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# PHARMACEUTICAL ORGANIC CHEMISTRY – I

## UNIT 2

TOPIC :

- **Alkanes, Alkenes and Conjugated dienes\***

SP<sup>3</sup> hybridization in alkanes, Halogenation of alkanes, uses of paraffins.

Stabilities of alkenes, SP<sup>2</sup> hybridization in alkenes

E1 and E2 reactions– kinetics, order of reactivity of alkyl halides, rearrangement of carbocations, Saytzeffs orientation and evidences. E1 verses E2 reactions, Factors affecting E1 and E2 reactions. Ozonolysis, electrophilic addition reactions of alkenes, Markownikoff's orientation, free radical addition reactions of alkenes, Anti Markownikoff's orientation.

Stability of conjugated dienes, Diel-Alder, electrophilic addition, free radical addition reactions of conjugated dienes, allylic rearrangement

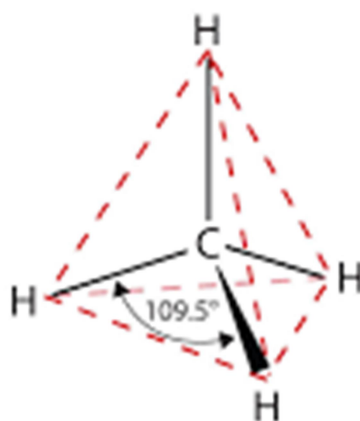


# Alkanes

- Alkanes are the simplest hydrocarbons or organic compounds.
- Alkanes are acyclic saturated hydrocarbons that means all the carbon-carbon bonds in alkanes are single bond.
- The general formula of alkanes is  $C_nH_{2n+2}$
- Alkanes contain strong. C-C&C-H Covalent bonds.
- Since alkanes contain strong covalent bands, hence they are relatively chemically inert.
- Methane is the simplest alkane.
- They are also known as Paraffins.
- Examples:  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$  etc.

## Structural Properties of Alkanes

- Each carbon atoms in alkanes are  $sp^3$  hybridized.
- All the carbon - carbon and carbon hydrogen bonds in alkanes are strong sigma bonds.
- The bond length of alkanes between Carbon-Carbon atom =  $1.54 \text{ \AA}$
- Carbon - hydrogen atom =  $1.12 \text{ \AA}$
- Alkanes forms tetrahedral structure with bond angle  $109.5^\circ$



# Halogenation

## Mechanism : Halogenation of Alkanes

→ The halogenation of alkane is a three step process via Free Radical Formation.

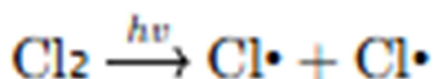
→ Free radicals are those substances that contain single unpaired electron.

→ These are the following three steps:

1. Chain Initiation
2. Chain Propagation
3. Chain Termination

### 1. Chain Initiation Step

➤ In chain initiation step chlorine molecule gets splitted by homolytic fission to form chlorine free radical



### 2. Chain Propagation Step

➤ Chain propagation is further divided into two steps:

**Step First :** In first step chlorine free radical attacks on  $\text{CH}_4$  to produce methyl free radical

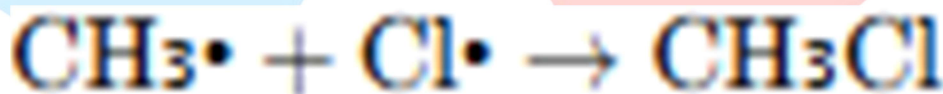


**Step Second :** In second step methyl free radical again attacks on chlorine molecule to form chlorine free radical and chloromethane



