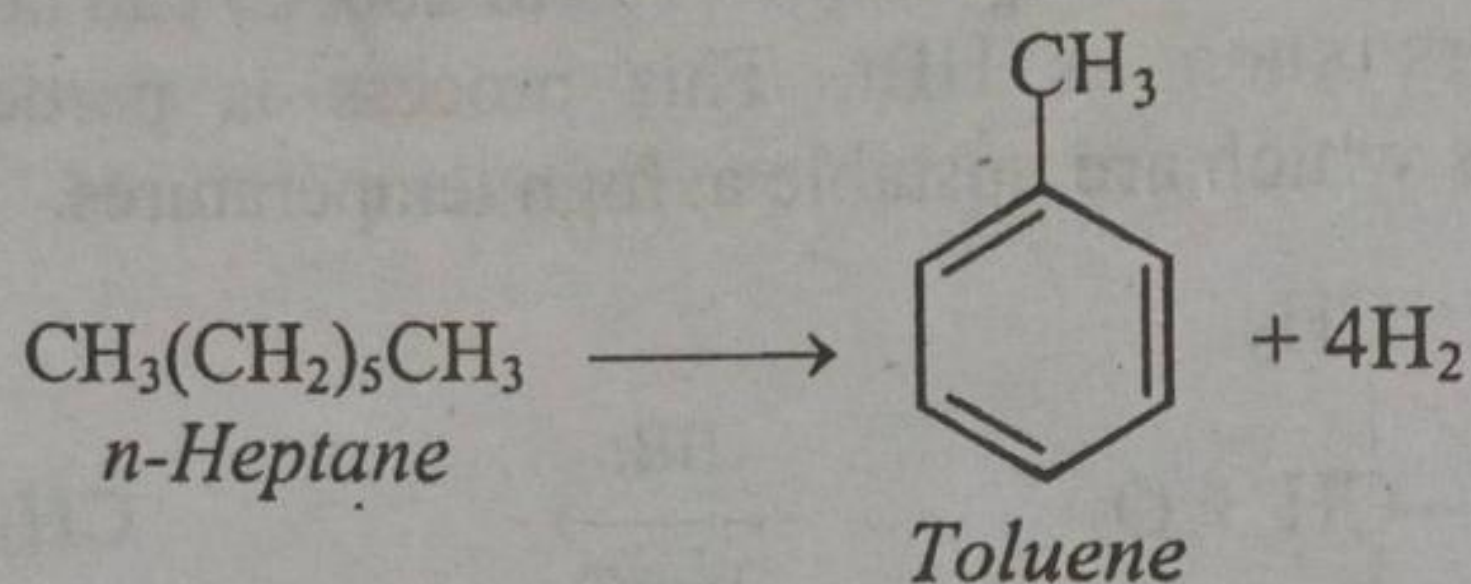
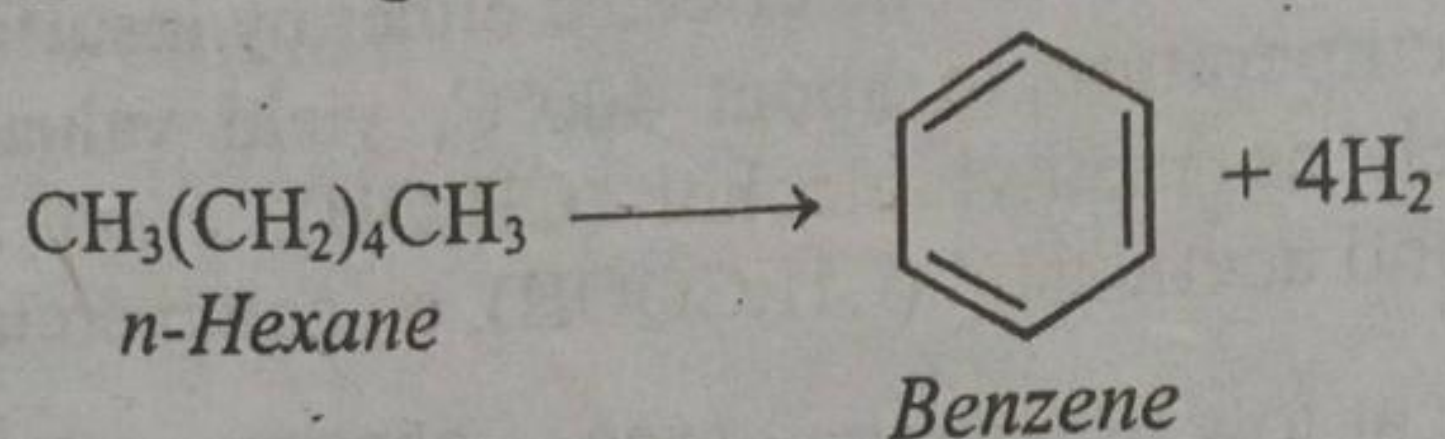


