2. **Formation of Alkyl Hydrogen Sulphate (Addition Reaction)**

Condition: Cold conc. H_2SO_4 (0–20 °C)

Reaction: $CH_3CH_2CH_2OH + H_2SO_4 \longrightarrow CH_3CH_2CH_2OSO_3H + H_2O$ (Propyl hydrogen sulphate)

3. **Oxidation:**

In presence of oxidizing agents like $K_2Cr_2O_7/H_2SO_4$, propanol is oxidized:

Primary alcohol → Aldehyde → Carboxylic acid

$$CH_3CH_2CH_2OH \xrightarrow{[O]} CH_3CH_2CHO \xrightarrow{[O]} CH_3CH_2COOH$$

Propanal (aldehyde), propanoic acid

b) Name the following alkenes

i) $CH_3C(CH_3)=CH-CH_3$ ii) $CH_2=CHCH(CH_3)_2$

Ans:

$CH_3-C(CH_3)=CH-CH_3$ — 2-methyl-2-butene

$CH_2=CH-CH(CH_3)-CH_3$ — 3-methyl-1-butene

c) Draw the structural formulas of the following alkenes.

i) 3-Methyl-2-butene

Ans: Correction: 2-Methyl-2-butene is the right structure.

$$CH_3-C(CH_3)=CH-CH_3$$

2-methyl-2-butene

ii) 2-Methyl-4-ethyl-2-pentene

Ans. (This is not correct). It may be **2, 4-dimethyl-2-hexene.**

$$\overset{1}{H_3C}-\overset{2}{C}(CH_3)=\overset{3}{CH}-\overset{4}{CH}(CH_3)-\overset{5}{CH_2}-\overset{6}{CH_3}$$

2, 4-dimethyl-2-hexene

d) Give the dehydrohalogenation reaction of bromopropane?

Ans. $CH_3-CH_2-CH_2-Br + KOH_{(alcoholic)} \xrightarrow{Heat} CH_3-CH=CH_2 + KBr + H_2O$ (Propene)

e) Can propanol undergo dehydration? If yes give reactions involving dehydration.

Ans. Yes, $CH_3-CH_2-CH_2-OH \xrightarrow[140-170°C]{75\% H_2SO_4} CH_3-CH=CH_2 + H_2O$

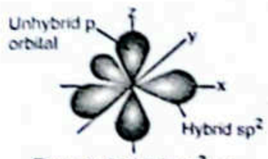
STRUCTURE AND REACTIVITY OF ALKENES

Structure of Alkenes

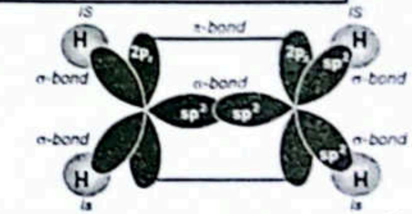
- Ethene (C_2H_4) is the simplest alkene. Each carbon atom in ethene is **sp^2 hybridized** and forms three equivalent sp^2 hybrid orbitals which lie in the same plane. The unhybrid p orbital lies perpendicular (90°) to the plane of hybrid orbitals (as shown in Figure).
- These sp^2 orbitals are formed by mixing of the 2s orbital with two 2p orbitals leaving one unhybrid p orbital. In ethene, each carbon uses two sp^2 orbitals to form two C – H bonds each. The remaining sp^2 orbital on each carbon is used to form a carbon-carbon σ bond by linear overlap as in Figure.
- The unhybrid p-orbitals of each carbon atom which are parallel to each other overlap laterally to form another carbon-carbon bond. This bond formed by the lateral overlap of p-orbitals is called a π bond.

Interesting Information!

Plants produce ethene as a natural ripening hormone. For efficiency harvesting and transportation to market, fruits and vegetables are often picked unripe and exposed to ethene so they could ripen in short time.



The set of orbitals sp² + p



- The two carbon atoms forming a double bond and the four atoms attached directly to them lie in the same plane. The remaining p-orbital on each carbon is used to form the π bond.
- The sp^2 hybridization results in a trigonal planar arrangement around each carbon atom. The bond angles are approximately 120°, leading to a planar molecule as shown in Figure.

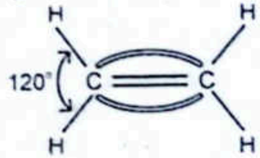


Figure: Structure of ethene

Reactivity of π bond

Comparison of Reactivity of Alkanes and Alkenes: Alkenes are more reactive than alkanes due to the presence of the double bond. The probability of finding electron is away from the line joining the two nuclei. Due to this reason π-electrons are less firmly held between the nuclei. A π bond is, therefore, a weak bond as compared to a σ-bond. During a reaction it breaks comparatively easily rendering alkenes as reactive group of compounds. Moreover, the loosely held π-electrons are more exposed to attack by the electrophilic reagents. Alkenes, therefore, undergo electrophilic addition reactions very easily.

Rack Your Mind!

3. Differentiate between electrophiles and nucleophiles.

Did You Know?

Electrophile is a species that can act as electron pair acceptor, it is represented by E^+. Alkenes act as nucleophile because they contains pi electrons. **Nucleophile** is a species that can act as a donor of a pair of electrons, it is represented by Nu^{-}.

Rack Your Mind!

4. Which of the following is not a nucleophile?

(A) H_2O (B) H_2S
(C) BF_3 (D) NH_3

QUICK CHECK 11.5

a) How does an alkane differ from an alkene in stability?

Ans. Alkanes are more stable than alkenes because:

- Alkanes have only single bonds ($σ^-$ bonds), which are stronger and less reactive.
- Alkenes contain a double bond ($σ^+$ π bond), the π bond is weaker and more reactive, making alkenes less stable.

b) Which of the following species is likely to act as a nucleophile? Why?

i) H_2 **ii) H^+** **iii) OH^-**

Ans. iii) OH^-

Explanation:

Nucleophile:

A nucleophile is a species that donates a pair of electrons to form a bond.

OH^- has a lone pair and a negative charge and is a strong nucleophile

c) Which of the following species is likely to act as an electrophile?

i) H_2 ii) H^+ iii) OH^-

Ans. ii) H^+

Explanation:

Electrophiles are electron-deficient species that "accept electrons" (Lewis acids).

H^+ has an empty 1s orbital and strongly attracts electrons.

The reactions of alkenes mostly proceed through the formation of carbocations. Therefore, before studying the addition reactions of alkenes, the concept of carbocations and their stability is very important.

Carbocation Stability and Inductive Effect of Alkyl Group

Carbocation is an alkyl group with a single positive charge on one of its carbon atoms.

Classification: Carbocations are classified into following types.

i. **Methyl Carbocation:** Carbocation which is bonded to H only is named as methyl carbocation.

ii. **Primary 1° Carbocation:** If carbocation is bonded to one C or alkyl substituent then it is named as primary 1° carbocation.

iii. **Secondary 2° Carbocation: If it is bonded to 2 carbons** (alkyl substituent) directly, then it is named as secondary 2° carbocation.

iv. **Tertiary 3° Carbocation:** It is named as tertiary 3° carbocation if it is directly bonded to 3 carbons (alkyl substituent).

Role of Inductive Effect:

The inductive effect of alkyl groups plays an important role in the stability of carbocation. The polarization of a σ bond due to electron withdrawing or electron donating effect of adjacent groups or atoms is referred to as inductive effect.

Electron Donating Inductive Effect: Alkyl groups have a slightly electron donating inductive effect. Electron donating species, are said to have **positive inductive effect (+I),** whereas electron withdrawing species, such as a halogen atom, have a negative inductive effect (–I).

The alkyl groups attached to the positively charged carbon atoms are electron donating groups. Due to the positive charge on the carbon atom, carbocation is electrophile. The inductive effect is shown by the arrowheads on the bonds to show the alkyl groups pushing electrons towards the positively charged carbon.

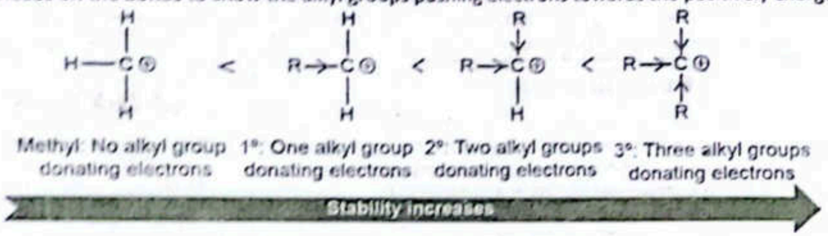


Figure: Inductive effect & stability of carbocation

As a result of this, the carbocation become less positively charged which makes it energetically more stable. The stability of carbocation ions increases with a number of alkyl groups due to their +I effect. This means that tertiary carbocation is the most stable as they have three electron-donating alkyl groups which energetically stabilize the carbocation Figure.

Electron withdrawing Inductive Effect

Electron withdrawing groups, such as a halogen atom, have a negative inductive effect (–I). Halogen withdraws bonded electrons from carbon to carbon bond and thus displays negative inductive effect. This causes a permanent dipole to arise in the molecule wherein the halogen atom holds a negative charge and carbon become partial positive Figure.

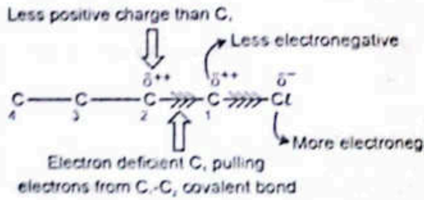


Figure: Inductive effect: Polarization of sigma bond

REACTIONS OF ALKENES

Alkenes are unsaturated hydrcarbons and they undergo electrophilic addition reactions mostly. Other minor types of reactions include oxidation, combustion and polymerization reactions.

Electrophilic Addition Reactions

The reactions in which an electrophile is added to the double bond of an alkene is called electrophilic addition reaction.

Mechanism of Electrophilic Addition in Alkenes

The C = C in alkenes is a region of high electron density making susceptible to attack by electrophiles. Alkenes reacts with an electrophile to give a carbocation intermediate that then reacts with a nucleophile. In the generalized mechanism Figure, X^+ represents an electrophile and Y^- represents a nucleophile.

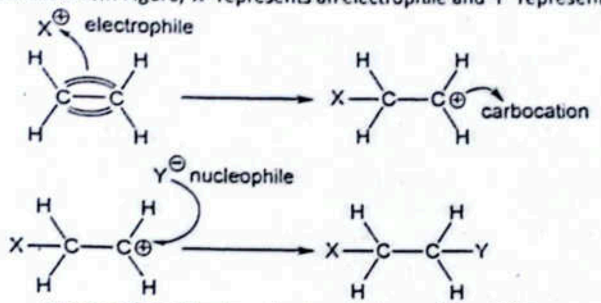


Figure: Generalized mechanism of electrophilic addition

QUICK CHECK 11.6

a) **How do alkenes react with an electrophile?**

Ans. Alkenes react with electrophiles through electrophilic addition. The general steps are:

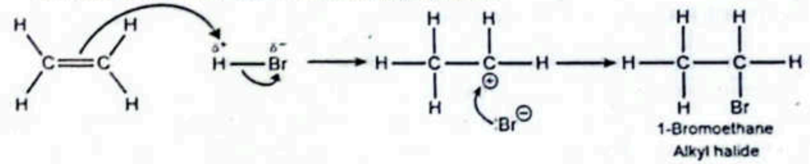
1. **Attack by π-electrons:** The alkene's π-electrons attack the electrophile (E^+), forming a carbocation intermediate.
2. **Nucleophilic attack:** A nucleophile (Nu^-) attacks the carbocation, forming the final product.

Example with HBr:

- **Step 1:** π-electrons attack H^+, forming a carbocation.
- **Step 2:** Br^- attacks the carbocation, yielding a bromoalkane.

Key Points:

- Follows Markovnikov's rule (H adds to the less substituted carbon).
- Carbocation stability determines the major product.



b) **Why the order of stability of carbocation is 3° > 2° > 1°?**

Ans. The stability of carbocations follows **3° > 2° > 1°** due to:

1. **Hyperconjugation** – More alkyl groups donate electron density via σ bonds, stabilizing the positive charge.
2. **Inductive Effect** – Alkyl groups are electron-donating (+I effect), dispersing the positive charge.
3. **Resonance (if applicable)** – Delocalization further stabilizes the carbocation.

3° carbocations have the most alkyl groups, providing maximum stabilization, while **1°** has the least.

In this chapter, only the mechanism of halogen addition and hydrogen halide addition will be learnt.