### 3. Chain Termination Step

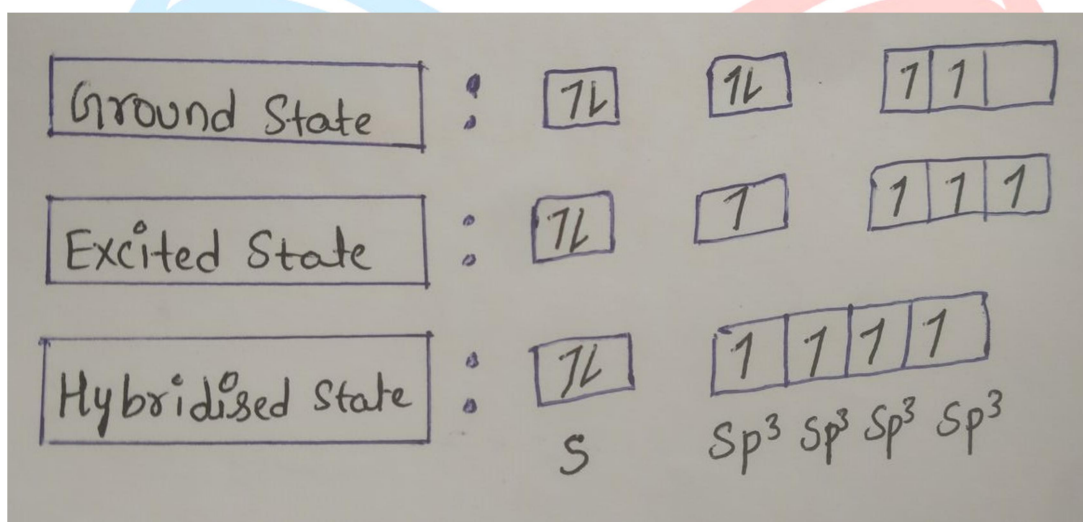
- In chain termination step all the free radicals combine or react with each other & no new free radical is forms which tends the reaction towards end.



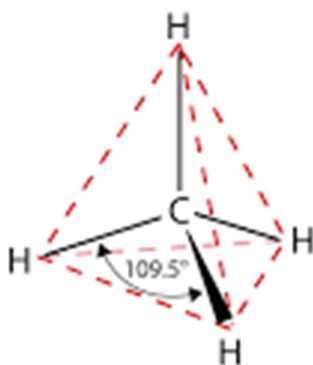
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## Sp<sup>3</sup> HYBRIDIZATION IN ALKANES

- All the carbons of alkanes show Sp<sup>3</sup> Hybridization.
- In Sp<sup>3</sup> hybridization one s orbital combines with three p orbitals to form four equivalent Sp<sup>3</sup> hybrid orbitals.
- Each Sp<sup>3</sup> hybrid orbital shows 25% s orbital characteristics and 75% p orbital characteristics.
- Example: Sp<sup>3</sup> hybridization of carbon in alkanes.



- The carbons of Alkanes show tetrahedral arrangement.
- The angle between two orbitals is 109.5°



# PARAFFINS

- Paraffins are nothing but simply the Alkanes
- The word "Paraffin" is derived from Latin:
  - *"Parum"* = *Little*
  - *"Affinis"* = *Affinity*
- Together meaning "Little Affinity" or Low Reactivity.
- This name reflects their chemical nature, as paraffins are relatively inert towards chemical reagents due to:
  - Presence of strong C-C and C-H sigma bonds
  - Lack of polar functional groups
  - No availability of free  $\pi$  electrons
- Hence, paraffins do not easily react with acids, bases, oxidizing agents, or reducing agents under normal conditions.
- They are non-polar, hydrophobic, and chemically stable, which makes them useful in various industries including fuel, pharmaceuticals, cosmetics, and agriculture.

## Uses of Paraffins

### ❖ Fuel for Engines:

- Paraffins are widely used as a fuel component in diesel and tractor engines due to their high energy content and clean combustion.

### ❖ Liquid Paraffin for Lamps:

- Liquid paraffin, a distilled and refined form of kerosene, is commonly used as a fuel in lamps, lanterns, and heating devices.

### ❖ Jet and Rocket Fuel:

- Certain paraffin-based fuels are used in jet engines and rockets for their high combustion efficiency.

### ❖ Medicinal Use:

- Liquid paraffin is a highly refined mineral oil with medicinal properties. It is widely used to:
  - Treat dry skin conditions (as a moisturizer).
  - Relieve constipation (as a mild laxative).

### ❖ Lubricant:

- Liquid paraffin is used as a lubricant in various industries, especially where non-reactive, smooth, and odorless oils are needed.

### ❖ Cooking Fuel:

- In some regions, paraffin oil is used as a cooking fuel due to its availability and affordability.

### ❖ Pharmaceutical Industry:

- Used in the production of penicillin and other antibiotics as part of fermentation processes.

### ❖ Cosmetic Industry:

- Widely used in the preparation of creams, lotions, petroleum jelly, lip balms, and skin ointments due to its moisturizing properties.

### ❖ Agricultural Use:

- Paraffin is used as an ingredient in many insecticides and pesticides, serving as a carrier or base material.



