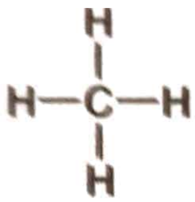
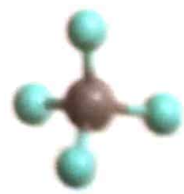
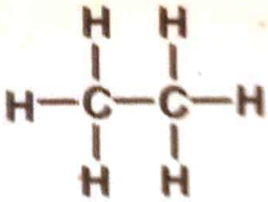
CH_4
Methane



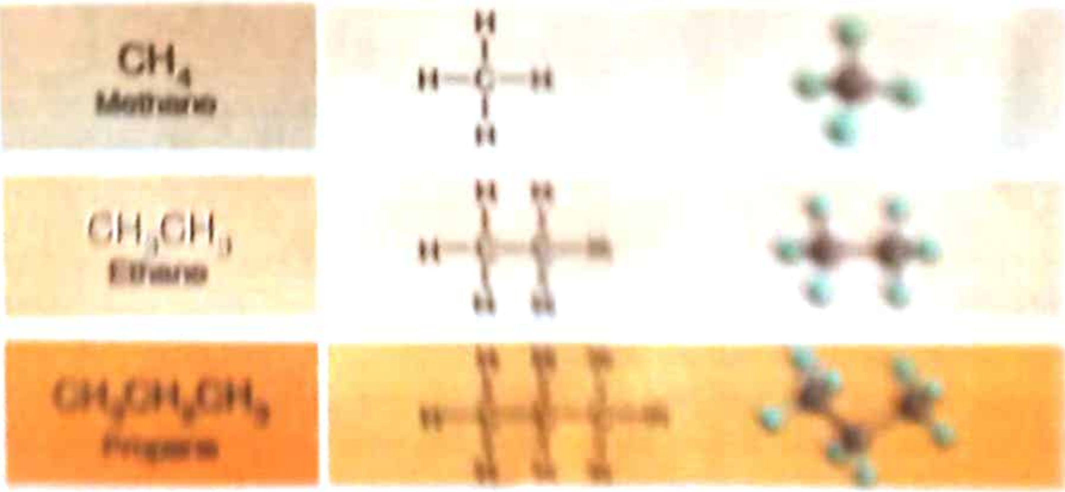


CH_3CH_3
Ethane



flare from a lake in Alaska

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



Carbon atoms in their molecules are bonded to each other by single covalent bonds. Each carbon atom bonded to enough hydrogen atoms to give maximum covalency of 4. Since the carbon chain 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 chemically almost inert. Hence they are sometimes referred to as **Paraffins** [illegible] affinity).

STRUCTURE

Let us consider methane (CH_4) and ethane (CH_3–CH_3) for illustrating the orbital [illegible] alkanes. In methane, carbon forms single bonds with four hydrogen atoms. Since the carbon is attached to four other atoms, it uses sp^3 hybrid orbitals to form these bonds. Each C–H bond [illegible] result of the overlap of an sp^3 orbital from carbon and an s orbital from hydrogen (Fig. 10.1). [illegible] bonds are σ bonds.

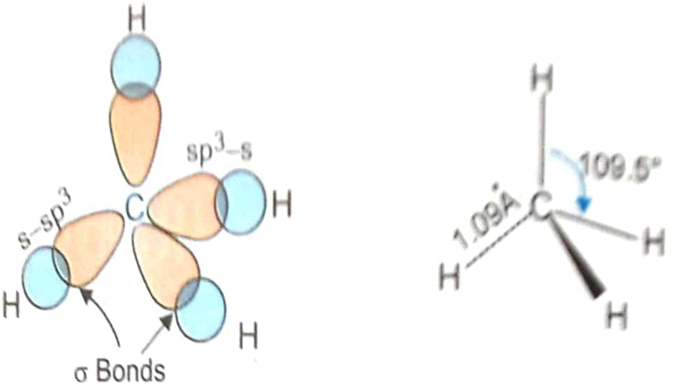


Fig. 10.1. Orbital structure of Methane.

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. 10.2). All C–H bonds and the C–C bond are σ bonds.