1. Halogenation

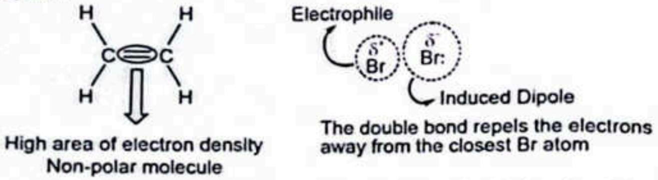
Halogenation means addition of halogens like chlorine or bromine. When bromine water (a solution of bromine in water having red-brown colour) is added to ethene in an inert solvent like carbon tetrachloride, its reddish brown colour is discharged at once. This reaction is used to identify the unsaturation of an organic compound.

$$CH_2=CH_2+Br_2 \xrightarrow{CCl_4} Br-CH_2-CH_2-Br$$

Mechanism:

The above reaction proceeds through a three-steps mechanism as given below:

i) Bromine (Br_2) is a non-polar molecule, however, when a bromine molecule gets closer to the double bond of an alkene, the high electron density in the double bond repels the electron pair in Br – Br away from the Br atom. As a result of this, the Br atom closest to the double bond is slightly positive and acts as an electrophile.



ii) The δ^+ bromine of Br_2 is attacked by the π electrons in the double bond and the partial positive bromine accepts a pair of electrons from the C = C bond in the alkene. This results in the formation of a highly reactive carbocation intermediate.

iii) This carbocation intermediate reacts with the Br^- (nucleophile) to make the product. Mechanism is shown below Figure.

Mechanism:

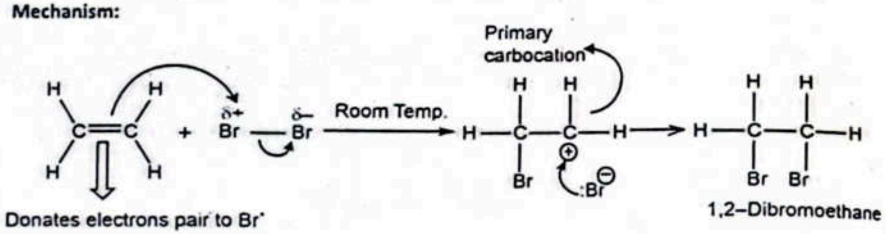


Figure: Electrophilic addition mechanism of ethene and Br_2

2. Hydrohalogenation

When an alkene reacts with dry gaseous hydrogen halide at room temperature, the product is a halogenoalkane.

$$\underset{\text{Ethene}}{CH_2=CH_2}+HBr \longrightarrow \underset{\text{Bromoethane}}{CH_3-CH_2-Br}$$

Hydrogen halides are among the simplest examples of polar substances having permanent dipoles that add to alkenes Figure 11.15. All hydrogen halides (HBr, HCl, HI, HF) give this reaction and add across C = C exactly the same way. But, the rate of reaction increases from HF to HI. The actual product formed depends upon whether the alkene is symmetrical or unsymmetrical.

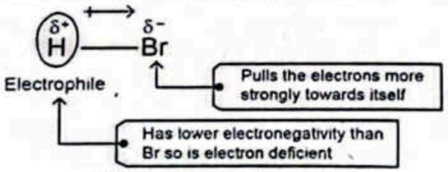


Figure: HBr molecule polarity

(Exercise L.Q.6)

Q. Describe the mechanism of electrophilic addition of hydrogen halides to alkenes. Discuss Markovnikov's Rule in the context of hydrogen halide addition.

i) **Addition to Symmetrical Alkenes:** When the alkene (e.g. ethene) is symmetrical only one product is theoretically possible. Let us look at the mechanism of addition of HBr to ethene.

Mechanism:

i. Nucleophilic pi-bond attacks the hydrogen in hydrogen halide. Hydrogen bromide gives a bromide ion (Br^-). Ethene is converted to carbocation by adding hydrogen to one of the double bonded carbons.

ii. The bromide ion (nucleophile) attacks the carbocation to give the addition product Figure.

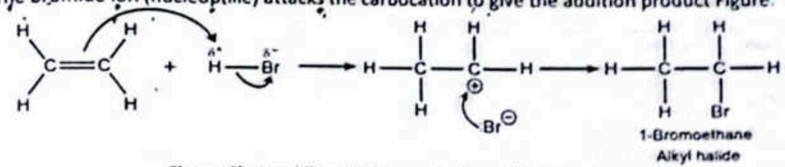


Figure: Electrophilic addition mechanism of HBr to ethene

ii) **Addition to Unsymmetrical Alkenes:** When the alkene is unsymmetrical, two products are theoretically possible. For example, the addition of HBr to propene can give two products. But experimentally, it has been found that under these conditions, the major product is 2-bromopropane and the minor product is 1-bromopropane.

Markovnikov's Rule:

Markovnikov's Rule is applicable for addition reactions in alkenes. According to this rule, "When a polar reagent adds to an unsymmetrical alkene, the negative part of the reagent attach to the double bonded carbon which bears the lesser number of hydrogen."

Mechanism:

Propene reacts with HBr in two ways. The mechanism of this reaction involves the following steps.

i. The pi electrons of C = C attacks on partial positive end of H – Br. Hydrogen bromide breaks heterolytically creating bromide ion (electrophile) and hydrogen is added to double bonded carbon with more number of hydrogen, creating a 2° carbocation.

ii. The bromide ion attacks the secondary carbocation to give the major product. The minor product is formed by the attack on primary carbocation Figure.

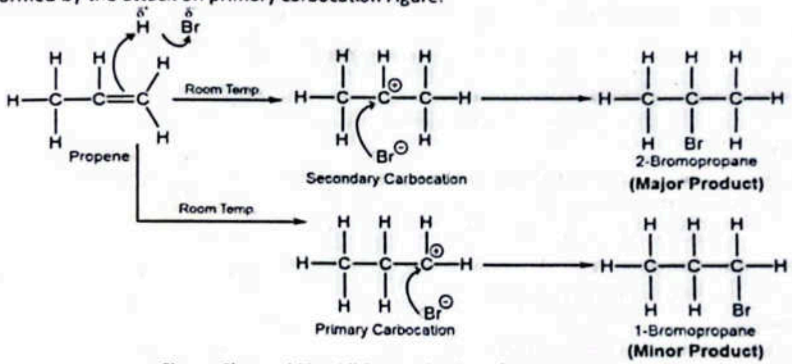


Figure: Electrophilic addition mechanism of HBr to propene

QUICK CHECK 11.7

a) Compare and explain the relative rates of addition to alkenes (reactivities) of HCl, HBr and HI

Ans. Order of Halogen Acid:

The reactivity order for addition of hydrogen halides to alkenes is:

HI ⟩ HBr ⟩ HCl

Explanation:

1. **Bond Strength** – The H-X bond strength decreases down the group (HCl > HBr > HI), making HI the easiest to break (fastest reaction).
2. **Electrophilicity** – **Iodine (I)** is less electronegative than Br or Cl, so HI is a better proton (H^+) donor, increasing its reactivity.
3. **Carbocation Stability** – The larger halide (I^-) stabilizes the intermediate carbocation better via polarizability, speeding up the reaction.

b) Explain the difference between an addition reaction and an elimination reaction?

Ans.

Feature	Addition Reaction	Elimination Reaction
Definition	Two molecules combine to form a single product.	A molecule splits into two or more products.
Substrate	Usually alkenes/alkynes (π bonds).	Usually alkyl halides/alcohols (sp^3 C–X).
Mechanism	Electrophilic/nucleophilic addition.	E1, E2 (unimolecular/bimolecular).
Bond Changes	π bond breaks; new σ bonds form.	σ bond breaks; new π bond forms.
Reagents	HX, X_2, H_2O (electrophiles/nucleophiles).	Base (OH^-, RO^-) + heat (for E2/E1).
Example	$C=C + HBr \rightarrow C-C-Br$	$R-CH_2-CH_2-Br \rightarrow C=C + HBr$
Product	Saturated (alkane) or functionalized molecule.	Unsaturated (alkene/alkyne) or smaller molecule.

c) How alkene react with an electrophile?

Ans. See Mechanism of Halogenation of Alkenes (a)

d) Explain how Markovnikov's rule is applied in addition of HBr to 2-pentene.

Ans.

$$H_3C-CH_2-CH_2-CH=CH_2 + H-Br \longrightarrow CH_3-CH_2-CH_2-\underset{|}{\overset{Br}{CH}}-CH_3$$

2-Bromopentane

3. Hydrogenation

Hydrogenation means addition of molecular hydrogen to an alkene in the presence of a catalyst (Ni/Pt) to form a saturated compound at 250 – 300°C.

$$H_2C=CH_2 + H_2 \xrightarrow[250-300^\circ C]{Ni} H_3C-CH_3$$

On industrial scale, this reaction is used to convert vegetable oil into margarine (Banaspati ghes).

$$Oil + H_2 \xrightarrow{Ni} \text{Margarine (Banaspati ghee)}$$

4. Hydration

Gaseous alkenes react with steam at high temperature and pressure in the presence of concentrated acid (H_2SO_4) as the catalyst to form alcohols.

$$H_2C=CH_2 + H_2O \xrightarrow{H_2SO_4} C_2H_5OH$$

Similar to hydrohalogenation, the alkene forms a carbocation intermediate, which is then attacked by OH^-.

5. Halohydration

Halohydration is a reaction where an alkene reacts with a halogen (such as bromine or chlorine) in the presence of water to form a halohydrin. For ethene (C_2H_4), the reaction specifically produces a bromohydrin or chlorohydrin, depending on the halogen used.

$$H_2C=CH_2 + Br_2 + H_2O \longrightarrow \underset{OH}{H_2C}-\underset{Br}{CH_2}$$

2-Bromoethanol

Rack Your Mind!

5. Write down the reaction of $H_2C=CH_2$ with HOCl.

Rack Your Mind!

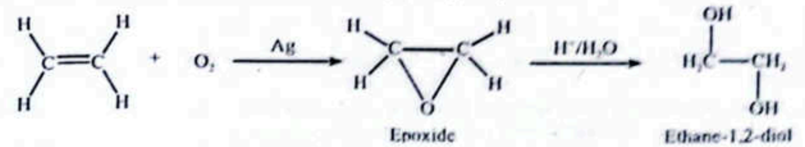
6. Write down the reaction of $CH_3-CH=CH_2$ with HOCl.

6. Epoxidation

The epoxidation of alkenes gives an oxygen-containing three-membered cyclic ether called epoxide. In the case of ethene (C_2H_4), this reaction can be accomplished using various oxidizing agents.

Catalyst: Ethene can also be converted to ethylene oxide using molecular oxygen and metal catalysts. A transition metal catalyst facilitates the reaction, forming an epoxide directly from the alkene.

Use: The epoxides can be converted in to diols by acid hydrolysis.



7. Ozonolysis

Ozonolysis is a method of oxidatively cleaving alkenes using ozone (O_3), a reactive allotrope of oxygen. Alkenes react with ozone (O_3) to form ozonides, which can be further reduced to carbonyl compounds (aldehydes or ketones), and ultimately to alcohols.

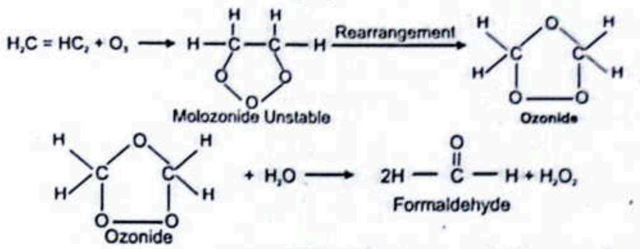
> Ozonolysis is used to detect the position and number of multiple bonds and structure of compounds.

Use: Ozonolysis is often used to identify the structure of unknown alkenes by breaking them down into smaller, more easily identifiable pieces.

Examples:

(i) Ozonolysis of Ethene: $C_2H_4 + O_3 \longrightarrow C_2H_4O_3 \longrightarrow 2CH_2O$

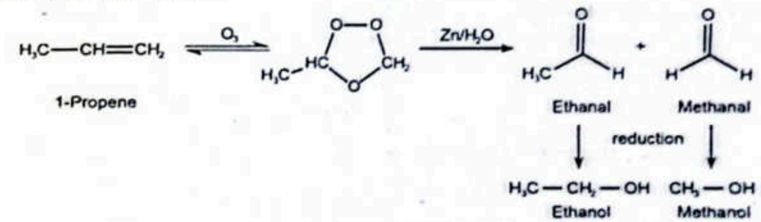
(OR)



$$H_3C-HC=CH_2 + O_3 \xrightarrow{Zn-H_2O} CH_3-\overset{O}{\overset{||}{C}}-H + H-\overset{O}{\overset{||}{C}}-H$$

Acetaldehyde Formaldehyde

(ii) Ozonolysis of Propene:



QUICK CHECK 11.8

a) Write the equation for the ozonolysis of ethene.

