**Sp3 Hybridization in Alkanes and Alkenes**

**Hybridization:**
The process of mixing of pure orbitals to give a set of new equivalent orbitals is called hybridization and the atom is said to be in hybridized state.

- **Classification of hybridization:**
  1) sp³ hybridization
  2) sp² hybridization
  3) sp hybridization

1) sp³ Hybridization
The process of intermixing of one s-orbital and three p orbitals to give a new hybridized orbital is known as sp³ hybridization.

  e.g. Methane – CH₄
  Ethane – C₂H₆

2) sp² Hybridization
The process of intermixing of one s-orbital and two p orbitals to give a new hybridized orbital is called as sp² hybridization.

  e.g. Ethene - C₂H₄
  Boron trichloride – BCl₃

3) sp hybridization
The process of intermixing of one s-orbital and one p orbital to give a new sp hybridization.

  e.g. Acetylene - C₂H₂
  Beryllium Chloride – BeCl₂

**sp³ Hybridization of Carbon:**
The electronic configuration of carbon in its ground state.

\[ \text{C (Ground state)} = 1s^2 \underbrace{2s^2} \underbrace{2px^1} \underbrace{2py^1} \underbrace{2pz^0} \]  
Valence shell

- In terms of energy level diagram, this electron configuration may be represented above. Since there are only two unpaired electrons it might be expected that only two single covalent bonds will be formed.
On this basis, carbon would combine with two hydrogen atoms (H = 1s\(^1\)) to form a molecule CH\(_2\). The two C – H bonds would be formed by overlap of the 2p orbitals (p\(_x\), p\(_y\)) with the 1s orbital of each hydrogen atom. Since the angle separating the p orbitals is 90\(^{\circ}\), the C – H bonds would be at right angles to each other. But from chemical analysis we know that the simplest stable compound that carbon forms with hydrogen is methane (CH\(_4\)) and this compound contains four identical C – H bonds.

Now, assume that one of the 2s electrons in the ground state is promoted to the empty p\(_z\) orbital. Since 2p\(_z\) orbital is at a higher energy level than the 2s orbital, this promotion process would require input of energy. This energy is supplied in the form of heat or light.

This new state of carbon is referred to as the excited state. The electron configuration of the carbon atom in its excited state is -

\[
\text{C (Excited state) = } 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1
\]

In terms of energy level diagram, this electron configuration may be represented as above. Since there are four unpaired electrons in the valence shell of the carbon atom in its excited state, it might be expected that four covalent bonds will be formed.

On this basis, carbon would combine with four hydrogen atoms to form a molecule CH\(_4\). The three C – H bonds would be formed by the overlap of three 2p orbitals (p\(_x\), p\(_y\), and p\(_z\)) with one s-orbital of each hydrogen atom. The fourth C – H bond will be formed by overlap of the 2s orbital of carbon with the 1s orbital of a hydrogen atom. Since the angle separating the p orbitals in an atom is 90\(^{\circ}\), the three C – H bonds may be expected to be at right angles to each other. The fourth C – H bond involving the overlap of s orbitals will not have any directional characteristics because s orbitals are spherically symmetrical. This implies that two different types of C – H bonds are involved in the formation of methane molecule. This is not true. Experimentally, methane has been shown to contain four identical C – H bonds that are directed towards the corners of a regular tetrahedron.
• To form four identical bonds, carbon must contribute a set of four equivalent orbitals. This can be achieved if the 2s and the three 2p orbitals (p_x, p_y and p_z) in the excited state are mixed or hybridized to give four new equivalent orbitals. These new orbitals are known as sp^3 hybrid orbital.

• The electronic configuration of the carbon atom in its sp^3 hybridized state is:

(Hybridized State) – 1s^2 2(sp^3)^1 2(sp^3)^1 2(sp^3)^1 2(sp^3)^1

The hybridized state electron configuration may be represented as follows:

![Diagram showing formation of four equivalent sp^3 hybrid orbitals of carbon.](image)

Fig. Q.1.1 Formation of four equivalent sp^3 hybrid orbitals of carbon.

Each sp^3 orbital contains one electron. Since each sp^3 orbital is obtained from one s and three p orbitals, it has 25 % s – character and 75 % p – character. As indicated each sp^3 orbital has a large lobe and small lobe.
The four new \( sp^3 \) orbitals obtained above are identical (same energy and shape) but differ only in their orientation in space with respect to each other. The four \( sp^3 \) orbitals are arranged in such a way that their axes are directed towards the corners of a tetrahedron with carbon located at the centre. The angle between any two orbitals is therefore, 109° 28′.

**Halogenation of Alkanes**

**Halogenation**: This involves the substitution of hydrogen atoms of alkanes with halogen atoms.

**e.g. 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.
Methane reacts with chlorine to give methyl chloride and HCl.

\[
\text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{UV light or } \Delta} \text{CH}_3\text{Cl} + \text{HCl} \quad \text{(Methyl chloride)}
\]

**Mechanism of halogenation**: 
It takes place through the formation of free radicals. 
For example, chlorination of methane involves the following steps.