# Alkenes

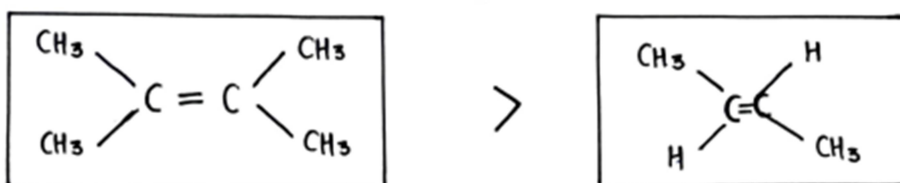
- Alkenes belongs to the class of hydrocarbons containing carbon-carbon double bond.
- Since they contain carbon- carbon double bonds, hence they are also known as Unsaturated Hydrocarbons.
- The general formula for alkenes =  $C_nH_{2n}$
- The first member or the smallest alkenes is Ethene ( $CH_2=CH_2$ ) also known as Ethylene.
- Alkenes are also known as Olefins.
- Example: Ethene, Propene, Butene etc.

## Stability of Alkenes

- Alkenes are less stable and more reactive compare to Alkanes.
- Different Alkenes show's different stability.
- Relative stability of alkenes depends on following factors:
  - Degree of substitution
  - On the basis of orientation
  - On the basis of conjugations

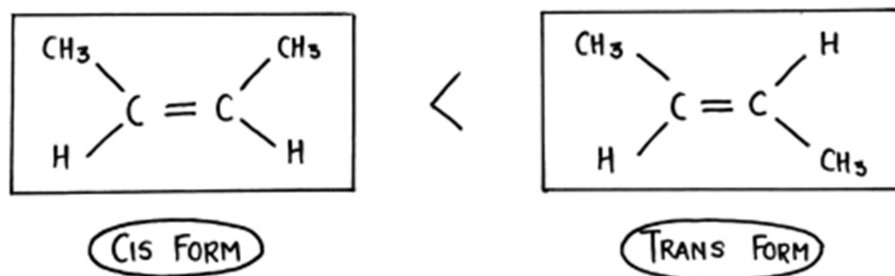
### 1. Degree of Substitution

- More the substituents (mainly alkyl group) attached to the double bonded carbon, more the stability of alkenes.



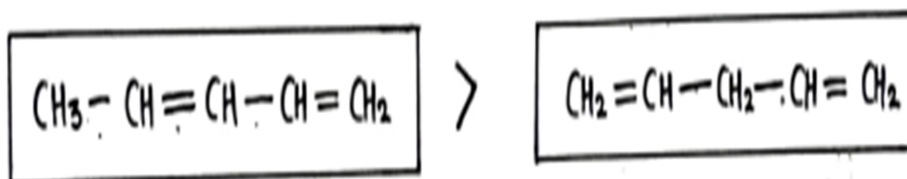
## 2. Orientation

→ Trans form of alkenes are more stable than cis form because trans form have opposite orientation of Alkyl groups on double bonded carbon atom.