Ans. See Above Point 7 Ozonolysis.

b) Give the epoxidation reaction of 2-Butene.

Ans.

$$CH_3-CH=CH-CH_3+\frac{1}{2}O_2\xrightarrow[300^{\circ}C]{Ag_2O}CH_3-\underset{\diagdown O \diagup}{CH-CH}-CH_3$$

c) How ozonolysis can indicate the position of a double bond in an alkene? Explain with the help of an example.

Ans. Position of double bond will affect the type of carbonyl compounds. e.g., if a double bond is at the end of alkene chain aldehyde will be formed. e.g., Ozonolysis of 1-butene.

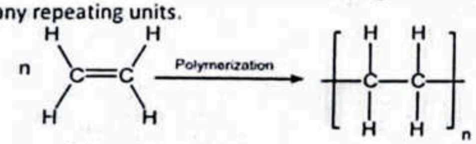
$$CH_3-CH_2-CH=CH_2+O_3\xrightarrow{Zn/H_2O}CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H+H-\overset{O}{\overset{\|}{C}}-H$$

8. **Polymerization**

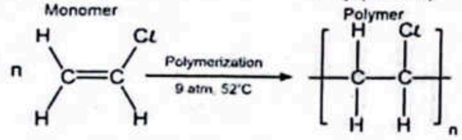
Polymerization is the formation of extremely long molecules (polymers) from small reactive molecules that join together (monomers). Addition polymerization is one of the most important addition reactions of alkenes which form the basis of the plastics industry.

Addition polymerization is the reaction in which many monomers containing at least one C = C double bond form long chains of polymers as the only product.

Just like in other addition reactions of alkenes, the π-bond in each C–C bond breaks and then the monomers link together to form new C–C single bonds. A polymer is a long-chain molecule that is made up of many repeating units.



Ethene Monomer — Poly (ethene) Polymer



Chloroethene (Vinyl Chloride) Monomer — Poly(chloroethene) (PVC) Polymer

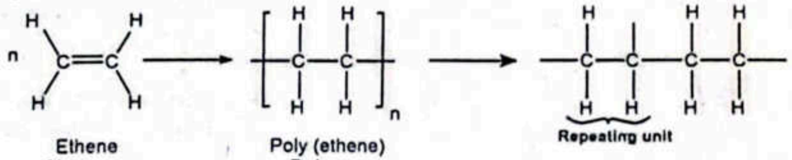
Interesting Information!

Alkenes, like ethene and propene, are used to create plastics through polymerization. Ethene, for instance, is polymerized to make polyethylene, one of the world's most common plastics used in bags, bottles, and packaging.

This ball pen is made of PVC

➢ Deducing Repeating Units

- A repeating unit is the smallest group of atoms that when connected one after the other make up the polymer chain. It is represented by square brackets in the displayed and general formula.
- In poly(alkenes) (such as poly(ethene)) and substituted poly(alkenes) (such as PVC) made of one type of monomer, the repeating unit is the same as the monomer except that the C – C double bond is changed to a C – C single bond.



Ethene Monomer — Poly (ethene) Polymer

QUICK CHECK 11.9

a) Ethene is a monomer used in the polymerization process to create polyethylene.

(i) Discuss how the chemical structure of ethene makes it suitable for polymerization.

Ans. See Above Topic Polymerization of Alkenes (Point 8).

(ii) Discuss the change in hybridization and bond angle during this reaction.

Ans.

Property	Ethene (Monomer)	Polyethylene (Polymer)
Hybridization (Carbon)	sp^2	sp^3
Geometry	Trigonal planar	Tetrahedral
Bond angle	120°	109.5°
Bonding	C = C double bond	C – C single bonds

b) Explain why an addition reaction increases the saturation of a molecule.

Ans. An addition reaction increases the saturation of a molecule because it involves the conversion of multiple bonds (double or triple bonds) into single bonds, allowing more atoms (typically hydrogen or halogens) to attach to the carbon atoms.

Example: Ethene + Hydrogen → Ethane

$$CH_2=CH_2+H_2\rightarrow CH_3-CH_3$$

CONJUGATED DIENES

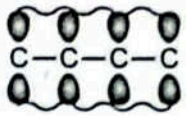
As the name indicates, a diene is a molecule containing two double bonds between carbon atoms. In a conjugated diene, the double bonds in the carbon chain are separated by a single bond. The adjacent double bonds in conjugated dienes allow for the overlap of p-orbitals on three or more adjacent atoms. This overlap leads to a delocalization of electrons, which can stabilize the molecule and affect its reactivity. In conjugated dienes pi-bond overlap extends over the entire system.

$$CH_2=CH-CH=CH_2$$

But-1,3-diene

$$CH_2=\underset{}{\overset{CH_3}{\overset{|}{C}}}-CH=CH_2$$

2-Methylbut-1,3-diene (Isoprene)



Delocalization of pi electrons

➢ **Significance:**

Conjugated alkenes are an important class of compounds in organic chemistry, featuring unique properties due to the arrangement of their double bonds. Conjugated dienes like 1,3-butadiene are used in the production of synthetic rubber. The conjugated structure allows for polymerization, leading to long chains that exhibit rubber-like properties.

QUICK CHECK 11.10

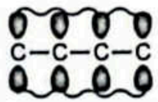
a) Draw the structure of simple conjugated dienes such as Penta-1, 3-diene.

Ans. $H_3C-CH=CH-CH=CH_2$

Pent-1,3-diene

b) Illustrate the delocalization of electrons in conjugated dienes.

Ans.



Delocalization of pi electrons

ISOMERISM

The concept of isomerism is an important feature of organic compounds.

Definition: Two or more compounds having the same molecular formula but different structural formulas and properties are said to be isomers and the phenomenon is called isomerism.

- The structural formula of a compound shows the arrangement of atoms and bonds present in it.
- The simplest hydrocarbon to have structural isomers is butane (C_4H_{10}). If we study the structural formula of butane or other higher hydrocarbons of the alkane family, we will observe that it is possible to arrange the atoms present in the molecule in more than one way to satisfy all valencies. This means that it is possible to have two or more different arrangements for the same molecular formula.
- **Example:** Chlorobutane molecule has two structural formulas:

$CH_3CH_2CH_2CH_2Cl$ (1-Chlorobutane) and $CH_3CHClCH_2CH_3$ (2-Chlorobutane)

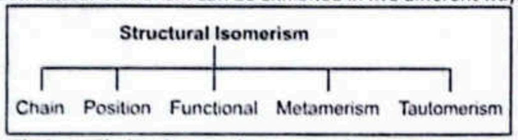
This fact has been supported by an experimental evidence that there are two compounds with different physical properties but with the same molecular formula of C_4H_9Cl. Isomerism is not only possible but common if the compound contains more than three carbon atoms. As the number of carbon atoms in a hydrocarbon increases, the number of possible isomers increase very rapidly. The five carbon compound, pentane, has three isomers.

Tip **Formula to find no. of chain isomers of Alkanes up to carbon no.7 is $2^{nc-4}+1$**
e.g., if nc = 6 (Hexane)
then,
$2^{6-4}+1 = 2^2+1 = 5$
- **For carbon no. 8 (Octane)**
$2^{nc-4}+2 = 2^{8-4}+2 = 2^4+2 = 16+2 = 18$
- **For carbon no. 9 (Nonane)**
$2^{nc-4}+3$
$= 2^{9-4}+3 = 2^5+3$
$= (2\times2\times2\times2\times2)+3 = 32+3 = 35$

➲ Types of Isomerism

A. Structural Isomerism:

The structural isomerism is not confined to hydrocarbons only. In fact, all classes of organic compounds and their derivatives show the phenomenon of structural isomerism. The structural isomerism arises due to the difference in the arrangement of atoms within the molecule. The structural isomerism can be exhibited in five different ways.



Rack Your Mind!

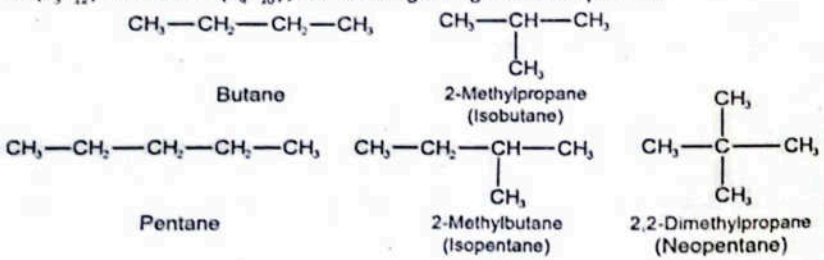
7. Number of isomers of C_4H_{10} is:
(A) 1 (B) 2
(C) 3 (D) 4

Rack Your Mind!

8. Five carbon compound, pentane has number of isomers:
(A) Five (B) Four
(C) Three (D) One

1. The Chain or Skeletal or Nucleus Isomerism

This type of isomerism arises due to the difference in the nature of the carbon chain. For example, for pentane (C_5H_{12}) and butane (C_4H_{10}), the following arrangements are possible.



Alkanes	No. of Isomers	Alkanes	No. of Isomers
Methane, Ethane, Propane	No Isomers	Butane (C_4H_{10})	2
Pentane (C_5H_{12})	3	Hexane (C_6H_{14})	5
Heptane (C_7H_{16})	9	Octane (C_8H_{18})	18
Nonane (C_9H_{20})	35	Decane ($C_{10}H_{22}$)	75
Icosane ($C_{20}H_{42}$)	366319	Triacontane ($C_{30}H_{62}$)	More than 4 billions

2. Position Isomerism

This type of isomerism arises due to the difference in the position of the same functional group or multiple bonds on the carbon chain. The arrangement of carbon atoms remains the same.

Examples:

C_3H_7Cl: $CH_3-CH_2-CH_2-Cl$ (**1-Chloropropane**); $CH_3-CH(Cl)-CH_3$ (**2-Chloropropane**)

C_3H_7OH: $CH_3-CH_2-CH_2-OH$ (**1-Propanol**); $CH_3-CH(OH)-CH_3$ (**2-Propanol**)

C_4H_8: $CH_3-CH_2-CH=CH_2$ (**1-Butene**); $CH_3-CH=CH-CH_3$ (**2-Butene**)

Pentane and 2-methyl butane have the same percentage composition.

Ethanal (acetaldehyde) does not show position isomerism.

Rack Your Mind!

9. Write down three position isomers of xylene.

3. Functional Group Isomerism

The compounds having the same molecular formula but different functional groups are said to exhibit functional group isomerism.

Examples

In the following examples, there are two or more compounds having the same molecular formulae but different arrangement of atoms.

C_2H_6O: CH_3-O-CH_3 (**Dimethyl ether**); CH_3-CH_2-OH (**Ethyl alcohol**)

C_3H_6O: $CH_3-CH_2-C(=O)-H$ (**Propionaldehyde (Propanal)**); $CH_3-C(=O)-CH_3$ (**Acetone (Propanone)**)

C_3H_8O: $CH_3-CH_2-CH_2-OH$ (**1-Propanol**); $CH_3-O-CH_2-CH_3$ (**Methoxy ethane**)

Rack Your Mind!

10. Both CH_3COOH and $HCOOCH_3$ show isomerism:
(A) Position (B) Chain
(C) Geometric (D) Functional group

Sr.No.	Formula	Functional Group Isomers
(i)	C_nH_{2n}	Alkene and cycloalkane
(ii)	C_nH_{2n-2}	Alkadiene, Alkyne and cycloalkene
(iii)	$C_nH_{2n+2}O$	Alcohol, ether
(iv)	$C_nH_{2n}O$	Aldehyde, ketone
(v)	$C_nH_{2n}O_2$	Carboxylic Acid, ester
(vi)	$C_6H_{12}O_6$	Glucose (aldohexose), Fructose (Ketohexose)
(vii)	$C_nH_{2n+1}CN$	Cyanides and Iso-cyanides e.g., CH_3CN = Ethane nitrile, CH_3NC = Methane isonitrile

4. Metamerism

This type of isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group. Such compounds belong to the same homologous series.

- Such compounds belong to the same homologous series or class of compounds.
- It is due to the presence of different alkyl groups attached to the same polyvalent functional group or atom.

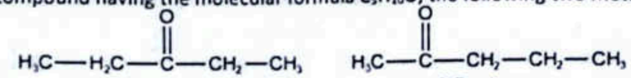
i.e., $-O-, -S-, -NH-, -\overset{O}{\overset{||}{C}}-, -\overset{O}{\overset{||}{C}}-O-$.