**I) Chain – Initiation step**: Chlorine molecule undergoes hemolytic fission to give chlorine free radicals

\[
\text{Cl}^- + \text{Cl} \xrightarrow{\text{UV light or } \Delta} \text{Cl}^* + \text{Cl}^*
\]

Chloride free radical

**II) Chain – Propagation steps**: 

a) Chlorine free radical attacks methane to produce HCl and methyl free radical.

\[
\text{Cl}^* + \text{H} : \text{CH}_3 \xrightarrow{} \text{H} : \text{Cl} + \text{CH}_3 \quad \text{Methyl radical}
\]

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

\[
\text{H}_3\text{C}^- : + \text{Cl} \xrightarrow{} \text{H}_3\text{C} : \text{Cl} + \text{Cl}^* \quad \text{Methyl Chloride}
\]

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

**III) Chain – Termination Step**: The above chain reaction comes to halt when any two free radicals combine.

For example,

\[
\text{Cl}^- + \text{Cl} \rightarrow \text{Cl} \cdot \text{Cl}
\]

\[
\text{CH}_3^- + \text{Cl} \rightarrow \text{CH}_3 \cdot \text{Cl}
\]

\[
\text{CH}_3^- + \text{CH}_3 \rightarrow \text{CH}_3 \cdot \text{CH}_3
\]
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.

Similarly, chloroform (CHCl₃) and carbon tetrachloride (CCl₄) are obtained by further chain reaction.

**Uses of Paraffin**

**Paraffin:**

i) Paraffin, also known as liquid paraffin, paraffin oil or kerosene, is a combustible hydrocarbon liquid that is burned, as a fuel.

ii) It is a mixture of different types of simple hydrocarbons, it is less volatile than gasoline and it boils at 302 – 527 degrees Fahrenheit.

iii) Paraffin can be extracted from coal, wood and oil shale, but it is primarily obtained from the distillation of petroleum which was first distilled in 1807 by geologist Abraham Gesner.

iv) Paraffin, when found is solid form, is called paraffin wax, while the liquid form is referred to as paraffin oil.

v) Liquid paraffin oil is a mineral oil that comes in two forms, either heavy liquid paraffin oil or light liquid paraffin oil. Paraffin is clean burning and maintains a high heat output.

**Paraffin Uses:**

i) Paraffin is a alkane hydrocarbon that has a variety of practical uses in industries such as medicine, agriculture and cosmetics.

ii) Paraffin is widely used as fuel or a fuel component for diesel and tractor engines.

iii) In centuries past, before electricity was invented, paraffin was used in lamps and lanterns as the main source of lighting.
iv) Today, paraffin is the most widely used heating oil in home, central heating systems in the UK and it is still used in less developed countries as the main fuel for cooking.

v) Paraffin is also used as a fuel in portable stoves during outdoor activities and mountaineering.

vi) Liquid paraffin can be used as a lubricant for machinery. Lubricants can help to extend the life of expensive machinery and equipment by reducing friction, binding and wear.

vii) Paraffin can also be used as a coolant for electrical systems, as a hydraulic fluid and as a solvent for greases and insecticides.

viii) Liquid paraffin also has medicinal properties. It is commonly used to treat dry skin, constipation, and eczema.

ix) Paraffin wax is also used as a water – harvesting soil treatment to supply runoff water to dry areas, as an adhesive and as a water – proofing agent.

Stabilities of Alkenes

**Stability of stearic effect :**

**Cis – isomer :**
The cis isomer is one in which two similar groups are on the same side of the double bond.

**Trans – isomer :**
The trans isomer is that in which two similar groups are on the opposite sides of the double bond.

- The trans isomers are more stable than the corresponding cis isomers.
- This is due to, in the cis isomer the bulky groups are on the same side of the double bond. So there is a steric hindrance.
- Because of this steric crowding, there are Vander Waals repulsive forces between the electron clouds of the groups.
- This decreases the stability of the cis alkene.
- In trans – 2 – Butene, the methyl groups are on opposite sides of the double bond and the repulsion does not occur.
Stability by Hyper-conjugation:

Hyper-conjugation is a modified resonance effect which involves delocalization of σ electron.

Stability of alkene increases with increased in number of alkyl group on the double bond. It is due to increased in number of contributing no bond resonance structure.

Example:

2 – butene is more stable than 1 – butene.

This is because there are six hydrogen involved in hyper-conjugation whereas there are only two hydrogen involved in 1 – butene. Hence contributing structure in 2 – butene are more and is more stable than 1 – butene.

1 – Butene:

\[
\text{CH}_3\text{–C–C} = \text{C}\longleftrightarrow \text{CH}_3\text{–C–C–CH}_2
\]
2 - butene:

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H-} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C}= & \quad \text{C} & \quad \text{CH}_3 \\
\text{H} & \quad & & & \quad \text{H} \\
\text{H} & \quad & & & \quad \text{H} \\
\end{align*}
\]
**E₁ versus E₂ Reaction**

**Elimination Reaction**

When two groups or atoms from adjacent carbon are eliminated with the formation of unsaturated compounds. This reaction is called as elimination reaction.

- **E₁ reaction**: When the rate of elimination reaction is dependent only on the concentration of substrate, the reaction is kinetically of a 1ˢᵗ order / Unimolecular. Such a unimolecular elimination reaction is designated as E₁.

- **Reaction**: Action of strong solution of alkali on 2 – bromo – 2 – methylpropane (tertiary butyl bromide) to form a 2 methyl propene.

\[
\begin{align*}
\text{CH}_3 & \quad \text{Br} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{CH}_3 + \text{OH}^- \rightarrow \text{CH}_3 \quad \text{C} = \text{CH}_2 + \text{H}_2\text{O} + \text{Br}^- \\
& \quad \text{2 – Methylpropene} \\
& \quad 2 – \text{Bromo – 2 – Methylpropane}
\end{align*}
\]

**Mechanism**: The E₁ mechanism is of two - step process:

**Step I**: Carbocation is generated due to slow heterolysis of substrate to release halide ion.

This is slow rate determining step which involves ionization of substrate forming a carbonium ion.