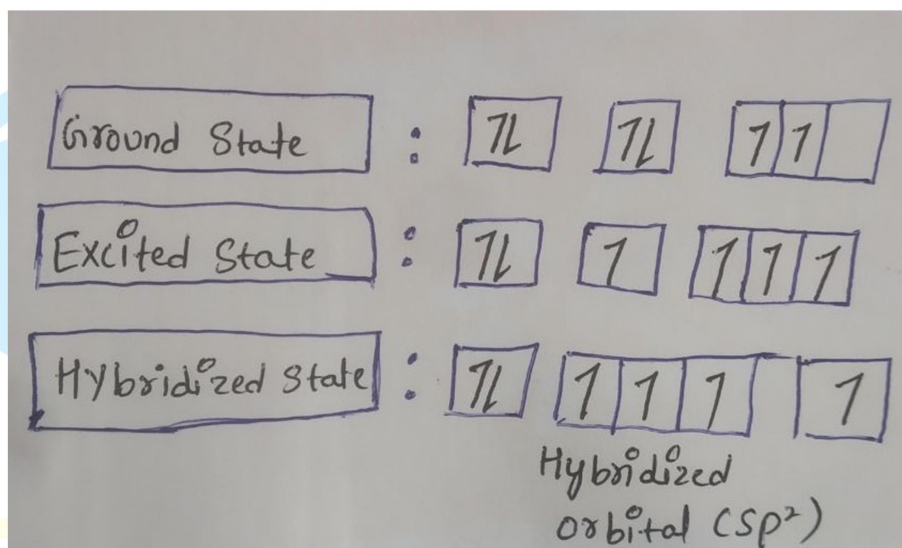
## 3. Conjugation

→ Conjugated alkenes are more stable than isolated alkenes

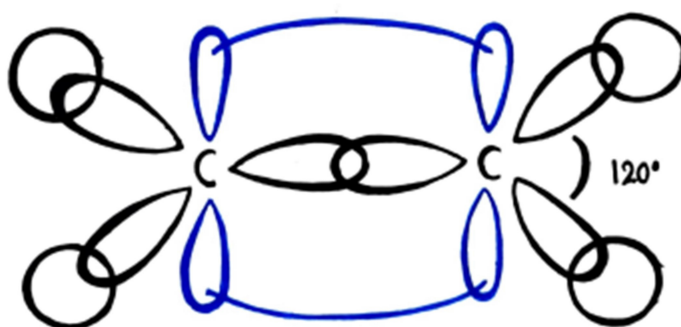


## sp<sup>2</sup> HYBRIDIZATION IN ALKENES

- When 1 s orbital combines with two p orbitals to form new hybrid orbitals of same size, shape and energy then this type of hybridization is known as sp<sup>2</sup> hybridization.
- The carbons of simplest alkene i.e. ethene shows sp<sup>2</sup> hybridization.



### Structure of Ethene



## Elimination Reaction

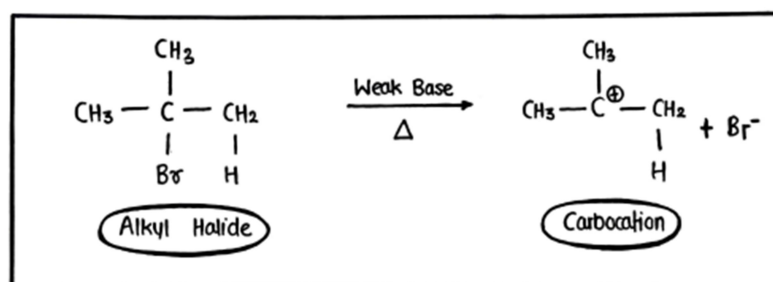
- An elimination reaction is an organic chemical reaction where two atoms or groups are removed from a molecule, forming a  $\pi$ -bond (usually a double bond). As a result, the degree of unsaturation in the molecule increases.
- There are two main types of elimination mechanisms:
  1. **E<sub>1</sub> Reaction** – *Elimination Unimolecular*
  2. **E<sub>2</sub> Reaction** – *Elimination Bimolecular*

### E<sub>1</sub> Reaction (Unimolecular Elimination Reaction)

- The E<sub>1</sub> reaction stands for Elimination Unimolecular Reaction. It is a type of elimination reaction where the reaction proceeds in two steps and involves the formation of a carbocation intermediate.
- This reaction follows first-order kinetics, meaning the rate of the reaction depends only on the concentration of the substrate, not the base.
- A weak base is sufficient to carry out E<sub>1</sub> reactions, and the reaction usually proceeds in the presence of a polar protic solvent such as water or alcohol.
- The reaction typically occurs at high temperature, which favors elimination over substitution.

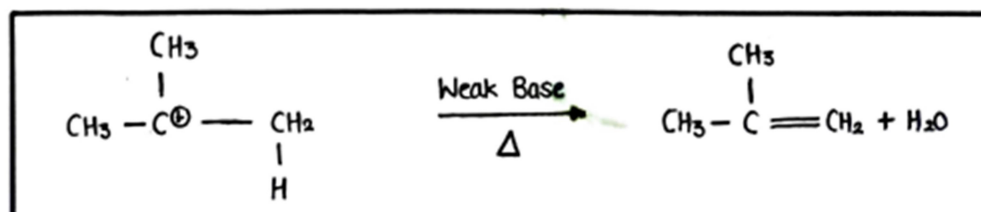
#### Step 1 :

Formation of Carbocation (Rate-Determining Step)



## Step 2 :

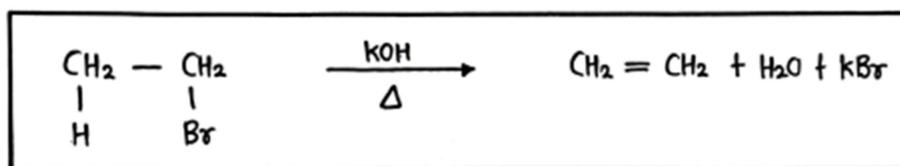
Loss of proton from the carbon atom adjacent to the carbon containing positive charge.