5. Pyrolysis. The thermal decomposition (cleavage by heat) of organic compounds is known as **pyrolysis**, the name derived from the Greek word *pyr* meaning 'fire' and *lysis* meaning 'losing'. Pyrolysis when applied to alkanes, is called **cracking**. When large alkane molecules are passed through a chamber heated to a high temperature (400–700°C), they undergo decomposition, through a free-radical mechanism, to a variety of smaller molecules of alkanes, alkenes, and even carbon and hydrogen. The extent of decomposition and the nature of the products depend on (i) structure of the original alkane, (ii) temperature and pressure at which cracking is carried out, (iii) time of heating and (iv) presence or absence of catalysts which are mostly metal oxides such as alumina, silica, etc. Methane itself is stable upto 700°C but the resistance of *n*-alkanes against heat decreases with increasing number of carbon atoms, and the branched-chain alkanes decompose more readily than the straight-chain isomers.

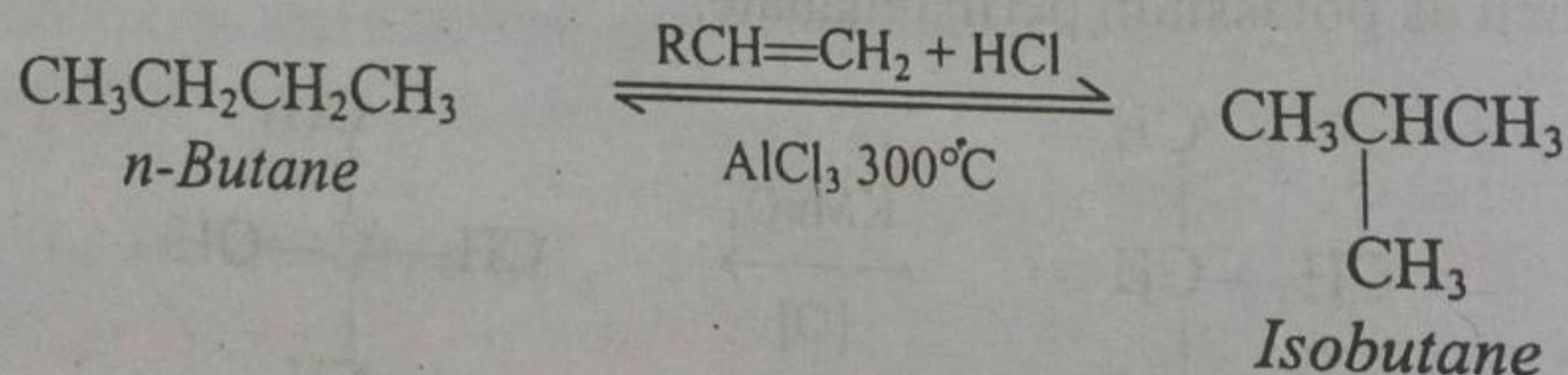
Of all the compounds produced in the process of cracking (particularly of petroleum), the most important are those containing four or fewer carbon atoms, e.g., methane, ethane, propane, butane, ethylene, propylene, butene, and isobutene. A modified process of cracking called **steam-cracking** in which an alkane is diluted with steam, heated to 700–900°C for a fraction of a second, and rapidly cooled, is used for the production of

alkenes such as ethylene, propylene, butadiene, and isoprene. These alkenes and the above hydrocarbons containing upto four carbon atoms, are widely used as raw materials in the chemical industry for the synthesis of aliphatic compounds on large scale. However, the main use of the process of cracking is to convert the higher fractions of petroleum into lower hydrocarbons suitable for use as motor fuel.

When alkanes containing six or more carbon atoms are heated at 450–550°C under pressure in the presence of a catalyst such as chromic oxide supported on alumina, they undergo dehydrogenation, cyclization and isomerization to form aromatic compounds. The process is called **hydroforming** or **catalytic reforming**.