- It is shown by ethers, thioether, ketones, esters, secondary amines, tertiary amines.
- Metamerism is due to the difference in alkyl groups joined with same divalent functional group present in the molecule.
- **Examples:** Diethyl ether and Methoxy methane.

$H_3C-H_2C-O-CH_2-CH_3$ (Ethoxy ethane) $H_3C-O-CH_2-CH_2-CH_3$ (Methoxy propane)

> • Alkenes do not show metamerism.
> • Butanone do not show metamerism.

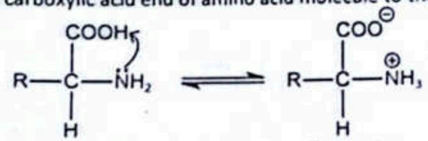
For a ketonic compound having the molecular formula $C_5H_{10}O$, the following two metamers are possible.



3-Pentanone 2-Pentanone

5. Tautomerism

This type of isomerism arises due to shifting of proton (H^+) from one atom to another in the same molecule. This is commonly seen in amino acids. They exist as zwitter ions which are formed when a proton is shifted from the carboxylic acid end of amino acid molecule to the amine group.



Amino acid Zwitter ion

➢ Keto-Enol Isomerism:

Keto-enol isomerism is exhibited only by such aldehydes and ketones which contain at least one α-hydrogen. Here one isomer has the carbonyl group and the other has an – OH group attached to a doubly bonded carbon known as enol. **E.g.,**

$$H_2C=\overset{OH}{\overset{|}{C}}-CH_3 \rightleftharpoons H_3C-\overset{O}{\overset{||}{C}}-CH_3$$

Prop-1-en-2-ol Acetone

B. Stereoisomerism:

Stereoisomers are such compounds which possess the same structural formula, but differ with respect to the positions of the identical groups in space.

There are two types of stereoisomerism:

i. Geometrical or cis trans isomerism

ii. Optical isomerism

Note: It is part of class 12 syllabus and will be covered there.

> **Rack Your Mind!**
>
> **11. Which type of structural isomerism involves differences in the arrangement of the carbon skeleton?**
> (A) Chain isomerism
> (B) Positional isomerism
> (C) Metamerism
> (D) Stereoisomerism

ORGANIC REDOX REACTIONS

Oxidation-Reduction reactions that involve organic compounds are called organic **redox reactions**. These reactions are characterized by the addition or removal of atoms/bonds. Normally, during organic oxidation oxygen is added or hydrogen is removed. During organic reduction, hydrogen is added or oxygen is removed. Some examples of oxidation and reduction reactions are given below:

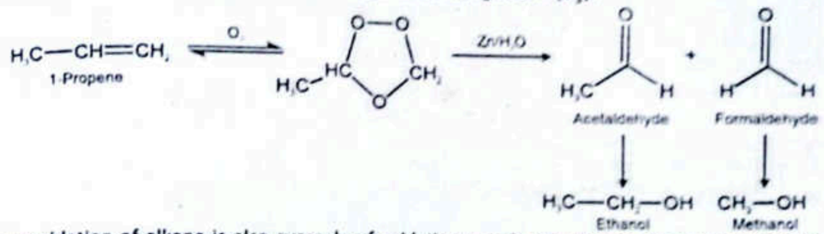
➲ Oxidation

Oxidation of organic compounds involving reaction with oxygen is usually the combustion reaction:

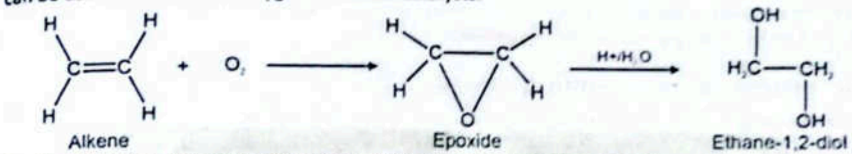
$$2C_2H_6+7O_2 \longrightarrow 4CO_2+6H_2O$$

Reactions of organic compounds with oxidizing agents. e.g.,

i) Ozonolysis is a method of oxidatively cleaving alkenes using ozone (O_3).



ii) The epoxidation of alkene is also example of oxidation reaction. In this reaction various oxidizing agents can be used like molecular oxygen and metal catalysts.



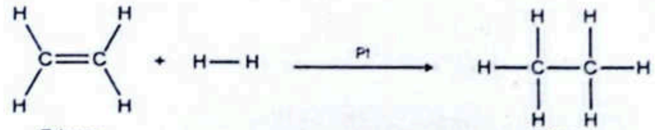
iii) Reaction of primary alcohols with acidified $K_2Cr_2O_7$ to make carboxylic acids,

(**Note:** Detail will be discussed in class 12 syllabus).

$$C_2H_5OH+2[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}CH_3COOH+H_2O$$

➢ Reduction

Addition of hydrogen to carbon-carbon double bond to form alkane is an example of organic reduction reaction.



Role of Reducing Agents in Organic Synthesis:

Various reducing agents are used in Organic synthesis. e.g.; $LiAlH_4$, $NaBH_4$.

(**Note:** Reduction of nitriles to amines, amides to amines, carboxylic acid to primary alcohols, nitrobenzene to phenylamine are all examples of reduction and will be studied in class 12 syllabus).

$$CH_3-\overset{O}{\overset{||}{C}}-H+2[H]\xrightarrow[\Delta]{LiAlH_4}CH_3-CH_2-OH$$

☑ QUICK CHECK 11.11

a) Draw the displayed formula and name an isomer of C_4H_8 that could be an example of positional isomerism?

Ans.

C_4H_8 $CH_3-CH_2-CH=CH_2$ (1-Butene) $CH_3-CH=CH-CH_3$ (2-Butene)

b) What type of isomers are ethoxy methane ether and propanol?

Ans.

C_3H_8O $CH_3-CH_2-O-CH_3$ (Ethoxy Methane (Methoxy ethane)) $CH_3-CH_2-CH_2-OH$ (1-propanol)

c) What are the different types of structural isomerism in alkenes?

Ans. The types of structural isomerism in alkenes are:

1. **Chain Isomerism** – Different carbon skeletons (e.g., 1-butene and 2-methylpropene).

2. **Position Isomerism** – Double bond at different positions (e.g., 1-butene and 2-butene).
3. **Functional Isomerism** – Same molecular formula but different functional groups (e.g., butene and cyclobutane).

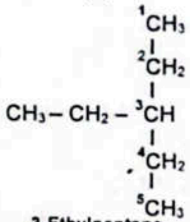
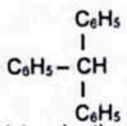
d) Write down different isomers of the compound $C_4H_9NH_2$.

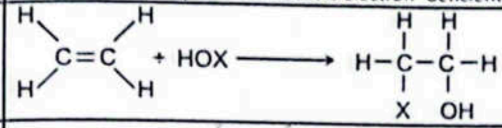
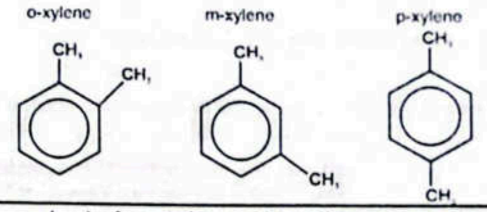
Ans. The molecular formula $C_4H_9NH_2$ represents **butylamine** (a primary amine with four carbons). It has four structural isomers due to different carbon chain arrangements and positions of the $-NH_2$ group.

Isomers of $C_4H_9NH_2$ (Butylamine):

1. **Straight-Chain Amines:**
   - **(a) 1-Butanamine (n-Butylamine)**
     $CH_3-CH_2-CH_2-CH_2-NH_2$
   - **(b) 2-Butanamine (sec-Butylamine)**
     $CH_3-CH_2-CH(NH_2)-CH_3$
2. **Branched-Chain Amines:**
   - **(c) 2-Methyl-1-propanamine (Isobutylamine)**
     $(CH_3)2CH-CH_2-NH_2$
   - **(d) 2-Methyl-2-propanamine (tert-Butylamine)**
     $(CH_3)3C-NH_2$

Solution File — Rack Your Brain!

Sr. #	Option	Explanation
1.	B	Toluene is the common name for methyl benzene, which is a benzene ring with one methyl group attached.
2.	S.Q	(a)  3-Ethylpentane (b)  Triphenylmethane
3.	S.Q	**Differences between Nucleophile and Electrophile:** **Nucleophile** • Nucleophile means nucleus loving. This is the reagent which seeks for a nucleus. • It has an unshared electron pair available for bonding. • In most cases it is basic in character. • It may be negatively charged or neutral. • Nucleophile is also called Lewis base. **Examples:** • It may be negatively charged e.g., $C_2H_5O^-$ Ethoxide, H_2S^- Hydrogen Sulphide ion, SCN^- Thiocyanate ion, Cl^- Chloride ion, Br^- Bromide ion, I^- Iodine ion, It may be neutral e.g. $H_2\ddot{O}:$, $\ddot{N}H_3$ • π-electron system $H_2C=CH_2$, $HC\equiv CH$ **Electrophile** • It is a specie which attracts electrons (electron loving). • In most cases, it is acidic in character. • The carbon atom of an alkyl group attached with the halogen atom and bearing a partial positive charge is called an electrophile or electrophilic center. • An electrophile may be neutral or positively charged. • Electrophile is also called Lewis acid. **Examples:** • It may be neutral or electron deficient e.g. $AlCl_3$, SO_3, BF_3, • It may be positively charged e.g., NH_4^+, Cl^+, Br^+, NO_2^+, R^+ etc.

Sr. #	Option	Explanation
4.	C	BF_3 is not a nucleophile because it is electron-deficient and acts as an electrophile.
5.	S.Q	
6.	S.Q	$CH_3-HC=CH_2 + \overset{\delta-}{HO}-\overset{\delta+}{Cl} \longrightarrow CH_3-\underset{OH}{HC}-CH_2-Cl$ (Propylene chlorohydrin or 1-Chloro-2-propanol)
7.	B	C_4H_{10} has two chain isomers, n-butane and iso-butane
8.	C	Pentane has three structural isomers: n-pentane, isopentane (methylbutane), and neopentane (dimethylpropane).
9.	S.Q	**Xylenes (C_8H_{10})** 
10.	D	They have the same molecular formula ($C_2H_4O_2$) but different functional group: carboxylic acid (–COOH) and ester (–COO–).
11.	A	Chain isomerism involves differences in the carbon skeleton (e.g., straight-chain vs. branched).

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. An alkene undergoes ozonolysis followed by reduction with zinc dust and water to yield propanone and methanal. The alkene is:
a) 1-Butene b) 2-Butene c) 2-Methylpropene d) 2-Methyl-2-butene

II. Which of the following reagents is typically used for the acid-catalyzed hydration of alkenes to form alcohols?
a) H_2 / Ni b) O_3 followed by Zn/H_2O
c) Dilute H_2SO_4 d) Br_2 in CCl_4

III. Halogenation of alkanes is an example of:
a) Electrophilic substitution b) Nucleophilic substitution
c) Free-radical substitution d) Oxidation

IV. Which of the following reactions can an alkane undergo?
a) Addition b) Substitution c) Polymerization d) Nitration

V. What is the first step in the electrophilic addition reaction of alkenes?
a) Formation of a carbocation b) Attack by a nucleophile
c) Attack by an electrophile on the double bond d) Formation of a free radical

VI. The addition of unsymmetrical reagent to an unsymmetrical alkene is in accordance with the rule/principle?
a) Markovnikov's Rule b) Hund's Rule c) Le Chatelier's Principle d) Aufbau Principle

VII. The most stable carbonium ion among the following is:
a) CH_3^+ b) $CH_3CH_2^+$ c) $(CH_3)_2CH^+$ d) $(CH_3)_3C^+$

VIII. Markovnikov's rule is applicable to:
a) $CH_2=CH_2$ b) $CH_3-CH_2-CH_3$ c) $CH_3-CH=CH-CH_3$ d) $(CH_3)_2C=CH_2$

IX. What intermediate is formed during the electrophilic addition of HBr to an alkene?
a) Carbocation b) Carbanion c) Radical d) Epoxide

X. The enhanced stability of conjugated dienes compared to isolated dienes is primarily attributed to:
a) Inductive effects of the double bonds.
b) Increased s-character of the hybridised orbitals.
c) Delocalisation of π electrons across the conjugated system.
d) Steric hindrance between the double bonds.