## E2 Reaction (Bimolecular Elimination Reaction)

- The E2 reaction stands for Elimination Bimolecular Reaction. It is a type of elimination reaction that occurs in a single concerted step, where the proton is removed and the leaving group leaves simultaneously, leading to the formation of a double bond (alkene).
- This reaction follows second-order kinetics, meaning the rate depends on both the substrate and the base:  
 $\text{Rate} = k [\text{substrate}][\text{base}]$
- A strong base is required to carry out E2 reactions, and the reaction generally takes place at a high temperature, which favors elimination over substitution.
- The reaction is generally endothermic because energy is required to break bonds and form a new  $\pi$ -bond.

## E2 Reaction Mechanism :



## E1 Versus E2 Reactions

Feature	E1 Reaction	E2 Reaction
<b>Full Form</b>	Elimination Unimolecular	Elimination Bimolecular
<b>Mechanism</b>	Two-step	One-step (concerted)
<b>Rate Law</b>	First-order: Rate = $k[\text{substrate}]$	Second-order: Rate = $k[\text{substrate}][\text{base}]$
<b>Intermediate</b>	Carbocation intermediate is formed	No intermediate (no carbocation)
<b>Base Required</b>	Weak base	Strong base
<b>Solvent</b>	Polar protic (e.g., water, ethanol)	Polar aprotic or protic
<b>Temperature</b>	High temperature required	High temperature required
<b>Substrate Preference</b>	Tertiary > Secondary >> Primary	Tertiary > Secondary > Primary
<b>Possibility of Rearrangement</b>	Possible (due to carbocation)	Not possible
<b>Stereochemistry</b>	No specific requirement	Requires anti-periplanar geometry
<b>Competes with</b>	SN1 reaction	SN2 reaction
<b>Major Product Orientation</b>	Saytzeff's product (more substituted alkene)	Saytzeff's product (unless bulky base used)
<b>Reaction Conditions</b>	Mild base, heat	Strong base, heat



## Factors Affecting E1 and E2 Reactions

### 1. Substrate (Alkyl Halide) Structure

- The nature of the carbon atom to which the leaving group is attached (primary, secondary, or tertiary) greatly affects the type of elimination reaction.
- **E1 Reaction:** Favors **tertiary** > **secondary** alkyl halides because **stable carbocations** are formed.
- **E2 Reaction:** Can occur with **primary, secondary, or tertiary** alkyl halides, but **tertiary** is most reactive due to stability and steric accessibility.

### 2. Base Strength

- The base is the species that abstracts the  $\beta$ -hydrogen during elimination. Its strength influences the reaction path.
- **E1 Reaction:** Requires a **weak base** (e.g.,  $\text{H}_2\text{O}$ ,  $\text{ROH}$ ), because the base is not involved in the rate-determining step.
- **E2 Reaction:** Requires a **strong base** (e.g.,  $\text{OH}^-$ ,  $\text{OR}^-$ ,  $\text{NH}_2^-$ ), as it must simultaneously remove a  $\beta$ -H during bond-breaking.

### 3. Leaving Group

- A leaving group is an atom or group that can depart from the molecule, taking along its bonding electrons.
- A **good leaving group** (like  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ ) stabilizes the transition state and speeds up both E1 and E2.
- In **E1**, since leaving group departure is the **rate-determining step**, it is **very crucial**.

#### 4. Solvent Type

- Solvents are the medium in which the reaction occurs and can influence ion stability and base strength.
- **E1 Reaction:** Favored in **polar protic solvents** (e.g., water, ethanol) because they **stabilize the carbocation** and the leaving group.
  - **E2 Reaction:** Favored in **polar aprotic solvents** (e.g., acetone, DMSO, DMF), which enhance the base strength and accelerate elimination.

#### 5. Temperature

- Temperature refers to the heat energy supplied to the system. It influences whether substitution or elimination predominates.
- Both **E1 and E2 reactions** are **endothermic** and are favored at **high temperatures**.
  - Higher temperature shifts the reaction toward **elimination** rather than substitution (SN<sub>1</sub>/SN<sub>2</sub>).