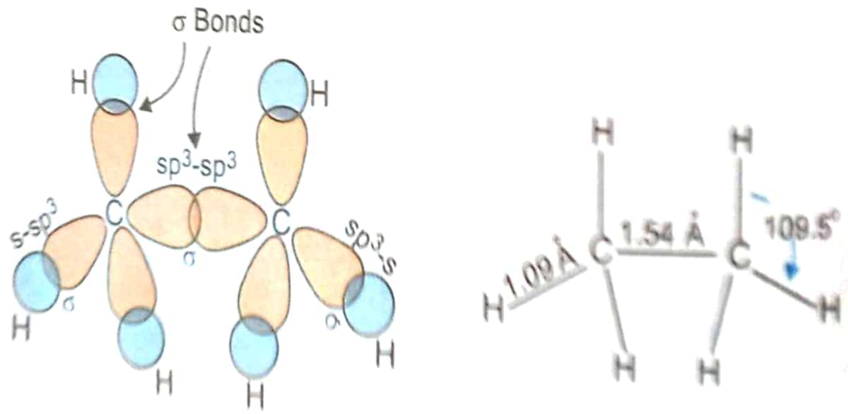


Fig. 10.2. Orbital structure of Ethane.

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 [illegible] carbons, *hexane* has *six*, and so forth (Table 10.1).

In the common system all isomeric alkanes have the same parent name. For example, the [illegible] 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 *n*- stands for normal.

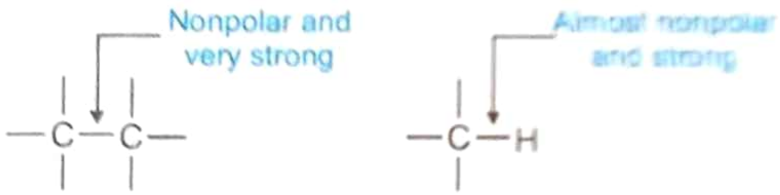
$CH_3CH_2CH_2CH_3$
n-Butane

$CH_3CH_2CH_2CH_2CH_3$
n-Pentane

near 1380 cm

CHEMICAL PROPERTIES

As already observed, alkanes are relatively stable to common reagents such as acids, alkalis, oxidizing agents, at room temperature. This is due to the fact that the electronegativities of carbon (2.60) and hydrogen (2.1) do not differ appreciably. Thus the bond electrons in C–H are practically equally shared between them and the bond is almost nonpolar. The C–C bond is completely nonpolar. Therefore, *polar reagents find no reaction sites on alkane molecules*. Furthermore, the C–H and C–C bonds are strong bonds. This explains why alkanes are stable to acids, alkalis, oxidizing agents etc., at room temperature.



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 diffuse 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.

$$CH_4 + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV light}} CH_3Cl + HCl$$

Methane → Methyl chloride (Chloromethane)

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

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

Methylene chloride (Dichloromethane)

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

Chloroform (Trichloromethane)

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

Carbon tetrachloride (Tetrachloromethane)

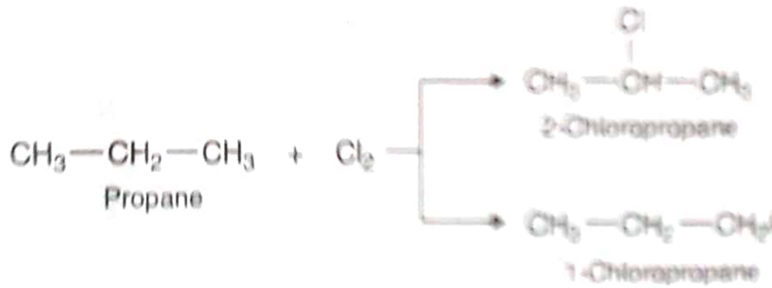
In actual practice, all the four substitution products (CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4) are obtained. The extent to which each product is formed depends upon the initial chlorine to methane ratio. Carbon tetrachloride is the major product if an excess of chlorine is used. Methyl chloride is the major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

$$CH_3CH_3 + Cl_2 \xrightarrow[\text{heat}]{\text{UV}} CH_3CH_2Cl + HCl$$

Ethane → Chloroethane

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.

$$Cl : Cl \xrightarrow[\text{or } \Delta]{\text{UV light}} Cl\cdot + Cl\cdot$$

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

$$Cl\cdot + H\text{—}CH_3 \longrightarrow HCl + \cdot CH_3$$

Methane → Methyl radical

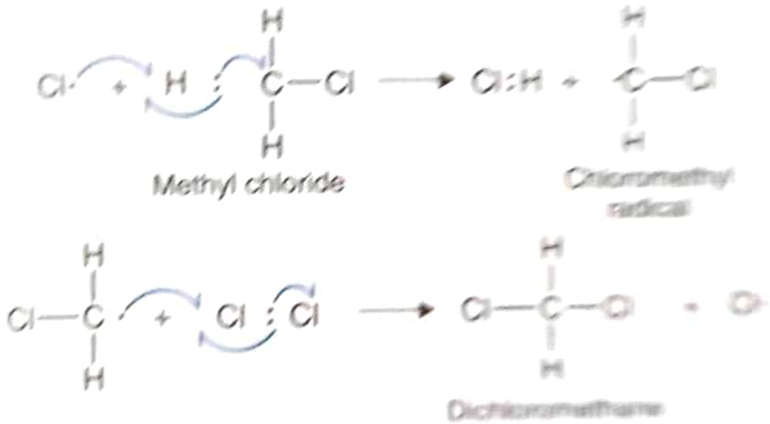
(*b*) Methyl free radical attacks chlorine molecule to give methyl chloride and chlorine free radical.