**Step II**: The carbonium thus form looses the β proton with the help of base which is generally the solvent itself.
**Kinetics of E₁ reaction:**

The E₁ reaction follows first order kinetics. The overall rate of reaction is determined only by the slow first step. Except for the many necessary solvent molecules, this rate determining step involves only substrate and its rate depends only on the concentration of substrate.

\[
\text{Rate} \propto [(\text{CH}_3)_3 \text{CBr}] \\
R = k[(\text{CH}_3)_3 \text{CBr}]
\]

The rate of an E₁ reaction is independent of base concentration because the reaction whose rate are measuring does not involve base.

It is the rate of formation of carbocations that determines how fast a reaction goes. Once formed, the carbocations rapidly react to yield product.

This mechanism was named E₁, that is elimination, uni-molecular because in the rate – determining step only one molecule, substrate, undergoes co-valency change.

**Define elimination reaction and write down reaction, mechanism and kinetics of E₂ reaction.**

**Elimination Reaction:**

When two groups or atoms from adjacent carbon are eliminated with the formation of unsaturated compounds. This reaction is called as elimination reaction.

- **E₂ reaction:**

When the rate of elimination reaction is dependent on both the concentration of substrate and catalyst reagent, the reaction is kinetically second order reaction / bio-molecular. Such a bimolecular elimination reaction is designated as E₂ reaction.

**Reaction:**

Action of sodium ethoxide on 1 – Bromopropane, propene is formed.

\[
\begin{align*}
\text{CH}_3 \text{CH} = \text{CH}_2 + \text{C}_2\text{H}_5\text{ONa} & \rightarrow \text{CH}_3 \text{CH} = \text{CH}_2 \\
\text{1 – Bromopropane} & \rightarrow \text{Propene} \\
+ \text{NaBr} + \text{C}_2\text{H}_5\text{OH}
\end{align*}
\]
**Mechanism:**

It is a single step reaction takes place via a formation of single transition state.

Base, Abstracts a proton from β - carbon, with simultaneous departure of a nucleophile takes place from the α carbon, through the intermediate transitional state.

The energy of transition state will be least when the two leaving groups are co-planar in the transition state. Also the two leaving groups should be trans to each other.

\[
\text{Transition state}
\]

\[
\begin{array}{c}
\text{OH}^- \\
\text{H} \\
\text{C - C - X} \\
\text{C = C}
\end{array}
\]

$E_2$ reaction is facilitated by:

- Strong base of high concentration is used
- Solvent of low polarity.

Polar solvent forms a strong solvent wall around the base restricting the attack.

**Kinetics of $E_2$ reaction:**

The $E_2$ reaction follows second – order kinetics. The rate determining step is the only step involves reaction between a molecule of alkyl halide and a molecule of base and its rate is proportional to the concentration of both reactants.

\[
\text{Rate} \propto [\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}] [\text{C}_2\text{H}_5\text{O}^-] \\
\text{Rate} = k [\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}] [\text{C}_2\text{H}_5\text{O}^-]
\]

This mechanism was named $E_2$ that is elimination bi-molecular, because in the rate – determining step two molecules undergo covalency changes.
reactivity of alkyl halides towards $E_1$ reaction.

The reactivity of alkyl halide is dependent on the stability of carbonium ion. Following reactions shows the formation of primary, secondary and tertiary carbonium ion.

i)

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H}_3\text{C} - \text{C} - \text{CH}_3 \\
\text{Br}
\end{array}
\xrightarrow{\text{Br}^-}
\begin{array}{c}
\text{CH}_3 \\
\text{H}_3\text{C} - \text{C} - \text{CH}_3 + \text{Br}^-
\end{array}
\]

Tertiary alkyl halide Tertiary carbocation

ii)

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H}_3\text{C} - \text{C} - \text{CH}_3 \\
\text{Br}
\end{array}
\xrightarrow{\text{Br}^-}
\begin{array}{c}
\text{H} \\
\text{H}_3\text{C} - \text{C} - \text{CH}_3 + \text{Br}^-
\end{array}
\]

Secondary alkyl halide Secondary carbocation

iii)

\[
\begin{array}{c}
\text{H} \\
\text{H}_3\text{C} - \text{C} - \text{H} \\
\text{Br}
\end{array}
\xrightarrow{\text{Br}^-}
\begin{array}{c}
\text{H} \\
\text{H}_3\text{C} - \text{C} - \text{H} + \text{Br}^-
\end{array}
\]

Primary alkyl halide Primary carbocation

The reactivity of alkyl halide is as follows:
Tertiary carbocation > secondary carbocation > primary carbocation

This is due to positive inductive effect associated with the alkyl groups. More the number of alkyl groups present on the positively charged carbon, more is the stability of the carbocation.

REARRANGEMENT OF CARBOCATIONS

Organic ions which contains a positively charged carbon atom are called carbonium ion or carbocation. They are formed by heterolytic bond fission.

\[
\text{C}_3\text{H}_2\text{A} \xrightarrow{\cdot} \text{C}^+ + \text{A}^-
\]

The stability of carbonium ion increases with increase in number of alkyl group due to their $+I$ effect. The alkyl groups releases electron towards the carbon bearing positive charge and thus stabilizes the ion.
The order of stability of carbonium ion is:

$$\begin{align*}
\text{Tertiary carbonium ion} & \quad \text{Secondary carbonium ion} & \quad \text{Primary carbonium ion} \\
R-C-R & \quad R-C-R & \quad R-C-H
\end{align*}$$

In case of tertiary carbocation, the number of alkyl group attach is more than that of secondary and primary carbocation. So, it releases more electron towards the positive carbon and stabilizes it. Hence, the tertiary carbocation is more stable than that of secondary and primary carbocation.