# Rearrangement of Carbocations

→ Carbocation rearrangement is a process where a less stable carbocation intermediate formed during a reaction reorganizes itself to become a more stable carbocation.

This happens through the migration of a hydride ion ( $\text{H}^-$ ) or an alkyl group from an adjacent carbon.

→ Carbocations are classified by their stability:

- **Tertiary ( $3^\circ$ ) > Secondary ( $2^\circ$ ) > Primary ( $1^\circ$ ) > Methyl**

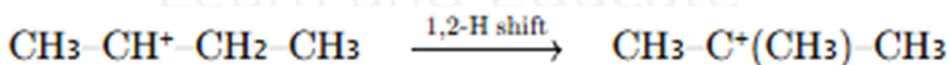
→ If a less stable carbocation is initially formed (like  $1^\circ$  or  $2^\circ$ ), it may rearrange to a more stable form (like  $3^\circ$ ) to lower its energy.

## Types of Rearrangement:

### 1. Hydride Shift (1,2-H Shift):

- A hydrogen atom (with its bonding pair of electrons) shifts from an adjacent carbon to the carbocation center.

**Example:**

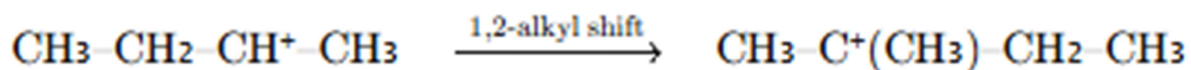


Here, a  $2^\circ$  carbocation rearranges to a  $3^\circ$  carbocation via a hydride shift.

### 2. Alkyl Shift (1,2-Alkyl Shift):

- An **alkyl group** (like  $\text{CH}_3$  or  $\text{CH}_2\text{CH}_3$ ) shifts from a neighboring carbon to the carbocation, along with its bonding electrons.

**Example:**

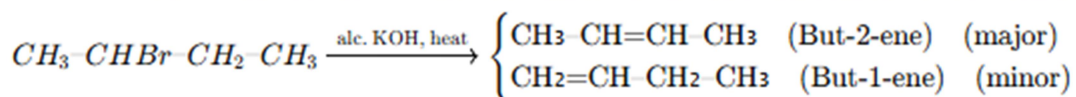


## Saytzeff's Rule (Zaitsev's Rule)

- Saytzeff's Rule, also spelled Zaitsev's Rule, states that:
- "In an elimination reaction, the major product is the more substituted alkene (the one with the greater number of alkyl groups attached to the double-bonded carbon atoms)."
- This orientation is followed in both E<sub>1</sub> and E<sub>2</sub> reactions under normal conditions (with a small, unhindered base).
- When elimination occurs, multiple alkenes can be formed depending on which β-hydrogen is removed.
- According to Saytzeff's rule, the hydrogen is eliminated from the β-carbon that has fewer hydrogen atoms and more alkyl groups, resulting in a more substituted and stable alkene.

Example:

**2-Bromobutane** undergoes elimination:



- But-2-ene is the Saytzeff product, formed in larger quantity because it is more substituted and more stable.

### Evidences Supporting Saytzeff's Rule

#### 1. Product Distribution in Elimination Reactions

- Reactions of secondary and tertiary alkyl halides show that the more substituted alkene predominates.
- For example, elimination of 2-bromo-2-methylbutane gives 2-methyl-2-butene as the major product.

## 2. *Thermodynamic Stability of Alkenes*

- Studies show that the heat of hydrogenation of more substituted alkenes is lower, proving they are more stable.
- More stable alkenes = more favored thermodynamic products.

## 3. *Isotopic Labeling Experiments*

- When  $\beta$ -hydrogens are isotopically labeled (e.g., deuterium), the preferred hydrogen is removed from the carbon with fewer H's, supporting the orientation.

## 4. *Computational and Spectroscopic Studies*

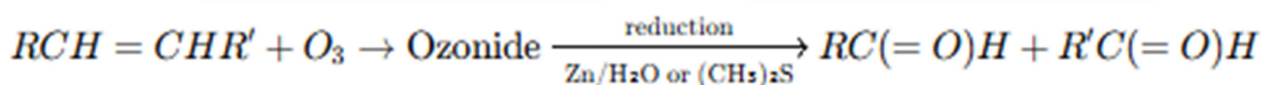
- Modern computational chemistry and NMR studies confirm that more substituted double bonds are lower in energy and thus thermodynamically favored.