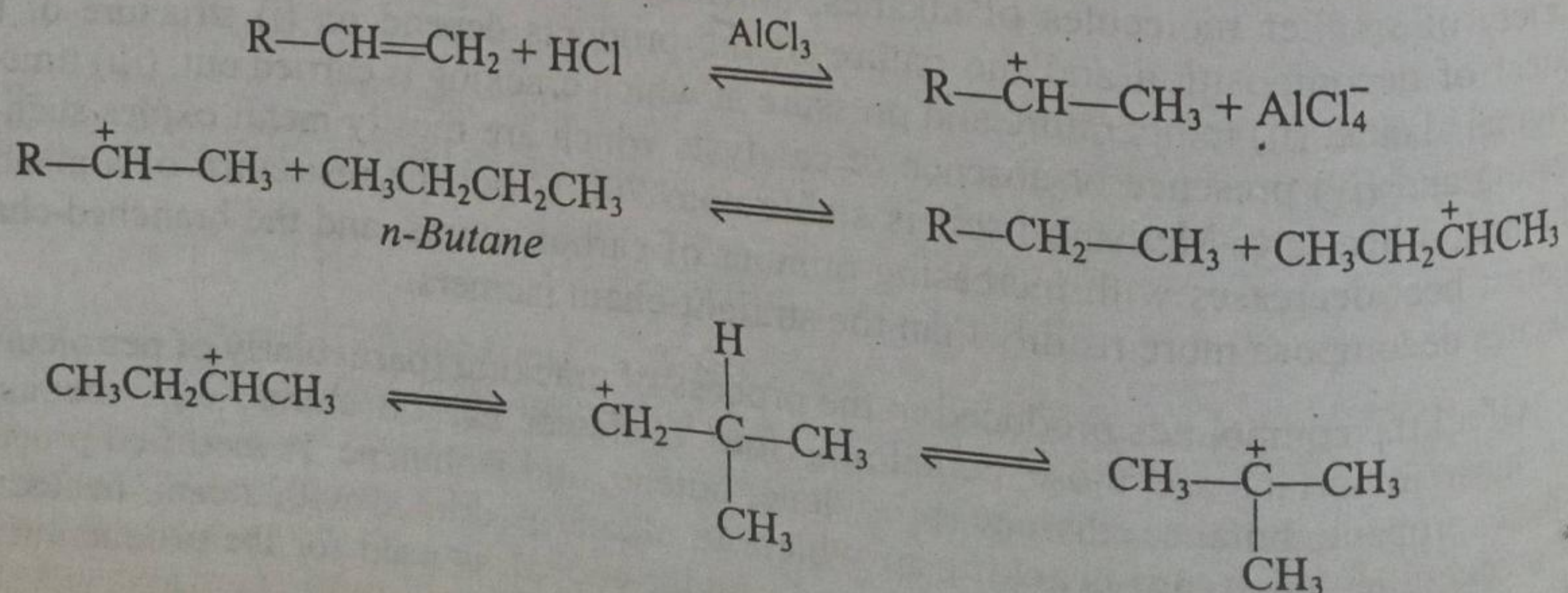


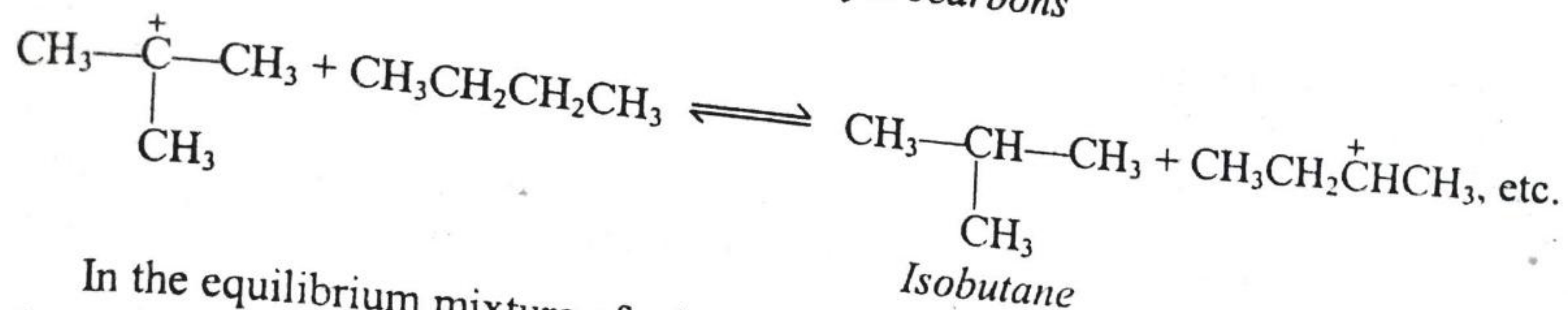
6. Isomerization. *n*-Alkanes on treatment with aluminium chloride at 300°C in the presence of a small amount of hydrogen chloride or a trace of water (to form HCl from AlCl₃) together with a trace of an alkene, are isomerized to branched-chain alkanes. For example, *n*-butane isomerizes to isobutane.



The reaction is reversible and an equilibrium mixture of *n*-butane and isobutane is obtained starting from either of the pure isomer. The isomerization of *n*-butane to isobutane is an important industrial process.

Isomerization is believed to be an ionic chain reaction involving carbocation that is formed from the alkene and HCl which are present in the reaction mixture in traces. The carbocation then initiates the chain reaction.





In the equilibrium mixture of *n*-butane and isobutane, the latter predominates because the tertiary carbocation is more stable than the secondary carbocation.