**Saytzeff Orientation and Evidences**

**Saytzeff rule orientation and evidences in $E_1$ and $E_2$ reaction.**

**$E_1$ reaction:**

**Saytzeff Rule orientation:**

Elimination by $E_1$ shows Saytzeff’s orientation.

The de-hydro-halogenation of an alkyl halide can yield more than one alkene, then according to the Saytzeff Rule, the main product is the most highly substituted alkene, i.e. the more highly branched, the more stable alkene, is the preferred product. Thus a substituted alkene is preferred over a mono-substituted alkene.

E.g. –

$$\begin{align*}
\text{H}_3\text{C} & \text{-CH} & \text{-CH} & \text{-CH}_3 \\
\text{H}_2\text{C} & \text{-CH} & \text{-CH} & \text{-CH}_3 \\
\text{CH}_3 & \text{-CH} & \text{CH} & \text{=CH} & \text{-CH}_3
\end{align*}$$

According to the Saytzeff’s Rule, the main product is the di-substituted alkene, 2 – Butene, rather than the mono-substituted, 1-butene.
Evidence for E₁ Mechanism:

1. The carbocation is generated in step - I undergo changes to form most stable confirmation before giving a proton. Therefore E₁ reaction is non - stereo - specific.

E.g.

In each of these examples the initially formed carbocation can rearrange by 1, 2 – shift to form a more stable carbocation.

i) 

![Diagram](image1)

(Secondary) Carbocation

(Tertiary) Carbocation

ii) 

![Diagram](image2)

(Secondary) Carbocation

(Tertiary) Carbocation

iii) 

![Diagram](image3)

(Secondary) Carbocation

(Tertiary) Carbocation
2. Isotope effect:
The hydrogen isotope effect is observed in $E_2$ reaction because breaking of $\beta$-carbon hydrogen bond occurs in rate determining step, since it does not occur in rate determining step i.e. step $I$ of $E_1$ reaction. Hence the isotope effect of hydrogen is not seen in $E_1$ reaction.

3. Structural effect:
The reactivity of alkyl halide is dependent on stability of carbonium ion. The reactivity decreases in order $3^o > 2^o > 1^o$.

E.g. –

i)

$$\begin{align*}
\text{CH}_3 - &\text{C} - \text{CH}_3 & \text{CH}_3 - &\text{C} - \text{CH}_3 \\
\text{Br} & & \Theta &
\end{align*}$$

Tertiary alkyl halide  Tertiary carbonium ion

ii)

$$\begin{align*}
\text{H} & \text{H} \\
\text{CH}_3 - &\text{C} - \text{CH}_3 & \text{CH}_3 - &\text{C} - \text{CH}_3 \\
\text{Br} & & \Theta &
\end{align*}$$

Secondary alkyl halide  Secondary carbonium ion

iii)

$$\begin{align*}
\text{H} & \text{H} \\
\text{CH}_3 - &\text{C} - \text{H} & \text{CH}_3 - &\text{C} - \text{H} \\
\text{Br} & & \Theta &
\end{align*}$$

Primary alkyl halide  Primary carbonium ion

4. Solvent and Base:
Change in solvent does not affect the rate of reaction because 1$^{st}$ step involves only reactant and its concentration affects the rate. Base does not affect the rate as it is added in the fast step. Hence, overall solvent and base does not affect the rate of reaction of $E_1$ mechanism.
**E₂ reaction:**

**Saytzeff Rule Orientation:**

- If the de-hydro-halogenation of secondary butyl bromide is carried out in presence of a base a mixture of 1 – butene and 2 – butene is obtained.

![Chemical Reaction Diagram](image)

- For example, sec-butyl bromide; attack by base at any one of three β - hydrogens (C - 1) can lead to the formation of 1 butene; attack at either of two β - hydrogens (on C - 3) can lead to the formation of 2 – butene and 2 – butene is the preferred product.
- The preferred product 2 – butene is a di-substituted alkene, whereas 1 – butene is a mono-substituted alkene, that is, in 2 – butane there are two alkyl groups attached to the doubly bonded carbons, and in 1 – butene there is only one alkyl group.
- The rule state that, in de-hydro-halogenation the preferred product is the alkene that has the greater number of alkyl groups attached to the doubly bonded carbon atoms.
- Now, de-hydro-halogenation is an irreversible reaction, so that once again orientation is determined by the relative rates of competing reactions. More 2 – butene than 1 – butene is obtained from sec-butyl bromide because 2 – butene is formed faster then 1-butene.
- The alkene with the greater number of alkyl groups is the preferred product because it is formed at faster rate than alternative alkenes.
- Ease of formation of alkenes:

\[ R_2C = CR_2 > R_2C = CHR > R_2C = CH_2, \quad RCH = CHR > RCH = CH_2 \]
Evidence of E₂ Mechanism:

1. Isotope effects:
   - Isotope have different mass and also do not show identical chemical properties, they differ in the rate of reaction, so the difference in the rate of reaction due to a difference in the isotope present in the reactant is called an isotope effect.
   - If a particular atom is less tightly bound in the transition state of a reaction than in the reactant the reaction involving the heavier isotope of that atom will go more slowly.
   - The hydrogen isotopes have the greatest proportional differences in mass: deuterium (D) is twice as heavy as protinus (H), and tritium (T) is three times as heavy.
   - When an elimination reaction is carried out by replacing hydrogen with its isotope deuterium, the reaction slows down. Breaking a carbon—deuterium bond is slower than breaking a similar carbon—hydrogen bond.

\[
\begin{align*}
K^H & \quad \text{Rate of reaction with hydrogen} \\
K^D & \quad \text{Rate of reaction with deuterium}
\end{align*}
\]

\[
\begin{align*}
\text{i) } & \quad \text{with hydrogen} \\
\text{C} - \text{H} + Z & \rightarrow [\cdots \text{C} \cdots \text{H} \cdots Z] \rightarrow \text{C} + \text{H} - Z \\
\text{ii) } & \quad \text{with deuterium} \\
\text{C} - \text{D} + Z & \rightarrow [\cdots \text{C} \cdots \text{D} \cdots Z] \rightarrow \text{C} + \text{D} - Z
\end{align*}
\]
The rate of reaction can be measured in two ways:

1. In intermolecular competition, a mixture of labeled and unlabeled reactants compete for a limited amount of reagent and the relative amount of the product formed is measured thus indicating the rate of the reaction.

2. In intermolecular competition, a single reactant is used in which same equivalent positions are labeled and others are not labeled. This reacts with the reagent and the amount of product is studied thus showing the reaction site and the rate of the reaction.

Let us consider de-hydro-halogenation of 2-phenyl ethyl bromide with \( \text{C}_2\text{H}_5\text{ONa} \) of labeled 2-phenyl ethyl bromide which contains deuterium at both \( \beta \)-positions.

Eg. 1)

\[
\text{H} \quad \text{C}_6\text{H}_5 \quad \text{H} \quad \text{Br} \\
\text{C} \quad \text{CH}_2 + \text{C}_2\text{H}_5\text{ONa} \quad \longrightarrow \quad \text{C}_6\text{H}_5\text{CH} = \text{CH}_2
\]

2-phenyl ethyl bromide

Eg. 2)

\[
\text{D} \quad \text{C}_6\text{H}_5 \quad \text{H} \quad \text{Br} \\
\text{C} \quad \text{CH}_2 + \text{C}_2\text{H}_5\text{ONa} \quad \longrightarrow \quad \text{C}_6\text{H}_5\text{CD} = \text{CH}_2
\]

2-Phenylethyl bromide (Labeled)

where, \( \frac{K^H}{K^D} = 7 \) i.e. rate of reaction with 2-phenyl ethyl bromide was 7 times that of rate with labeled 2 phenyl ethyl bromide.

This shows that \( \beta \)-C – hydrogen bond break in rate determining step.

2. Absence of hydrogen exchange:

Let us consider another mechanism for de-hydro-halogenation via the formation of carbanion.

\[
\text{C} \quad \text{C} + \ddot{\beta} \quad \text{C} \quad \text{C} + \ddot{\Theta} \\
\text{Alkyl halide base} \quad \text{Alkene halogen}
\]
Mechanism:

Step I: The reaction involve abstraction of the proton by a base leaving behind its pair of electron thus forming a carbanion.

\[ \text{Alkyl halide} + \text{B} \rightarrow \text{Carbanion} \, + \, \text{HB} \]

Step II: Loss of halide to give the product alkene. This is an acid base reaction.

\[ \text{Alkene} + \text{X}^- \]

This mechanism is called \( E_{1(\text{cb})} \).

- Consider, the de-hydro-halogenation of 2-phenyl bromide with a \( C_2H_5\text{ONa} \) in presence of labeled ethanol as a solvent. Consider if carbanion were formed reversibly they would regain hydrogen. From the solvent before actually losing the halide ion to yield alkene. Since the ethanol used deuterium the carbanion would be gaining a deuterium and not a proton.

- The reaction was interrupted in between and un_consumed 2-phenyl ethyl bromide was recovered. It showed no presence of deuterium.

This showed that \( E_2 \) mechanism does not involve hydrogen exchange and thus showing as that carbanion are not formed.

\[ \text{C}_6\text{H}_5\text{CH} \rightarrow \text{CH} = \text{CH}_2 \]

\[ \text{Labeled halide} \]

\[ \text{Carbonion} \]

\[ \text{Alkene} \]
3. **Rearrangement does not take place:**
   This is consistent with a mechanism which does not involve carboxylation as intermediate thus indicating the reaction to be a single step process.

4. **Elemental effect:**
   The reaction shows a large – elemental effect. This effect was studied to understand whether rate at which the halide ion is last affect the rate of reaction. In the elimination reaction reactivity of alkyl halides is as follows:
   
   \[ R – I > R – Br > R – Cl > R – F \]
   
   Alkyl bromides react 40 to 60 times as fast as the chlorides, alkyl iodides react more than 25,000 times as fast as the fluorides.

Thus, the rate of breaking the carbon – halogen bond does affect the overall rate of elimination.

**Factors Affecting \( E_1 \) and \( E_2 \) Reactions**

**Factors affecting \( E_1 \) reaction:**

Different factors that influence the rate of \( E_1 \) reaction are:

1. **Type of substrate and reactivity:**
   Carbocation is the intermediate in \( E_1 \) elimination. So rate of reaction depends on the stability of carbocation formed, groups with + I effect would stabilize the carbocation.