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# Ozonolysis

- Ozonolysis is an organic reaction in which alkenes or alkynes react with ozone ( $O_3$ ) to form ozonides, which are then cleaved using a reducing or oxidative agent to give carbonyl compounds such as aldehydes, ketones, or carboxylic acids.
- It is a cleavage reaction used to break  $C=C$  double bonds and identify the structure of unknown alkenes.

## General Reaction:



## Types of Ozonolysis

### 1. Reductive Ozonolysis:

- Uses zinc and water ( $Zn/H_2O$ ) or dimethyl sulfide (DMS) as a reducing agent.
- Products: Aldehydes or ketones

### 2. Oxidative Ozonolysis:

- Uses oxidizing agents like  $H_2O_2$  or  $NaOH$ .
- Products: Carboxylic acids (aldehydes are further oxidized)

## Mechanism (Reductive Ozonolysis of Alkenes)

### 1. Step 1: Ozone Addition

- Ozone ( $O_3$ ) adds to the double bond of the alkene forming a **molozonide** intermediate (unstable).

### 2. Step 2: Molozonide Rearrangement

- Molozonide rearranges to form a **stable ozonide**.

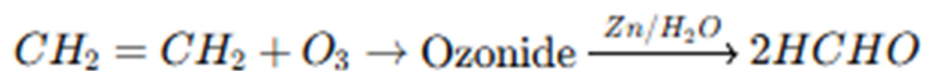
### 3. Step 3: Ozonide Cleavage



- Ozonide is cleaved with **Zn/H<sub>2</sub>O** or **(CH<sub>3</sub>)<sub>2</sub>S** to give **carbonyl compounds** (aldehydes/ketones).

### Examples of Ozonolysis

#### 1. Ethene



**Product : Formaldehyde**



# Electrophilic Addition Reactions of Alkenes

- An electrophilic addition reaction is a type of organic reaction in which an electrophile (electron-deficient species) adds to the carbon-carbon double bond of an alkene, resulting in the formation of a saturated product.
- Alkenes are rich in  $\pi$ -electrons, so they readily react with electrophiles.

## General Reaction



Where:

- $E^+$  = Electrophile
- $Nu^-$  = Nucleophile (usually added in the second step)

## Mechanism of Electrophilic Addition (Two-Step Process)

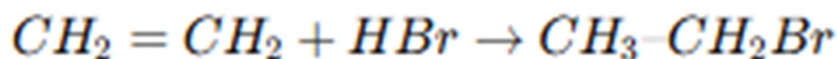
### 1 Attack of the Electrophile ( $E^+$ ):

- The  **$\pi$ -electrons** of the double bond attack the electrophile.
- This forms a **carbocation intermediate**.

### 2 Nucleophilic Attack:

- The **nucleophile** ( $Nu^-$ ) attacks the carbocation.
- This gives the final **addition product**.

Example 1: Addition of HBr to Ethene



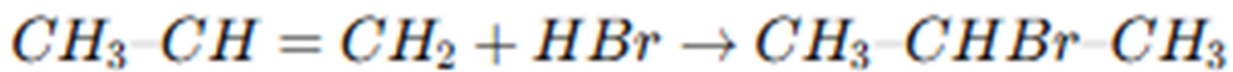
## Mechanism:

- Step 1: Double bond attacks  $H^+$  → carbocation is formed.
- Step 2:  $Br^-$  attacks the carbocation → product formed.

## Markovnikov's Orientation (Markovnikov's Rule)

- "When a protic acid (HX) is added to an unsymmetrical alkene, the hydrogen ( $H^+$ ) atom attaches to the carbon that already has more hydrogen atoms, and the halide ( $X^-$ ) goes to the carbon with fewer hydrogen atoms."
- This rule helps predict which product will be major when adding HX,  $H_2O$ , or alcohol to alkenes.

General Example



In this case

- The  $H^+$  adds to  $CH_2$  (which has more H's)
- The  $Br^-$  adds to  $CH$  (which has fewer H's)

**Product : 2-bromopropane (major product)**

Mechanism Behind Markovnikov's Rule (Electrophilic Addition)

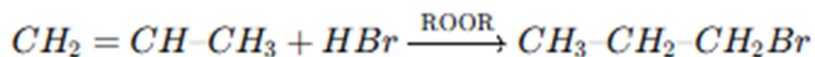
- Step 1: Electrophilic attack ( $H^+$ )**
  - The  **$\pi$ -electrons of the double bond** attack the  $H^+$ .
  - A **carbocation** intermediate is formed on the more substituted carbon (more stable).
- Step 2: Nucleophile attack ( $X^-$ )**
  - The **halide ion ( $Br^-$  or  $Cl^-$ )** attacks the carbocation, giving the final product.