XI. Which of the following carbocations would be the least stable?
a) $(CH_3)_2CH^+$ b) $CH_3CH_2^+$ c) CH_3^+ d) $(CH_3)_3C^+$

XII. Which of the following is the repeating unit in the polymer poly(ethene) (polyethylene)?
a) $-CH_2CH_2-$ b) $-CH=CH-$ c) $-CH_2CH_2-$ d) $-CH(CH_3)CH_2-$

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	c	2-Methylpropene	• Ozonolysis of 2-methylpropene ($(CH_3)_2C=CH_2$) gives propanone (CH_3COCH_3) and methanol (HCHO).
II.	c	Dilute H_2SO_4	• Dilute H_2SO_4 catalyzes the hydration of alkenes to form alcohols.
III.	c	Free-radical substitution	• Halogenation of alkanes (e.g., $CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl$) proceeds via free-radical chain mechanism.
IV.	b	Substitution	• Alkanes undergo substitution (e.g., halogenation) but not addition (no π bonds) or polymerization.
V.	c	Attack by an electrophile on the double bond	• The first step is electrophilic attack (e.g., H^+ in HBr) on the π electrons of the alkene.
VI.	a	Markovnikov's Rule	• Unsymmetrical reagents (e.g., HBr) add to unsymmetrical alkenes such that the H attaches to the less substituted carbon.
VII.	d	$(CH_3)_3C^+$	• Tertiary carbocations (3°) are most stable due to hyperconjugation and inductive effects.
VIII.	d	$(CH_3)_2C=CH_2$	• Markovnikov's rule applies to unsymmetrical alkenes (e.g. $(CH_3)_2C=CH_2$).
IX.	a	Carbocation	• Electrophilic addition of HBr forms a carbocation intermediate (e.g., $CH_3CH^+CH_3$).
X.	c	Delocalisation of π electrons across the conjugated system	• Conjugated dienes (e.g., buta-1,3-diene) are stabilized by π-electron delocalization over 4+ carbons.
XI.	c	CH_3^+	• Methyl cation (CH_3^+) is least stable (no alkyl groups to stabilize the positive charge).
XII.	c	$-CH_2CH_2-$	• Poly(ethene) is formed by polymerization of ethene ($CH_2=CH_2$) with repeating unit $-CH_2-CH_2-$

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. Define the following:
i) Cycloalkanes ii) Isomerism iii) Conjugated dienes iv) Inductive effect

Ans.

i) **Cycloalkanes:** Cycloalkanes are saturated hydrocarbons with carbon atoms arranged in a ring structure, containing only single bonds.
General formula: C_nH_{2n}

ii) **Isomerism**
Two or more compounds having the same molecular formula but different structural formulas and properties are said to be isomers and the phenomenon is called isomerism.

iii) **Conjugated dienes**
Conjugated dienes are organic compounds that contain two double bonds separated by a single bond. The double bonds are alternating (i.e., conjugated) in the carbon chain.

iv) **Inductive effect**
The inductive effect refers to the transmission of charge through a chain of atoms in a molecule by the polarization of sigma bonds. It occurs when an atom or group of atoms in a molecule either donates electron density (electron-donating) or withdraws electron density (electron-withdrawing) through the sigma bonds.

b. Differentiate between:
i) Aliphatic and Aromatic hydrocarbons ii) Homolytic and Heterolytic Fission
iii) Electrophile and Nucleophile

Ans.

i) **Aliphatic and Aromatic hydrocarbons**

Property	Aliphatic Hydrocarbons	Aromatic Hydrocarbons
Structure	Open-chain (straight or branched) or non-aromatic rings	Contain one or more **benzene rings** (aromatic rings)
Bonding	May have single, double, or triple bonds	Contain **delocalized π-electrons** in a ring structure
Stability	Less stable than aromatics	Highly stable due to resonance
Types	Alkanes, alkenes, alkynes, and cycloalkanes	Benzene, toluene, naphthalene, etc.
Reactivity	Generally more reactive	Less reactive toward addition reactions
Examples	Ethane (C_2H_6), Propene (C_3H_6), Butyne (C_4H_6)	Benzene (C_6H_6), Toluene (C_7H_8)

ii) **Homolytic and Heterolytic Fission**

Feature	Homolytic Fission	Heterolytic Fission
Bond breaking	Bond breaks evenly	Bond breaks unevenly
Electron distribution	Each atom gets one electron	One atom gets both bonding electrons
Produces	**Free radicals**	**Ions (cation and anion)**
Occurs in	Non-polar solvents or under high energy (e.g. UV light)	Polar solvents or in presence of electrophiles/nucleophiles
Example	$Cl-Cl \rightarrow Cl^{\bullet} + Cl^{\bullet}$	$H-Cl \rightarrow H^+ + Cl^-$

iii) **Electrophile and Nucleophile**

Property	Electrophile	Nucleophile
Definition	Electron-deficient species	Electron-rich species
Electron behavior	Accepts electron pairs	Donates electron pairs
Charge	Often positively charged or neutral	Often negatively charged or neutral
Affinity	Attracted to electron-rich centers	Attracted to electron-deficient centers
Role in reactions	Acts as a Lewis acid	Acts as a Lewis base
Examples	H^+, NO_2^+, $AlCl_3$, BF_3	OH^-, NH_3, Cl^-, CN^-

c. Explain why alkanes do not undergo addition reactions.

Ans. Alkanes do **not undergo addition reactions** because:

- They are **saturated hydrocarbons**, meaning all carbon-carbon bonds are **single (σ) bonds.**
- These σ-bonds are **strong and stable**, and there are **no regions of high electron density** like double or triple bonds for an electrophile to attack.
- Addition reactions typically occur with **unsaturated compounds** (like alkenes or alkynes), which have **π-bonds** that are more reactive.

In short, Alkanes lack π-bonds, making them chemically inert toward addition reactions and more likely to undergo substitution reactions instead.

d. How elimination reaction is considered the opposite of an addition reaction.

Ans. An elimination reaction is considered the opposite of an addition reaction because:

- In an addition reaction, atoms or groups are added to a molecule, typically converting a double or triple bond into a single bond.
- In an elimination reaction, atoms or groups are removed from a molecule, typically forming a double or triple bond from a single bond.

Alkanes do not undergo elimination reactions under normal conditions because:

- Elimination reactions require a molecule to have a leaving group (like –OH, –Br, –Cℓ) on one carbon and a β-hydrogen (on an adjacent carbon).
- Alkanes consist of only C–C and C–H single bonds and do not have good leaving groups naturally.
- They are also non-polar and chemically stable, making it hard to break bonds without strong reagents or high energy.

In short, Alkanes lack both the leaving groups and reactive centres needed for elimination, so they do not undergo elimination reactions unless first converted to more reactive derivatives (like alkyl halides).

e. Compare the carbocation stability in propene and 2-butene.

Ans.

(i) Propene (CH_3–CH=CH_2)

- If a proton is removed from the double bond, the most likely carbocation formed is the allyl carbocation ($CH_2 = CH–CH_2^+$).
- This allylic carbocation is resonance-stabilized, meaning the positive charge is delocalized over two carbon atoms.
- **Stability:** Relatively stable due to resonance.

(ii) 2-Butene (CH_3–$CH = CH$–CH_3)

- Ionization typically leads to a secondary carbocation ($CH_3–C^+H–CH=CH_3$).
- There is no resonance stabilization unless rearrangement occurs.
- **Stability:** Less stable than the allylic carbocation of propene.

f. Given the molecular formula C_5H_{10}, list all possible structural isomers that are alkenes.

Ans. C_5H_{10} Alkene Isomers:

(i) Pent-1-ene
$CH_2=CH–CH_2–CH_2–CH_3$

(ii) Pent-2-ene
$CH_3–CH=CH–CH_2–CH_3$

(iii) 2-Methylbut-1-ene
$CH_2=C(CH_3)–CH_2–CH_3$

(iv) 3-Methylbut-1-ene
$CH_2=CH–CH(CH_3)–CH_3$

(v) 2-Methylbut-2-ene
$CH_3–C(CH_3)=CH–CH_3$

g. When propene (C_3H_6) undergoes electrophilic addition with HBr, it forms 2-bromopropane as the major product. Explain why 2-bromopropane is favored over 1-bromopropane, using the concept of carbocation stability.

Ans. When propene ($CH_3–CH=CH_2$) reacts with HBr, the reaction proceeds via an electrophilic addition mechanism. The major product is 2-bromopropane, and this can be explained using carbocation stability:

Explanation:

1. **Electrophilic attack:**
   The **π electrons** of the double bond attack the H^+ from HBr.
   This can lead to two possible carbocations:
   - Path A (less stable): H^+ adds to the CH_2 end, forming a primary carbocation ($CH_3–CH–CH_2^+$)
   - Path B (more stable): H^+ adds to the CH end, forming a secondary carbocation ($CH_3–C^+H–CH_3$)
2. **Carbocation stability:**
   - Primary carbocations are less stable
   - Secondary carbocations are more stable due to hyperconjugation and inductive effects from surrounding alkyl groups
3. **Nucleophilic attack:**
   - Br^- then attacks the more stable secondary carbocation, leading to 2-bromopropane.

Conclusion:

2-bromopropane is the major product because its formation proceeds through a more stable secondary carbocation, following Markovnikov's rule.

h. Explain why conjugated alkenes may show different reactivity compared to isolated alkenes.

Ans. Conjugated alkenes show different reactivity compared to isolated alkenes due to delocalization of π-electrons across alternating double and single bonds.

Aspect	Conjugated Alkenes	Isolated Alkenes
Structure	Alternating double and single bonds.	Double bonds separated by two or more single bonds.
Electron delocalization	π-electrons are **delocalized** across the system.	π-electrons are **localized** between two atoms.
Stability	More stable due to **resonance.**	Less stable.
Reactivity	Can undergo **special reactions** (e.g. 1, 4-addition).	React through **normal electrophilic addition** only.
UV/Visible absorption	Often absorb at **longer wavelengths.**	Less likely to absorb in the visible range.

i. Explain how inductive effects from alkyl groups stabilize carbocations in alkenes.

Ans. Inductive effects from alkyl groups help stabilize carbocations in alkenes by donating electron density through sigma (σ) bonds toward the positively charged carbon.

- Carbocations are electron-deficient species (positively charged carbon).
- Alkyl groups (like $–CH_3$ or $–CH_2CH_3$) have a slight electron-releasing character.
- Through the inductive effect, they push electron density toward the carbocation, reducing its positive charge and making it more stable.

Relative stability of carbocations due to inductive effects:

- **Tertiary carbocation** (3 alkyl groups) → Most stable
- **Secondary carbocation** (2 alkyl groups)
- **Primary carbocation** (1 alkyl group)
- **Methyl carbocation** (no alkyl groups) → Least stable

j. Write the equation for each reaction.

i. $CH_3CH_2CH=CH_2$ with H_2 (Ni catalyst)
ii. $CH_3CH=CH_2$ with $C\ell_2$
iii. $CH_3CH_2CH=CHCH_2CH_3$ with $H_2O(H_2SO_4$ catalyst)

Ans.

i. $CH_3CH_2CH=CH_2$ with H_2 (Ni catalyst)

This is a hydrogenation reaction of an alkene.

$$CH_3CH_2CH = CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_2CH_3$$

ii. $CH_3CH=CH_2$ with Cl_2

This is an electrophilic addition of chlorine to an alkene.

$$CH_3CH=CH_2 + Cl_2 \longrightarrow CH_3CHClCH_2Cl$$

iii. $CH_3CH_2CH=CHCH_2CH_3$ with $H_2O(H_2SO_4$ catalyst)

It is Hydration of hex-2-ene with H_2O in the presence of H_2SO_4 catalyst

$$CH_3CH_2CH=CHCH_2CH_3 + H_2O \xrightarrow{H_2SO_4} CH_3CH_2CH(OH)-CH_2CH_2CH_3$$

k. Write structural formulas for each of the following compounds.