   Order of stability of carbocation:
   
   \[ 3^\circ > 2^\circ > 1^\circ \]

   Therefore, order of reactivity is \( 3^\circ > 2^\circ > 1^\circ \) substrate. But bridged halides do not undergo this reaction because the intermediate carbocation cannot assume planar triagonal geometry and is highly strained.

2. **Nature and Concentration of the base:**
   \( E_1 \) reactions are independent of nature and concentration of the base. Therefore the reaction can be carried out using weak base usually in the form of the solvent.

3. **Nature of leaving group:**
   Least basic groups are good leaving groups, thus order of leaving group reactivity is,
   
   \[ H_2O > R – OH > CH_3COO^- > RO^- \]
   
   \[ I^- > Br^- > Cl^- > F^- \]
4. **Nature of solvent:**
Rate of reaction of $E_1$ reaction increases by using polar solvents due to the carbocation intermediate solvents of low polarity and low nucleophilicity favour $E_1$ reactions.

5. **Temperature:**
Increase in temperature favours $E_1$ reaction and hence increases the rate of reaction as the activation energies of elimination are higher than those of the substitution reaction.

**Factors affecting rate of $E_2$ reaction:**

1. **Nature of Substrate:**
Rate of $E_2$ reaction increases with the presence of electron withdrawing group on the $\beta$ - carbon as the I – effect of these groups increase the acidity of the $\beta$ - H stabilizing the carbanion character. Also presence of more number of alkyl or aryl groups increases the rate of reaction when present on the carbon atom where a new double bond would be developed.

2. **Nature of leaving group:**
With increase in the size of the group, the ability of a leaving group also increases and thus increasing the rate of reaction.

   e.g. Increase in size of halogen atom increases the rate of reaction i.e. I > Br > Cl > F.

3. **Nature and concentration of the base:**
Rate of reaction increases with increase in basicity and concentration of the base. Order of basicity is,

   $\text{NH}_2 > \text{OEt} > \text{OH}$

4. **Nature of Solvent:**
Decrease in solvent polarity increases the rate of reaction.

5. **Temperature:**
Increase in the temperature increases the rate of $E_2$ reaction.
Alkenes belong to the group of unsaturated hydrocarbons that is one molecule of alkene contains at least one double bond. Due to the presence of pi electrons they show addition reactions in which an electrophile attacks the carbon-carbon double bond to form the addition products. These reactions are known as electrophilic addition reactions of alkenes. Sometimes these addition reactions follow free radical mechanism too. Oxidation and ozonolysis reactions are also some of the prominent reactions of alkenes. Some of these reactions are discussed below:

Electrophilic addition reactions of alkenes: Alkenes exhibit wide range of electrophilic addition reactions. Addition of hydrogen halides such as hydrogen bromide and hydrogen chloride is an example of electrophilic addition reactions of alkenes. The general trend of hydrogen halide is given as: HI > HBr > HCl. For symmetrical alkenes such as ethene it is quite easier to predict the end product in comparison to unsymmetrical alkenes such as propene. For example:

\[
\text{CH}_2 = \text{CH}_2 + \text{H}^–\text{Br} \rightarrow \text{CH}_3\text{–CH}_2\text{–Br}
\]
Markovnikov proposed a rule called Markovnikov rule for the prediction of major product in such cases. Markovnikov rule states that negative part of the adding molecule gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus, 2-bromopropane is the expected product by this rule. This can further be explained with the help of mechanism of electrophilic substitution reactions of alkenes. The general mechanism is explained below:

An electrophile, H⁺ is generated from hydrogen bromide which attacks on double bond to form carbocation.

Since, the secondary carbocation is more stable than the primary carbocation, the secondary carbocation predominates the formation of ions.

Finally, Br⁻ attacks the carbocation to form alkyl halides.
Ozonolysis, electrophilic addition reactions of alkenes

- When ozone is passed through an alkene in an inert solvent, it adds across the double bond to form an ozonide.
- Ozonides are explosive compounds.
- They are not isolated on warming with zinc and water.
- Ozonoides cleave at the site of double bond.
- The products are aldehydes, ketones or an aldehyde and a ketone, depending on the structure of the alkene.

- The two-step process of preparing the ozonide and then decomposing it to get the carbonyl compounds is called ozonolysis. For example,

\[ \text{Ethylene} \xrightarrow{i) O_3 \ \text{ii) Zn/H}_2\text{O}} \text{Formaldehyde (2 Molecules)} \]

\[ \text{2 – Methyl – 2 – Butene} \xrightarrow{i) O_3 \ \text{ii) Zn/H}_2\text{O}} \text{Acetone acetaldehyde} \]

- Ozonolysis is probably the best method for locating the position of the double bonds in unknown alkenes.
The oxygenated carbons in carbonyl compounds obtained by ozonolysis are the ones that were joined by a double bond in the original alkene. Suppose an alkene on ozonolysis gives the carbonyl compounds.

\[ \text{CH}_3 \quad \text{H} \]
\[ \text{H}_3\text{C} - \text{C} = \text{O} \quad \text{and} \quad \text{O} = \text{C} - \text{CH}_3 \]

Acetone \quad \text{Acetaldehyde}

Joining the oxygenated carbons by a double bond, we get the following structure of the unknown alkene.

\[ \text{CH}_3 \quad \text{H} \]
\[ \text{CH}_3 - \text{C} = \text{C} - \text{CH}_3 \]

2-Methyl-2-Butane

**Markownikoff's Orientation:**

**Markownikoff's Rule:**

When an unsymmetrical reagent adds to an unsymmetrical alkene, the positive part of the reagent becomes attached to the double bonded carbon which bears the greatest number of hydrogen atoms.
For example,

When unsymmetrical propene reacts with hydrogen bromide it gives two product: isopropyl bromide and \( n \)-propyl bromide.