Step [illegible] 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

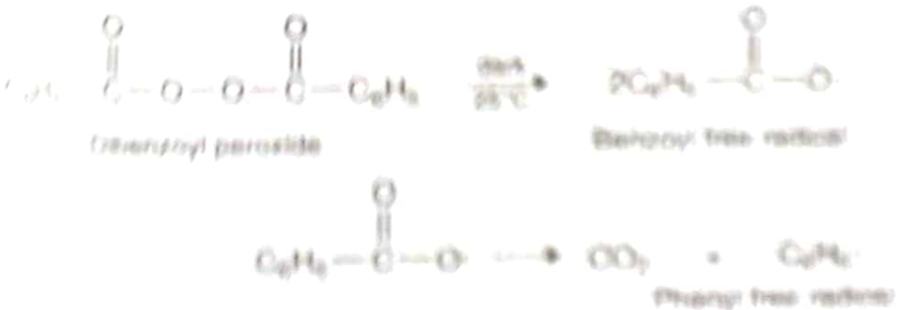
$$Cl\cdot + \cdot Cl \longrightarrow Cl{-}Cl$$
$$CH_3\cdot + \cdot Cl \longrightarrow CH_3{-}Cl$$
$$CH_3\cdot + \cdot CH_3 \longrightarrow CH_3{-}CH_3$$

A chlorine free radical can also attack methyl chloride to form chloromethyl free radical. This free radical participates further in the chain reaction to yield methylene chloride (dichloromethane).



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

PROOF OF FREE RADICAL MECHANISM. If the reaction actually follows the above mechanism, then the addition of substances that are sources of free radicals should initiate the reaction in the dark at room temperature. This is actually so. For example, methane reacts with chlorine in the dark at room temperature in the presence of catalytic amounts of dibenzoyl peroxide.



Phenyl free radical then reacts with chlorine molecule to produce a chlorine free radical.

$$C_6H_5\cdot + Cl{:}Cl \longrightarrow C_6H_5{-}Cl + Cl\cdot$$

Chlorobenzene Chlorine free radical

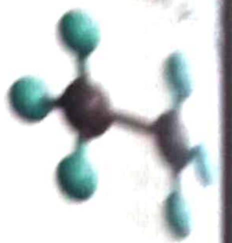
Once the chlorine free radicals are produced, the reaction can proceed in the manner described above.

(ii) Bromination. Bromine reacts with alkanes in a similar manner [illegible].

(iii) Iodination. Iodine reacts with alkanes reversibly. The hydrogen iodide formed [illegible] is a powerful reducing agent and is capable of reducing the iodoalkane to the alkane.

Uses. Methane is used (1) as a domestic fuel in the form of natural gas; (2) in the ... methanol ; (3) in the manufacture of carbon black which is used in printing inks, ... gramophone records, and rubber tyres.

ETHANE, $CH_3–CH_3$



Ethane occurs to the extent of 10-20 per cent along with methane in *Natural Gas*.

Preparation. Ethane can be prepared :

(1) By heating sodium propionate with soda-lime in a pyrex test-tube.

$$\underset{\text{Sodium propionate}}{CH_3CH_2COONa} + NaOH \xrightarrow{\Delta} \underset{\text{Ethane}}{CH_3CH_3} + Na_2CO_3$$

(2) By the reduction of ethyl iodide, using nascent hydrogen, formed by the action of ... zinc-copper couple.

$$\underset{\text{Ethyl iodide}}{CH_3CH_2I} + 2[H]\ (\textit{from couple}) \longrightarrow \underset{\text{Ethane}}{CH_3CH_3} + HI$$

(3) By the action of sodium metal on methyl iodide in dry ether solution. (*Wurtz Reaction*)

$$\underset{\text{Methyl iodide}}{CH_3I} + 2Na + ICH_3 \xrightarrow{\text{ether}} \underset{\text{Ethane}}{CH_3CH_3} + 2NaI$$

Thin slices of sodium metal are suspended in dry ether contained in a small flask fitted with a reflux condenser and a tap-funnel. Methyl iodide is slowly added from the tap-funnel and the ... evolved is collected over water.