(i) Isobutylene (ii) 2,3,4,4-Tetramethyl-2-pentene (iii) 2,5-Heptadiene
(iv) 4,5-Dimethyl-2-hexene (v) Vinyl acetylene (vi) 1,3-Pentadiene
(vii) 1-Butyne (viii) 3-n-Propyl-1,4-pentadiene (ix) Vinyl bromide
(x) But-1-en-3-yne (xi) 4-Methyl-2-pentyne (xii) Isopentane

Ans. Structural Formulae

(i) Isobutylene $CH_3-C=CH_2$ | CH_3 (IUPAC Name = 2-Methylpropene)	(ii) 2,3,4,4-Tetramethyl-2-pentene CH_3 | ${}^5CH_3-{}^4C-{}^3C={}^2C-{}^1CH_3$ | | | CH_3 CH_3 CH_3
(iii) 2,5-Heptadiene ${}^7CH_3-{}^6CH={}^5CH-{}^4CH_2-{}^3CH={}^2CH-{}^1CH_3$	(iv) 4,5-Dimethyl-2-hexene ${}^6CH_3-{}^5CH-{}^4CH-{}^3CH={}^2CH-{}^1CH_3$ | | CH_3 CH_3
(v) Vinyl acetylene $H_2C=CH-C\equiv CH$	(vi) 1,3 – Pentadiene ${}^5CH_3-{}^4CH={}^3CH-{}^2CH={}^1CH_2$
(vii) 1-Butyne ${}^4CH_3-{}^3CH_2-{}^2C\equiv{}^1CH$	(viii) 3-n-Propyl-1,4-pentadiene ${}^5CH_2={}^4CH-{}^3CH-{}^2CH={}^1CH_2$ | $CH_2-CH_2-CH_3$
(ix) Vinyl bromide $H_2C=CH-Br$	(x) But-1-en-3-yne ${}^1CH_2={}^2CH-{}^3C\equiv{}^4CH$
(xi) 4-Methyl-2-pentyne ${}^5CH_3-{}^4CH-{}^3C\equiv{}^2C-{}^1CH_3$ | CH_3	(xii) Isopentane ${}^4CH_3-{}^3CH_2-{}^2CH-{}^1CH_3$ | CH_3

l. Write down names of the following compounds according to IUPAC-System.

(i) $H_3C-CH=CH(CH_2)_2CH_3$ (ii) $(CH_3)_2C=CH_2$

(iii) $CH_3-CH_2-CH_2-C=CH_2$ with $CH(CH_3)_2$ on C (iv) $CH_2=CH-CH=CH_2$

(v) $CH_2=C-CH_2CH_2CH_3$ with C_2H_5 on C (vi) $(CH_3CH_2)_3CH$

(vii) $CH_3CH_2C(CH_3)2CH(CH_2CH_3)CH_3$ (viii) $CH_2=CH-C\equiv C-CH=CH_2$

(ix) $(CH_3)_3C-CH_2-C(CH_3)_3$ (x) $CH_2=CH-C\equiv CH$

(xi) $CH_3C(CH_3)_2(CH_2)CH_3$

(a)
$H_3C-CH_2-CH-CH_2-CH_2-CH_3$
\|
CH_2-CH_3

(b)
$(CH_3)_2CH-CH-CH(CH_3)_2$
\|
CH_3

(c)
$H_3C-CH_2-CH_2-CH(CH_3)_2$ (CH bearing two CH_3 groups)

Ans. IUPAC Names

(i) $H_3C^1-{}^2CH={}^3CH-{}^4CH_2-{}^5CH_2-{}^6CH_3$ 2-Hexene	(ii) CH_3 | $CH_3-C=CH_2$ 2-Methylpropene
(iii) ${}^5CH_3-{}^4CH_2-{}^3CH_2-{}^2C={}^1CH_2$ | $CH_3-HC-CH_3$ 2-Isopropyl-1-pentene	(iv) $CH_2=CH-CH=CH_2$ 1,3 – Butadiene
(v) ${}^1CH_2={}^2C-{}^3CH_2{}^4CH_2{}^5CH_3$ | C_2H_5 2-Ethyl-1-pentene	(vi) ${}^1CH_3$ | ${}^2CH_2$ | $CH_3-CH_2-{}^3CH$ | ${}^4CH_2$ | ${}^5CH_3$ 3-Ethylpentane
(vii) CH_3 | $H_3{}^1C-{}^2CH_2-{}^3C-{}^4CH-CH_3$ | | CH_3 ${}^5CH_2$ | ${}^6CH_3$ 3,3,4-Trimethylhexane	(viii) ${}^1CH_2={}^2CH-{}^3C\equiv{}^4C-{}^5CH={}^6CH_2$ 1,5-Hexadien-3-yne
(ix) CH_3 CH_3 | | $H_3C-C-CH_2-C-CH_3$ | | CH_3 CH_3 2,2,4,4 - tetramethylPentane	(x) ${}^1CH_2={}^2CH-{}^3C\equiv{}^4CH$ 1-Buten-3-yne
(xi) CH_3 | $H_3C-C-CH_2-CH_3$ | CH_3 2,2 - dimethylbutane	(a) $H_3{}^1C-{}^2CH_2-{}^3CH-{}^4CH_2-{}^5CH_2-{}^6CH_3$ | CH_2-CH_3 3-ethylhexane
(b) ${}^1CH_3-{}^2CH-{}^3CH-{}^4CH-{}^5CH_3$ | | | CH_3 CH_3 CH_3 2, 3, 4 - trimethylpentane	(c) $H_3{}^5C-{}^4CH_2-{}^3CH_2-{}^2CH-{}^1CH_3$ | CH_3 2-MethylPentane

DESCRIPTIVE QUESTIONS

Q.3 **Describe the free radical halogenation of methane using Cl_2 as an example.**

Ans. See Page No. (385)

Q.4 **Describe the following methods for the preparation of alkenes:**
i) Dehydrohalogenation of alkyl halides **ii) Dehydration of alcohols**

Ans. See Page No. (389)

Q.5 **Describe the mechanism of electrophilic addition of hydrogen halides to alkenes. Discuss Markovnikov's Rule in the context of hydrogen halide addition.**

Ans. See Page No. (395)

Q.6 **Explain the following reactions of alkenes with examples:**
a) Halogenation **b) Ozonolysis** **c) Epoxidation** **d) Polymerization**

Ans. See Reactions of Alkenes (Point No. 1, 7, 6, 8) in theory.

ADDITIONAL SLOs BASED MCQs

1. **The most likely reaction alkanes undergo is:**
A. electrophilic addition B. free radical substitution
C. nucleophilic addition D. electrophilic substitution

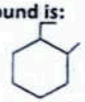
2. **The condensed structural formula of the major product obtained by hydrobromination of 2-methylpent-2-ene is:**
A. $CH_3CH(Br)CH(CH_3)CH_2CH_3$ B. $(CH_3)_2C(Br)(CH_2)_2CH_3$
C. $(CH_3)_2CHCH(Br)CH_2CH_3$ D. $CH_2(Br)CH(CH_3)(CH_2)_2CH_3$

3. **Which one of the following is a possible propagation step in chlorination of ethane?**
A. $C_2H_6 + Cl \rightarrow C_2H_5Cl + H$ B. $C_2H_5Cl + Cl \rightarrow C_2H_4Cl + HCl$
C. $C_2H_5 + Cl \rightarrow C_2H_5Cl$ D. $C_2H_4Cl_2 + Cl \rightarrow C_2H_4Cl + Cl_2$

4. **Which one of the following is the most stable (least reactive) hydrocarbon?**
A. hex-1-ene B. propene C. penta-1,2-diene D. hepta-1,3,5-triene

5. **The most striking factor held responsible for the less reactivity of alkanes is:**
I. their non-polar bonds II. absence of functional group
III. their strong sigma (δ) bonds IV. Long C – C bond lengths
A. I &II only B. II & III only C. I, II & III only D. III & IV only

6. **The systematic name of the following compound is:**



A. 2-ethylmethylcyclohexane B. 2-methyethylcyclohexane
C. 1-ethylmethylcyclohexane D. 1-ethyl-2-methylcyclohexane

7. **Dehydration of propan-1-ol gives:**
A. propene B. propane C. propanone D. propanal

8. **Which one of the following compounds can show geometric isomerism?**
A. 2,2-dimethylbut-2-ene B. 2-methylhex-1-ene C. hex-3-ene D. 2-methylpropene

9. **A racemic mixture must contain:**
A. 90 levorotatory isomers
B. equimolar quantities of levorotatory and dextrorotatory isomers
C. meso isomers and levorotatory isomers
D. 80 dextrorotatory and 20% levorotatory isomers

10. **Which set of compounds are consecutive members of same homologous series?**
A. CH_3OH, CH_3CHO, HCHO B. CH_3COOH, C_2H_5COOH, C_3H_7COOH
C. CH_4, CH_3Cl, CH_2Cl_2 D. C_2H_2, C_2H_4, C_2H_6

11. **The molecule of ethane possesses which hybridization;**
A. sp^3 B. sp^2 C. sp D. sp^2d

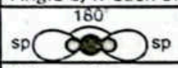
12. **The sp^2 hybrid orbitals are oriented in space at one angle;**
A. 109.5° B. 180° C. 100° D. 120°

13. **The geometry of acetylene is:**
A. angular B. bent C. trigonal D. linear

14. **Which reaction is used as test for the presence of alkene;**
A. reaction of cold diluted alkaline $KMnO_4$ B. combustion
C. polymerization D. catalytic hydrogenation

15. **The general formula of alkane is;**
A. C_nH_{2n+2} B. C_nH_n C. C_nH_{2n} D. C_nH_{2n-2}

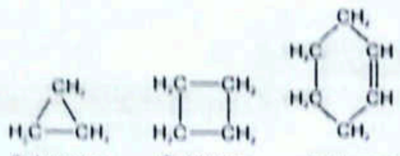
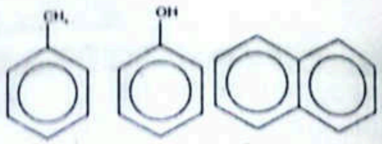
Answer Key with Explanations

Sr.#	Ans.	Explanations
1.	B	Alkanes are most likely to undergo free radical substitution reactions, such as the chlorination and bromination of alkanes, which involve the formation of free radicals.
2.	C	The hydrobromination of 2-methylpent-2-ene follows Markownikov's rule, where the bromine atom attaches to the more substituted carbon atom, resulting in 3-bromo-2-methylpentane.
3.	C	During the chlorination of ethane, a propagation step involves the ethyl radical (C_2H_5) reacting with a chlorine atom to form chloroethane (C_2H_5Cl).
4.	B	Stability decreases with increasing number of double bonds and conjugation. Propene, with a single double bond, is more stable than dienes or trienes.
5.	C	Alkanes are less reactive due to their non-polar bonds, absence of functional groups, and strong sigma bonds.
6.	D	The correct IUPAC name indicates the substituents' positions and follows the alphabetical order of naming.
7.	A	Dehydration of propan-1-ol results in the formation of propene through the elimination of water.
8.	C	Geometric isomerism (cis-trans) can occur in compounds with double bonds that have different substituents on each carbon of the double bond. Hex-3-ene fits this criterion.
9.	B	A racemic mixture contains equal amounts of both enantiomers, which cancel out each other's optical activity.
10.	B	These compounds are carboxylic acids and differ by a CH_2 unit, fitting the definition of a homologous series.
11.	A	In ethane, there is C – C so each carbon is sp^3 hybridized.
12.	D	Angle b/w each orbital is 120°.
13.	D	
14.	A	When alkenes are treated with mild oxidizing reagents like dilute (1%) alkaline $KMnO_4$ solution (Baeyer's Reagent) at low temperature, hydroxylation of double bond occurs resulting in the formation of dihydroxy compounds known as vicinal glycols. The pink colour of $KMnO_4$ solution is discharged during the reaction.
15.	A	The general formula of alkane is C_nH_{2n+2}.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Differentiate between Alicyclic and Aromatic compounds.

Ans.

Alicyclic Compounds	Aromatic Compounds
• The homocyclic compounds which contain ring of three or more carbon atoms and resembling the aliphatic compounds are called alicyclic compounds.	• The homocyclic compounds which contain atleast one benzene ring are called aromatic compounds.
• They may be saturated or unsaturated.	• They may contain one or more benzene rings.
• They have low percentage of carbon.	• They have high percentage of carbon.
Examples:  Cyclopropane, Cyclobutane, Cyclohexene	**Examples:**  Toluene, Phenol, Naphthalene

Q.2 Define the term Isomerism. Give examples.

Ans. Isomerism:

"Two or more compounds having the same molecular formula but different structural formulas and properties are said to be isomers and the phenomenon is called isomerism."

Examples:

C_5H_{12}:

$CH_3-CH_2-CH_2-CH_2-CH_3$ (n-pentane)

$CH_3-CH(CH_3)-CH_2-CH_3$ 2-Methylbutane (Iso-pentane)

$CH_3-C(CH_3)_2-CH_3$ 2, 2-Dimethylpropane (Neo-pentane)

Q.3 How functional group isomerism differs from metamerism? Give examples.

Ans.