**Mechanism:**

The mechanism of this reaction involves the following steps:

**Step I:** HBr ionizes to give a proton (electrophile) and a bromide ion (nucleophile).

\[
\text{HBr} \rightarrow \text{H}^+ + \text{Br}^- \\
\text{Proton} \quad \text{Bromide ion}
\]

**Step II:** The proton attacks the double bond to form a more stable carbonium ion.

**Step III:** The bromide ion attacks the more stable secondary carbonium ion to give the major product.
Free radical addition reactions of alkenes

To illustrate, consider the alkoxy radical-catalyzed, anti-Markovnikov reaction of hydrogen bromide to an alkene. In this reaction, a catalytic amount of organic peroxide is needed to abstract the acidic proton from HBr and generate the bromine radical, however a full molar equivalent of alkene and acid is required for completion.

![Chemical reactions diagram]

Note that the radical will be on the more substituted carbon. Free-radical addition does not occur with the molecules HCl or HI. Both reactions are extremely endothermic and are not chemically favored.
Free radical addition reactions example

\[ \text{Initiation:} \quad \text{peroxides or } h\nu \quad \rightarrow \quad \text{Rad}^\cdot \]

\[ \text{Reaction:} \quad \text{Rad}^\cdot + \text{HBr} \quad \rightarrow \quad \text{RadH} + \text{Br}^\cdot \]

\[ \text{Propagation:} \quad \text{Br}^\cdot + \text{HBr} \quad \rightarrow \quad \text{BrH} + \text{Br}^\cdot \]
Anti-Markownikoff’s Rule / Peroxide effect / Kharasch effect:

The addition of HBr to unsymmetrical alkene in the presence of organic peroxides \((R - O - O - R)\) takes a course opposite to that suggested by Markownikoff’s rule. This phenomenon of anti-Markownikoff’s addition of HBr caused by the presence of peroxides is known as peroxide effect.

For example,

When propylene reacts with HBr in the presence of a peroxide, the major product is \(n\) - propyl bromide, whereas in the absence of a peroxide the major product is isopropyl bromide.

\[
\begin{align*}
\text{H}_2\text{O}_2 & \quad \rightarrow \quad \text{CH}_3-\text{CH}-\text{CH}_2-\text{Br} \\
\text{CH}_3-\text{CH}==\text{CH}_2 + \text{HBr} & \quad \rightarrow \quad \text{Br} \\
& \quad \rightarrow \quad \text{CH}_3-\text{CH}-\text{CH}_3
\end{align*}
\]

\(n\) - Propyl bromide 
(Anti-Markownikoff’s product) 
Isopropyl bromide 
(Markownikoff’s product)

**Mechanism:**

Propylene reacts with HBr in the presence of a peroxide by a free radical mechanism.

Following steps are involved.

**Step 1:** Peroxide dissociates to give alkoxy free radicals.

\[
R - O - O - R \xrightarrow{\Delta} 2R - O^* \\
\text{Alkoxy free radical}
\]
**Step II**: Alkoxy free radical attacks HBr to form a bromine atom (a free radical).

\[
\text{R-O + H:Br} \rightarrow \text{R-\textcolor{red}{O}H + Br^{'}} \\
\text{Bromine atom}
\]

**Step III**: Bromine atom can attack propylene to give a primary free radical and a secondary free radical.

\[
\begin{align*}
\text{Br} & + \text{CH}_3\text{CH=CH}_2 \rightarrow \text{CH}_2=\text{CH}-\text{CH}_2 \\
\text{Propylene} & \quad \text{(1\textsuperscript{st} Free radical)}
\end{align*}
\]

\[
\begin{align*}
\text{Br} & + \text{CH}_3\text{CH=CH}_2 \rightarrow \text{CH}_3\text{CH}-\text{CH}_2 \\
\text{Propylene} & \quad \text{(2\textsuperscript{nd} Free radical)}
\end{align*}
\]

The order of stability of free radicals is \(3^\circ > 2^\circ > 1^\circ\). Therefore, the more stable secondary free radical is formed predominantly.

**Step IV**: More stable secondary free radical attacks the H – Br molecule to form anti – Markownikoff’s product and a bromine atom. The bromine atom goes back to step 3.

\[
\begin{align*}
\text{CH}_3\text{-CH-CH}_2\text{-Br} + \text{H:Br} & \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br} + \text{Br} \\
\text{n-Propyl bromide}
\end{align*}
\]
Stability of Conjugated Dienes

Conjugated dienes:
The dienes in which double bonds are separated by one single bond, is called as conjugated dienes.
E.g.

\[ \text{Conjugated double bonds} \]

Stability of conjugated dienes:
Conjugated dienes are more stable than non-conjugated dienes (both isolated and cumulated) due to factors such as delocalization of charge through resonance and hybridization energy. This can also explain why alicyclic radicals are much more stable than secondary or even tertiary carbocations. This is all due to the positioning of the pi orbitals and ability for overlap to occur to strengthen the single bond between the two double bonds.

i) Resonance Effect: The resonance structure shown below gives a good understanding of how the charge is delocalized across the four carbons in this conjugated diene. This delocalization of charges stabilizes the conjugated diene.
ii) **Hybridization energy**: For example,

In 1, 3 – butadiene the carbons with the single bond are sp² hybridized unlike in non-conjugated dienes where the carbons with single bonds are sp³ hybridized. This difference in hybridization shows that the conjugated dienes have more ‘s’ character and draw in more of the pi electrons, thus making the single bond stronger and shorter than an ordinary alkane C – C bond (1.54 Å).