The **more stable carbocation** forms, leading to the **Markovnikov product**.

## Anti-Markovnikov's Orientation

- "In certain addition reactions to unsymmetrical alkenes, the hydrogen ( $H^+$ ) atom adds to the carbon atom with fewer hydrogen atoms, and the other group (such as halide or OH) attaches to the carbon with more hydrogen atoms."
- This rule is opposite to Markovnikov's Rule and is observed in free radical addition reactions, especially in the presence of peroxides.
- It typically occurs during the addition of HBr to alkenes in the presence of peroxides (ROOR). This reaction proceeds via a free radical mechanism, not a carbocation mechanism.
- Anti-Markovnikov orientation is seen only in the presence of peroxides and only with HBr, not with HCl or HI.

### General Reaction



Here

- The **Br** adds to the **less substituted carbon** ( $CH_2$ )
- The **H** adds to the **more substituted carbon** ( $CH$ )

**Product : 1-bromopropane** (Anti-Markovnikov product)

### Mechanism: Free Radical Addition (Peroxide Effect)

#### Step 1: Initiation

- Peroxides ( $RO-OR$ ) break down into free radicals under heat/light:



- $RO\cdot$  reacts with  $HBr \rightarrow Br\cdot$  radical is formed.

#### Step 2: Propagation

1.  $\text{Br}^\bullet$  attacks alkene to form the most stable free radical intermediate (adds Br to less substituted carbon).
2. The free radical abstracts H from another HBr molecule  $\rightarrow$  gives the final Anti-Markovnikov product and regenerates  $\text{Br}^\bullet$ .

### Step 3: Termination

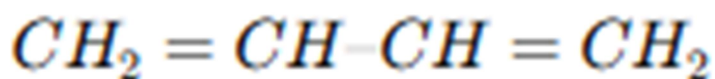
- Radicals combine and stop the chain.



# Conjugated Dienes

- A diene is an organic compound that contains two double bonds (C=C) in its carbon chain.
- A conjugated diene is a specific type of diene in which the two double bonds are separated by one single bond (C=C-C=C).
- The  $\pi$ -electrons in conjugated dienes are delocalized over four carbon atoms, which increases their stability and reactivity.

General Formula



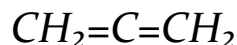
Example : 1,3-Butadiene

Types of Dienes

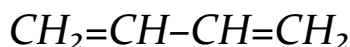
1. **Isolated Dienes** – Double bonds separated by two or more single bonds



2. **Cumulated Dienes (Allenenes)** – Double bonds share a common carbon



3. **Conjugated Dienes** – Double bonds separated by one single bond



Uses of Conjugated Dienes

- Raw material for synthetic rubber (e.g., tires)
- Used in the Diels–Alder synthesis of cyclic compounds
- Intermediate in manufacturing of pharmaceuticals and plastics

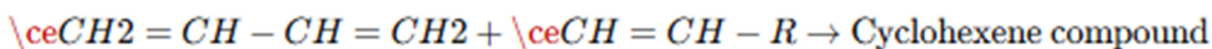


# Diels–Alder Reaction

- The Diels–Alder reaction is a [4+2] cycloaddition reaction between a conjugated diene and a dienophile (an alkene or alkyne) to form a six-membered cyclic compound.
- It is a concerted reaction (occurs in one step without intermediates) and is widely used in the synthesis of cyclic organic compounds.
- The reaction was given by Otto Paul Hermann Diels and Kurt Alder.
- They also awarded with Nobel Prize in 1950 for their discovery.
- The Diels–Alder reaction is an organic chemical reaction between a conjugated diene and an Alkene to form Cyclohexene.

## General Reaction

Conjugated Diene + Dienophile → Cyclohexene derivative



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## Mechanism of Diel's Alder Reaction

- Diel's Alder reaction is a single step process.
- Electrons from the dienophile attacks on Carbon (C) 1 on the diene resulting in the formation of single bond between C1 & C6
- Double bond between C1 & C2 relocates to between C2 & C3
- Double bond between 3 & 4 broken e electrons form a single bond between 4 and 5 to form our final product.
- Finally Cyclohexene forms.