Functional Group Isomerism	Metamerism
• The compounds having the same molecular formula but different functional groups are said to exhibit functional group isomerism.	• This type of isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group.
• Such compounds belong to different homologous series.	• Such compounds belong to the same homologous series.
Examples: C_3H_6O: $CH_3-CH_2-\overset{O}{\overset{\Vert}{C}}-H$ Propanal	**Example:** $C_4H_{10}O$: $CH_3-CH_2-O-CH_2-CH_3$ Diethyl ether; $CH_3-O-CH_2-CH_2-CH_3$ Methyl-n-propyl ether

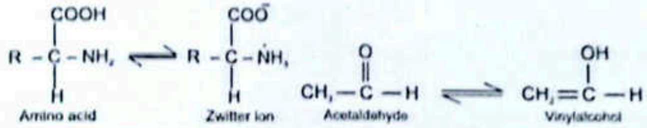
C_3H_6O: $CH_3-\overset{O}{\overset{\Vert}{C}}-CH_3$ Propanone; $CH_2CH_2-CH_2-OH$ 1-Propanol; $CH_3-O-CH_2-CH_3$ Methoxy Ethane	$C_5H_{10}O$: $CH_3-CH_2-\overset{O}{\overset{\Vert}{C}}-CH_2-CH_3$ Diethyl ketone (Pentan-3-one); $CH_3-\overset{O}{\overset{\Vert}{C}}-CH_2-CH_2-CH_3$ Methyl-n-propyl ketone (Pentan-2-one)

Q.4 Define Tautomerism with an example.

Ans. Tautomerism:

This type of isomerism arises due to shifting of proton (H^+) from one atom to other in the same molecule.

Examples:



Q.5 Justify that in alkanes sigma bonds are inert.

Ans. Inertness of σ-bond:

In a σ-bond, the electrons are very tightly held between the two nuclei which makes it a very stable bond. A lot of energy is required to break it. Moreover, the electrons present in a σ-bond can neither attack on any electrophile nor a nucleophile can attack on them. Due to the inertness of σ-bonds, alkanes are unreactive.

Q.6 Why alkanes are called paraffins?

Ans. Alkanes are Paraffins:

The word "paraffins" is derived from Latin words 'parum' = little, 'affins' = affinity. Alkanes are called paraffins due to:

(i) Non-polar Nature:

The electronegativity values of carbon **(2.5)** and hydrogen **(2.1)** do not differ appreciably and the bonding electrons between C – H and C – C are equally shared making them almost non-polar. In view of this, the ionic reagents such as acids, alkalies, oxidizing agents, etc. find no reaction site in the alkane molecules to which they could be attached.

(ii) Inertness of σ-bond:

In a σ – bond, the electrons are very tightly held between the nuclei which makes it a very stable bond. A lot of energy is required to break it. Moreover, the electrons present in a σ – bond can neither attack on any electrophile nor a nucleophile can attack on them.

Q.7 Differentiate between hydrogenolysis and hydrogenation.

Ans.

Hydrogenolysis	Hydrogenation
1. The addition of hydrogen accompanied by bond cleavage is called hydrogenolysis."	1. The addition of hydrogen to an unsaturated compound in the presence of a catalyst is called hydrogenation."
2. It is carried out in Pd-charcoal cavity.	2. It is carried out in the presence of Ni, Pt or Pd etc.
Examples: (i) $R-X+H-H \xrightarrow[\Delta]{Pd-Charcoal} R-H+HX$ (Alkane) (ii) $CH_3-Cl+H-H \xrightarrow[\Delta]{Pd-Charcoal} CH_4+HCl$	**Examples:** (i) $CH_2=CH_2+H_2 \xrightarrow[200^\circ C]{Ni} CH_3-CH_3$ (Ethene → Ethane) (ii) Vegetable oil $+H_2 \xrightarrow[200^\circ C]{Ni}$ vegetable Ghee

Q.8 Give general mechanism of electrophilic addition reactions of alkene.

Ans. General Mechanism of Electrophilic Addition Reactions of Alkene:

It involves three steps:

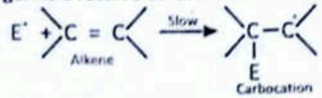
Step 1: To Generate Electrophile:

The reagent E – Nu ionizes to give an electrophile and nucleophile.

$$E - Nu \longrightarrow E^{+} + :Nu^{-}$$

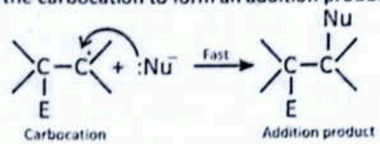
Step 2: Attack of Electrophile and Formation of Carbocation:

The electrophile attacks the carbon – carbon double bond and forms a covalent bond with one carbon and other carbon bears positive charge. As a result a carbocation is formed.



Step 3: Attack of Nucleophile:

The nucleophile now attacks the carbocation to form an addition product.



Since the reaction is initiated by addition of electrophile, so it is called electrophilic addition reaction.

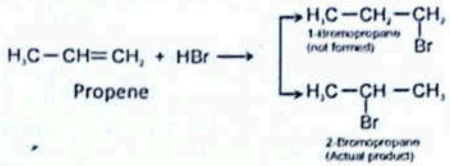
Q.9 What is Markownikov's rule? Give example also.

Ans. Markownikov's Rule:

Statement:

"In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, constituting the double bond, which has least number of hydrogen atoms."

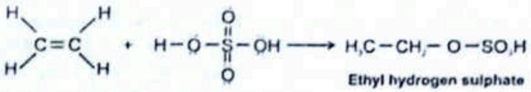
Example:



Q.10 How would you convert ethene into ethyl alcohol?

Ans. Conversion of Ethene into Ethyl Alcohol:

When ethene is treated with cold concentrated sulphuric acid (H_2SO_4), it is dissolved because it forms ethyl hydrogen sulphate.



The ethyl hydrogen sulphate on boiling with water decomposes to give ethyl alcohol.

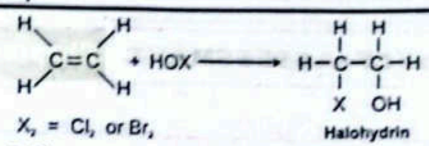
$$H_3C-CH_2-O-SO_3H + H_2O \xrightarrow{100^{\circ}C} H_3C-CH_2-OH + H_2SO_4$$

Q.11 Convert ethene to (a) Halohydrin (b) Ethylene oxide

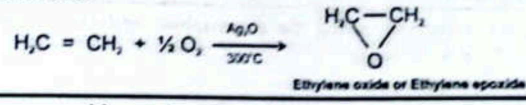
Ans. (a) Ethene to Halohydrin:

If the halogenation of an alkene is carried out in an aqueous solution, haloalcohol is formed called a Halohydrin.In this reaction, molecules of the solvent become reactants too.

$$X_2 + H_2O \longrightarrow HOX + HX$$



(b) Ethene to Ethylene Oxide:



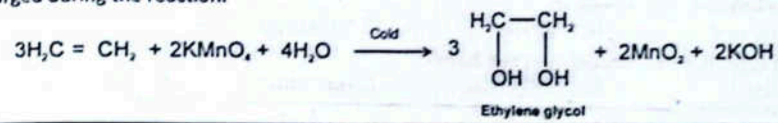
Q.12 How Ethylene Glycol is prepared from ethene?

Ans. Baeyer's Test:

- Dilute 1% alkaline $KMnO_4$ solution is called Baeyer's reagent.
- It is pink in colour and acts as mild oxidizing agent.
- Baeyer's reagent is used to test the presence of unsaturation in the molecules.

Reaction:

When alkenes are treated with Baeyer's reagent at low temperature, hydroxylation of double bond occurs resulting in the formation of dihydroxy compounds known as vicinal glycols. The pink colour of $KMnO_4$ is discharged during the reaction.



Q.13 What is ozonolysis? Describe it giving example. Also give its mechanism.

Ans. Ozonolysis:

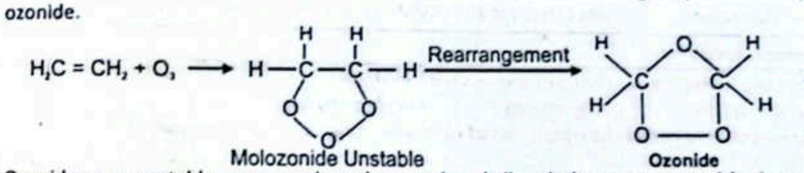
"The cleavage of an unsaturated molecule by reacting with ozone is called ozonolysis."

Ozone (O_3) is a highly reactive allotropic form of oxygen. It reacts vigorously with ethene (or other alkenes) to form formaldehyde (or other **carbonyl compounds.)**

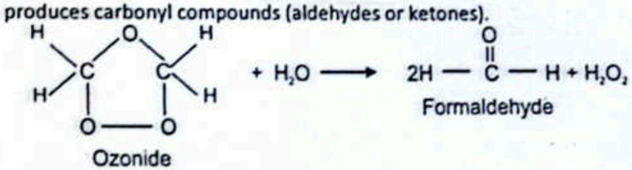
$$CH_2 = CH_2 + O_3 \xrightarrow{Zn} 2HCHO$$

Mechanism:

(i) Ozone reacts with ethene to form molozonide. Molozonoide rearranges spontaneously to form an ozonide.



(ii) Ozonides are unstable compounds and are reduced directly by treatment with zinc and H_2O. The reduction produces carbonyl compounds (aldehydes or ketones).



$$Zn + H_2O_2 \longrightarrow ZnO + H_2O$$

◈◈◈◈◈

SELF-ASSESSMENT Chapter # 11

Total Mark: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) What intermediate is formed during the electrophilic addition of HBr to an alkene?
A. Carbocation B. Carbanion C. Radical D. Epoxide

(ii) Markownikov's rule is applicable to :
A. $CH_2 = CH_2$ B. $CH_3 - CH_2 - CH_3$ C. $CH_3 - CH = CH - CH_3$ D. $(CH_3)_2 - C = CH_2$

(iii) Which of the following reagents is typically used for the acid-catalyzed hydration of alkenes to form alcohols?
A. H_2/Ni B. O_3 followed by Zn/H_2O C. Dilute H_2SO_4 D. Br_2 in CCl_4

(iv) Alkanes are generally unreactive toward polar reagents because:
A. They have double bonds B. They are aromatic
C. Their bonds are non-polar D. They are ionic

(v) An alkene undergoes ozonolysis followed by reduction with zinc dust and water to yield propanone and methanal. The alkene is:
A. 1-Butene B. 2-Butene C. 2-Methylpropene D. 2-Methyl-2-butene

(vi) What type of isomerism exists in but-2-ene?
A. Chain B. Geometrical C. Functional D. Position

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Differentiate between aliphatic and aromatic hydrocarbons with one example each.
(ii) Write the IUPAC name of the following:
a) $CH_2 = CH - CH = CH_2$ b) $CH \equiv C - CH = CH - C \equiv CH$
(iii) Why do branched alkanes have lower boiling points than the straight-chain alkanes?
(iv) What is homolytic and heterolytic bond fission?
(v) Why the order of stability of carbocation is 3° > 2° > 1°?
(vi) Write down the structural formulas for 2-methylbutane and 2, 2-dimethylpropane.
(vii) Give the dehydrohalogenation reaction of bromopropane?
(viii) Given the molecular formula C_5H_{10}, list all possible structural isomers that are alkenes.

Q.3 Extensive Questions. (2 × 4 = 8)

(a) Explain the following reactions of alkenes with examples:
a) Halogenation b) Ozonolysis c) Polymerization
(b) Describe the free radical halogenation of methane using Cl_2 as an example.

Chapter 12 NITROGEN AND SULPHUR

Student Learning Outcomes

After studying this chapter, students will be able to:

- Explain the lack of reactivity of nitrogen due to its triple bond strength and lack of polarity. **(Understanding)**
- Describe the basicity of ammonia using the Bronsted-Lowery theory. **(Understanding)**
- Identify the structure of the ammonium ion and explain how it is formed by an acid-base reaction. **(Understanding)**
- Describe how ammonia can be displaced from ammonium salts through an acid-base reaction. **(Understanding)**
- Describe natural and man-made occurrences of oxides of nitrogen and their catalytic removal from exhaust gases of internal combustion gases. **(Understanding)**
- Explain the role of NO and NO_2 in the formation of photochemical smog, specifically in the reaction with unburned hydrocarbons to form peroxyacetyl nitrate (PAN). **(Understanding)**
- Differentiate between nitrification and de-nitrification. **(Knowledge)**
- Explain the lack of reactivity of sulfur, with reference to its bonding and stability of its compounds. **(Understanding)**
- Describe the different oxidation states of sulfur and their relative stability. (Understanding)
- Describe the properties and uses of sulfuric acid, including its production and industrial applications. **(Understanding)**
- Describe the chemical reactions and processes involving sulfur, such as combustion and oxidation. **(Understanding)**
- Explain the uses of sulfur compounds in industry and everyday life, such as in fertilizers, gunpowder, and rubber, and in synthetic organic chemistry, including the synthesis of dyes, drugs, and fragrances. **(Understanding)**

NITROGEN

➢ **Occurrence:**
Nitrogen belongs to group 15 of the periodic table.