Another useful resource to consider are the heats of hydrogenation of different arrangements of double bonds since the higher the heat of hydrogenation the less stable the compound. It is shown below that conjugated dienes (~ 54 kcal) have a lower heat of hydrogenation than their isolated (~ 60 kcal) and cumulated diene (~ 70 kcal).

\[
\begin{align*}
\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 & \quad \text{CH}_2 = \text{CH} - \text{CH}_2 = \text{CH}_2 \\
1, 3 – \text{Butadiene} & \quad 1, 4 – \text{Pentadiene} \\
(~ 54 \text{ kcal}) & \quad (~ 60 \text{ kcal}) \\
\text{Conjugated diene} & \quad \text{Non – conjugated diene}
\end{align*}
\]

From above it is concluded that, conjugated 1, 3 – Butadiene is more stable than non – conjugated 1, 4 – Pentadiene.

**Diels – Alder Reaction**:

- α, β unsaturated carbonyl compounds undergo an exceedingly useful reaction with conjugated dienes, known as the Diels – Alder reaction.
- This is an addition reaction in which C – 1 and C – 4 of the conjugated diene system become attached to the doubly bonded carbons of the unsaturated carbonyl compound to form a six – membered ring.
- The alkene or alkyne used in Diels – Alder reaction is referred to as Dienophile (dien - lover). The product of Diels – Alder reaction is called the Adduct. The net result is the formation of two new σ bonds and one new π bond of the expense of three original π bonds.
- The simplest example of a Diels – Alder reaction is the reaction of 1, 3 butadiene with reaction of 1, 3 butadiene with ethylene. No catalyst is required.
- The Diel – Alder reaction is useful not only because a ring a generated, because it takes place so readily for a wide variety of reactants.

Although the dienophile can be simple alkene, electron – attracting groups (such as – CN, - CHO, - COR, - COOH, - COOR) facilitate the reaction.

For example,
Electrophilic addition reaction of conjugated diene

- The addition of hydrogen bromide to 1, 3 – butadiene, two products are formed. One is the result of addition to one of the double bonds, 1, 2 – addition.

- The second product involves addition across the ends of the conjugated diene, 1, 4 – addition.

- Formation of both 1,2 – and 1, 4 – addition products occurs not only with halogens, but also with other electrophile such as the hydrogen halides.

- The reaction of 1,3 – butadiene with hydrogen chloride. The first step, as with alkenes, is formation of carbocation. However, with 1, 3 – butadiene, if the proton is added to Cl, the resulting cation has a substantial delocalization energy, with the charge distributed over two carbons. Attack of Cl as a nucleophile at one or the other of the positive carbons yields the 1, 2 – or the 1, 4 – addition product.
An important feature of reactions in which 1, 2 and 1, 4 additions occur in competition with one another is that the ratio of the products can depend on the temperature, the solvent and also on the total time of reaction.

**Free radical addition of conjugated diene:**

The conjugated dienes also undergo addition reactions by radical chain mechanisms. Here the addition product almost always is the 1, 4 adduct. Thus radical addition of hydrogen bromide to 1, 3 - butadiene gives 1 – bromo – 2 – butene.

**Mechanism:**

**Step I: Initiation**

\[ \text{HBr} \rightarrow \text{H}^+ + \text{Br}^- \]

**Step II: Propagation:**

\[ \text{Br} + \text{CH}_2=\text{CH} - \text{CH} = \text{CH}_2 \rightarrow \text{BrCH}_2-\dot{\text{CH}}-\text{CH} = \text{CH}_2 \]

\[ \text{BrCH}_2-\dot{\text{CH}}-\text{CH} = \text{CH}_2 + \text{H} : \text{Br} \]

\[ \text{BrCH}_2-\dot{\text{CH}}-\text{CH} = \text{CH}_2 + \dot{\text{Br}} \]
Allylic Rearrangement

**Ans.** : Allylic compounds are those which have a functional group on a carbon atom \( \alpha \) to an olefinic bond.

\[
\begin{array}{c}
\text{C=C-C-X} \\
\hline
\end{array}
\]

The double bond (and the functional group) in these compounds undergo acid or base catalyzed migration to form a new compound.

\[
R-\text{C}=\text{C}-\text{C}\text{-OH} \xrightarrow{\text{H}^+ \text{ or } \text{OH}^-} R-\text{C}-\text{C}=\text{C} \\
\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{OH} \xrightarrow{\text{H}^+} \text{CH}_3-\text{CH}-(\text{OH})=\text{CH}=\text{CH}_2 \\
\alpha - \text{Methylallyl Alcohol}
\]

The incoming and outgoing nucleophiles may not be the same.

\[
\begin{array}{c}
\text{CH}_3-\text{CH (Cl)}=\text{CH}-\text{CH}_2 \\
\alpha - \text{Methylallyl chloride} \\
\downarrow \text{EtOH}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3-\text{CH(OEt)}=\text{CH}-\text{CH}_2 \quad + \quad \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{OEt} \\
3 - \text{Ethoxybutene - 1} \quad 3 - \text{Ethoxybutene - 2}
\end{array}
\]

Such transformations which involve migration of the double bond and the functional group from one carbon to another is known as allylic rearrangement.