CYCLOALKANES

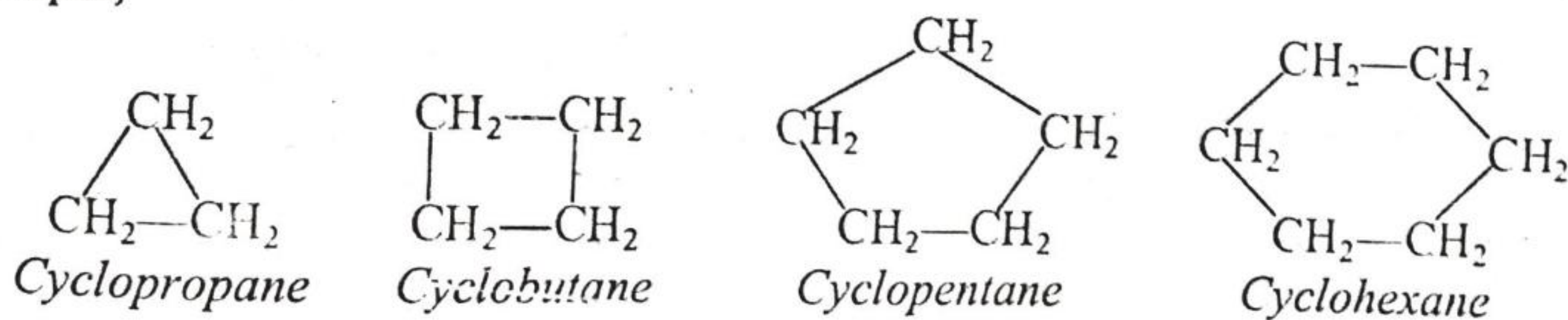
Cycloalkanes are aliphatic saturated hydrocarbons in which the sp^3 hybridized carbon atoms are arranged in a ring, and except for cyclopropane and cyclobutane all have tetrahedral geometry. These are represented by the general formula C_nH_{2n} which shows that these have two hydrogen atoms fewer than alkanes. In fact, two carbons of the molecule utilize one of their valence bonds each in the formation of the ring. If the molecular formula of a saturated hydrocarbon corresponds to the general formula C_nH_{2n-2} the compound contains two rings in its molecule and the general formula C_nH_{2n-4} shows the presence of three rings in the molecule.

Since cycloalkanes are *aliphatic* in nature and have *cyclic* structure, these are also commonly known as **alicyclic** compounds. These are also sometimes called **carbocyclic** compounds to differentiate them from heterocyclic compounds (compounds containing at least one atom other than carbon in their ring).

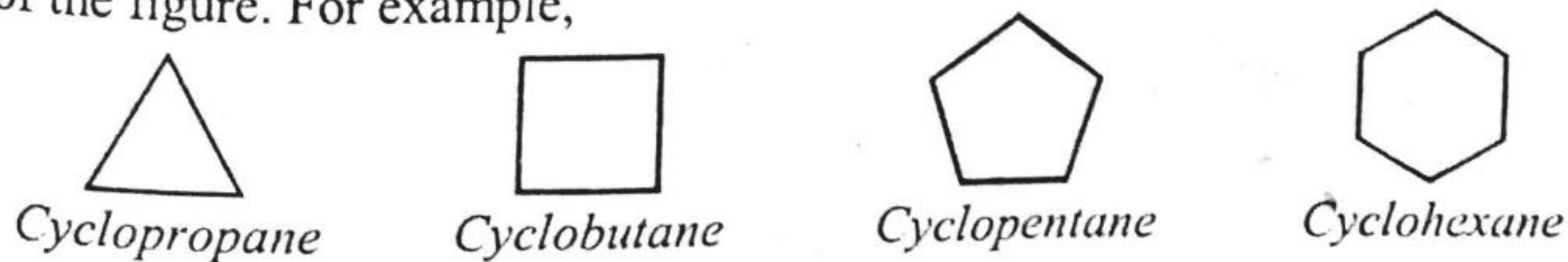
Nomenclature of Cycloalkanes

In the IUPAC system, the cycloalkanes are named according to the following rules:

1. The cycloalkanes with only one ring are named by attaching the prefix *cyclo-* to the name of the unbranched alkane having the same number of carbon atoms as the ring. For example,



For convenience, cycloalkanes are often represented by simple geometric figures, e.g., cyclopropane by a regular triangle, cyclobutane by a square, cyclopentane by a pentagon, cyclohexane by a hexagon, and so on. A carbon atom with its two attached hydrogens (unless some other substituent is indicated) is understood to be present at each corner of the figure. For example,



2. The substituted cycloalkanes are named by placing the names of the substituents along with their numbers showing their relative positions before the names of the cycloalkanes. If there is only one substituent, it is not necessary to designate its position