(4) By passing a mixture of ethylene and hydrogen over heated nickel catalyst.

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2 \xrightarrow[\Delta]{Ni} \underset{\text{Ethane}}{CH_3CH_3}$$

(5) By hydrolysis of ethylmagnesium bromide.

$$\underset{\text{Ethylmagnesium bromide}}{CH_3CH_2MgBr} + H_2O \longrightarrow \underset{\text{Ethane}}{CH_3CH_3} + Mg(OH)Br$$

Properties. Ethane is a colorless gas. It is sparingly soluble in water but dissolves in organic solvents like ethanol, ether, and benzene. It gives all the general reactions of alkanes.

CONFORMATIONS OF ALKANES

Free rotation is possible around C–C single bonds (s bonds). **The different spatial arrangements of a molecule that can be obtained by rotation around C–C single bonds are called Conformations or Conformation Isomers.**

Fig. 10.4. Free rotation is possible around C–C single bonds (σ bonds). The different spatial arrangements of a molecule that result from rotation about a single bond are called conformations.

Conformations of Ethane. Let us consider ethane, H_3C-CH_3, as an example. The two tetrahedral methyl groups can rotate about the carbon-carbon bond axis yielding several arrangements.

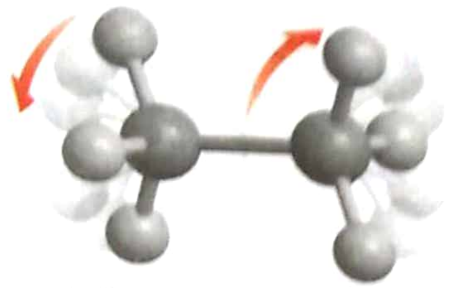


Fig. 10.5. In ethane, the two methyl groups can rotate about the C–C σ bonds. As a result, an infinite number of spatial arrangements (conformations) of ethane are possible.

The two extreme arrangements of ethane represented by ball-and-stick models are shown in Fig. 10.6.

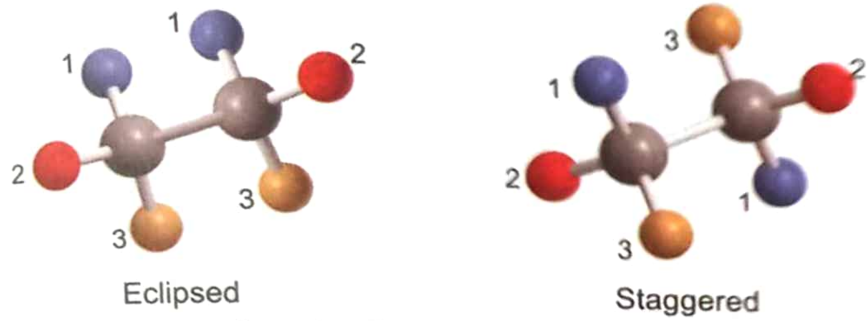


Fig. 10.6. Ball-and-Stick models of eclipsed and staggered conformations of ethane.

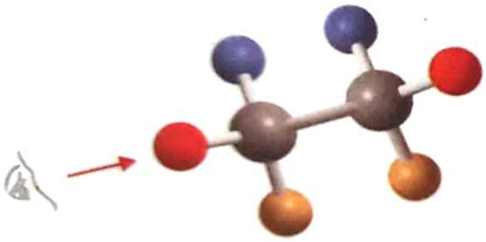


Fig. 10.7

When viewed from one end of the model along C–C axis (Fig. 10.7), the models shown above represent the following conformational forms.

(1) The **Eclipsed Form** in which the rear methyl group is completely eclipsed and only the one nearer the eye is visible.

(2) The **Staggered Form** in which the rear methyl group has been rotated upside down (Fig. 10.6) and all the six H atoms of the two methyl groups are staggered symmetrically.

(3) Evidently there could be several other arrangements or forms possible in between the eclipsed form and the staggered form. Such an arrangement lying anywhere between the two extreme forms is called a **Skew Form**.

As suggested by Melvin Newman, in ethane the front carbon atom is represented by the intersection of bonds from it, while the rear carbon appears as a circle (Fig. 10.8).

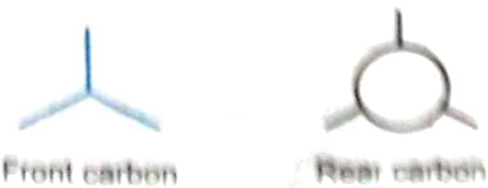


Fig. 10.8