➢ **Preparation:**
(i) In industrial processes, nitrogen is typically obtained by cooling air until it becomes a liquid. Liquid nitrogen is commonly used for rapid cooling purposes.
(ii) In laboratory settings, nitrogen can be generated by slowly heating a solution of ammonium nitrite.

$$NH_4NO_{2(aq)} \xrightarrow{\Delta} N_{2(g)} + 2H_2O_{(l)}$$

Table: Physical Properties of Nitrogen ($_7N^{14}$)

Atomic number	7
Relative atomic mass	14.007 Da
Physical appearance	Colourless Gas
Electronic configuration	[He]$2s^2\ 2p^3$
Melting point	$-210^\circ C$
Boiling point	$-195.8^\circ C$
Covalent radius	74 pm

Ionic radius (3-)	171 pm
1st Ionization energy	1402 kJ/mol
Electronegativity	3.0
Electron affinity	−8.0 kJ/mol
Density	$0.001145\ g/cm^3$
Principal oxidation states	3+ and 5+

REACTIVITY OF NITROGEN (N_2)

Reasons for Inertness of Nitrogen

Nitrogen is a significant component of the air, known for its low reactivity due to its small size, symmetrical electronic cloud, and nonpolar triple bond.

Rock Your Mind!

1. **Summarize the reasons for inertness of nitrogen.**

(i) High bond Energy

- Nitrogen has electronic configuration of $1s^2 2s^2 2p^3$.
- Nitrogen requires three electrons to complete its octet, forming a triple bond by sharing three electrons with another nitrogen atom (as shown in Figure). The bond has a bond enthalpy of $+944\ kJ\ mol^{-1}$. High energy is required to break this bond to form new bonds, making N_2 very unreactive.

(ii) Non-Polar Nature of N_2

- $N\equiv N$ is nonpolar.
- Both the atoms are the same having zero electronegativity difference. This causes equal sharing of the three bonded electrons between the two atoms making the bond nonpolar.

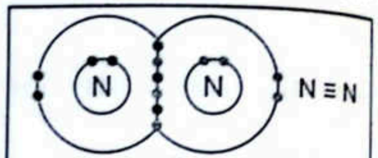


Figure: Bonding in N_2 molecule

Interesting Information!

Uses of Nitrogen:

(i) The high concentration of nitrogen in the air serves to dilute oxygen, preventing every spark in our atmosphere from igniting a massive fire.

(ii) In the case of large shipments of hydrocarbons or edible oils, it is crucial to utilize blankets of Nitrogen or any other inert gas on ships to safeguard them from oxygen and moisture.

(iii) It is also used in laboratory to carry out the reactions which require inert atmosphere.

AMMONIA (NH_3)

(Exercise LQ.1)

Q. Explain the preparation and basicity of ammonia.

Preparation of Ammonia:

- Ammonia (NH_3) is an important industrial compound of nitrogen, which is mainly used as a fertilizer.
- Ammonia is prepared industrially by Haber-Bosch process.

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{\Delta} 2NH_{3(g)}$$

Q. Ammonia behaves as a Lowry-Bronsted base. Explain.

Basicity of Ammonia

Ammonia behaves as a Lowry-Bronsted base by accepting a proton (H^+) from an acid to form ammonium ion.

$$NH_{3(aq)} + H^{+1}_{(aq)} \rightleftharpoons NH_4^{1+}{}_{(aq)}$$

Ammonia dissolves in water to form ammonium hydroxide (NH_4OH) and equilibrium is established between ammonia molecules and ammonium ions in the solution.

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH^{1+}_{4(aq)} + OH^{1-}_{(aq)} \qquad K_b = 1.8\times10^{-5}$$

Ammonia solution is a weak base due to the low basicity constant (K_b) and the equilibrium position being towards the far left side.

Structure of Ammonium (NH_4^{1+})

Ammonia molecule has **pyramidal shape** due to lone pair of nitrogen. But when nitrogen atom in ammonia utilizes this lone pair of electrons to form ammonium ion, this ion adopts a **tetrahedral** shape in which all the bonds are of equal length and strength, (as depicted in Figure).

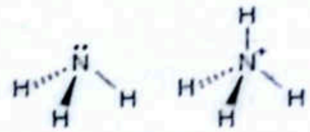


Figure: Pyramidal and tetrahedral shapes of ammonia and ammonium

Synthesis of Ammonia from Ammonium Salts

Preparation of Ammonia

- **In Laboratory:**

  In the laboratory, ammonia gas can be synthesized by heating an ammonium salt such as ammonium chloride ($NH_4C\ell$) with a base like calcium hydroxide ($Ca(OH)_2$) as shown in Figure.

$$2NH_4C\ell_{(s)} + Ca(OH)_{2(aq)} \longrightarrow CaC\ell_{2(aq)} + 2H_2O_{(\ell)} + 2NH_{3(g)}$$

  In this acid-base reaction, NH_4^+ acts as an acid by donating H^+ ions, while OH^- acts as a base by accepting H^+ ions. This reaction displaces ammonia gas from the ammonium salt and produces salt and water.

- **Use in Salt Analysis:**

  It is commonly used to identify ammonium in salt analysis. If a gas with a pungent smell is released and turns moistened red litmus paper blue, it indicates the presence of ammonium in the compound.

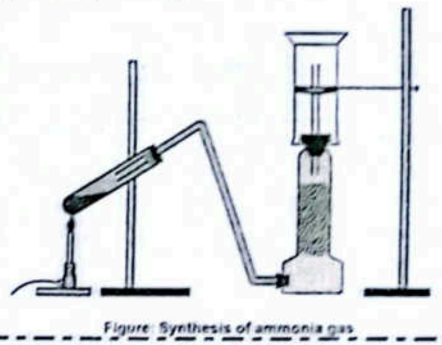


Figure: Synthesis of ammonia gas

QUICK CHECK 12.1

a) Why N_2 gas is used in food packaging?

Ans. N_2 gas is used in food packaging because it is inert and prevents oxidation and bacterial growth. By replacing oxygen (O_2) inside the package, N_2 slows down spoilage and keeps food fresh for longer. It is especially useful for snacks, chips, and ready-to-eat meals to maintain crispness and flavor.

b) Both CO and N_2 have triple bonds in their molecules. Why do you think CO is more reactive than N_2?

Ans. Although both CO and N_2 have triple bonds, CO is more reactive because:

- The bond is **slightly weaker** (bond energy 1072 kJ/mol as compared to bond energy of N_2 which is 946 kJ/mol).
- CO has a polar structure (C slightly positive, O slightly negative), making it more likely to react with other molecules compared to nonpolar N_2.

c) Ammonium salts such as $(NH_4)_2SO_4$ or $(NH_4)_2NO_3$ are commonly used as fertilizers. Why a farmer wouldn't treat a field with an ammonium fertilizer at the same time as using lime? What would be the chemical reactions?

Ans. Ammonium fertilizers like $(NH_4)_2SO_4$ react with lime ($Ca(OH)_2$ or CaO) to release ammonia gas (NH_3), reducing nitrogen content in the soil:

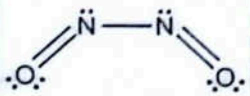
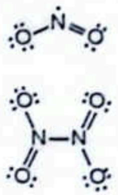
$$2NH_4^+ + Ca(OH)_2 \longrightarrow 2NH_3\uparrow + Ca^{2+} + 2H_2O$$

This reaction makes the fertilizer less effective and causes nitrogen loss, harming crop growth.

OXIDES OF NITROGEN

Oxides of nitrogen are NO, N_2O, NO_2, N_2O_4 and N_2O_5 in which oxidation states range from I+ to V+. N_2O_4 and N_2O_5 decay quickly to other oxides. NO and NO_2 are collectively called as NO_x. The structures, properties and uses of these oxides are given in Table.

Table: Properties of some common oxides of nitrogen

Name and formula of oxide	Structure	Formal oxidation state	Properties	Uses
Nitrous oxide/ Nitrogen oxide (Laughing gas) N_2O	:N≡N—Ö:	1+	Colourless gas, water-soluble, neutral, sweet smelling, helps in combustion.	Dental anaesthetic, propellant for whipped ice cream, synthesis of NaN_3.
Nitic oxide, Nitrogen dioxide NO, N_2O_2	:N≡Ö 	2+	Colourless gas, slightly water-soluble, neutral, NO is paramagnetic while N_2O_2 is diamagnetic, oxidizing as well as reducing in nature.	Biochemical messenger (Lowers blood pressure and role in other body functions), synthesis of nitrosyl carbonyls.
Nitrogen dioxide/Nitrogen peroxide, Nitrogen tetraoxide NO_2, N_2O_4 $2NO_2 \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4$ (Brown, Colourless)		4+	NO_2 is a reddish brown gas, paramagnetic, and reacts with water to form HNO_3 and HNO_2, N_2O_4 is colourless liquid or solid.	Rocket propellant, HNO_3 formation by Ostwald process, explosives.

Did You Know?
Name of Ammonia by IUPAC:
Another recommended name for ammonia by the International Union of Pure and Applied Chemistry (IUPAC) is **Azane** and for ammonium is **Azanium**. These names have been derived from Azote, a Greek name for nitrogen, meaning "no life". These names are used in naming derivatives of ammonia and ammonium e.g. sodium azide (NaN_3).

Rack Your Mind!
2. Peroxy acetyl nitrate (PAN) is an irritant to human being and it effects:
A) Ears B) Stomach
C) Eyes D) Nose

SOURCES OF OXIDES OF NITROGEN

The main categories of NO_x sources are:

Natural Sources of NO_x

Natural sources include lightning, volcanoes, biological decay, forest fires, soil microorganisms, oceans, etc. NO is produced when N_2 and O_2 in the air react during lightning. It is produced by microorganism using air N_2.

Anthropogenic (Man-made) Sources of NO_x

The main anthropogenic sources of NO_x are the combustion of fossil fuels in vehicles and power plants. Other sources include chemical plants, biomass burning, welding, etc.

ROLE OF NO & NO₂ IN SMOG & PAN FORMATION

(Exercise L.Q.4)

Q. How oxides of nitrogen (NO_x) cause the formation of photochemical smog and PAN? Give its mechanism.

NO_x is responsible for numerous harmful effects on living organisms.

Photochemical Smog

Photochemical smog (Los Angeles smog) forms in the atmosphere from NO_x and volatile organic compounds (VOCs) in the sunlight. It is oxidizing in nature. Photochemical oxidants, such as NO_2, ozone, and peroxyacyl nitrates (PANs) can react and oxidise specific compounds in the atmosphere. Photochemical smog is becoming more common than classical smog (London smog) due to increasing NO_x emissions.

Did You Know?
Lahore smog consists of volatile organic compounds (VOCs), NO_x, ground level ozone (O_3), particulate matter PM 2.5, CO and SO_2.

Rack Your Mind!
3. The yellow colour in photochemical smog is due to:
A) NO B) NO_2
C) N_2O D) N_2O_5

Chemical Reactions:

The formation of photochemical smog involves the following chemical reactions.

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$$
$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$
$$NO_{2(g)} \xrightarrow{h\nu} NO_{(g)} + O_{(g)}$$
$$O_{(g)} + O_{2(g)} \longrightarrow O_{3(g)}$$
$$RCH=CHR_{(g)} + O_{3(g)} \longrightarrow RCO^{\cdot}_{3(g)} + RCH^{\cdot}_{2(g)} \longrightarrow RC(O)OONO_2$$

Alternate Reactions
$RCH=CHR + O_3 \longrightarrow 2RCHO + O_2$
$RCHO + OH^{\cdot} \longrightarrow RC(O)O^{\cdot} + H_2O$
$RC(O)O^{\cdot} + NO_2 \longrightarrow RC(O)OONO_2$

Formation of Peroxyacyl Nitrates (PANs)

NO_x take part in a series of reactions leading to the formation of ozone (O_3), aldehydes, peroxyacyl nitrates (PANs) and peroxybenzoyl nitrate (PBN). PAN is one of the members of peroxyacyl nitrates as shown in Figure.

Rack Your Mind!
4. Mention the conditions which are required for the formation of smog?

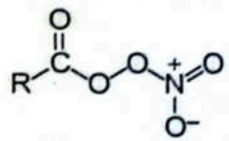


Figure: General structure of PANs

Rack Your Mind!
5. Differentiate between oxidizing and reducing smog.

The R group in peroxyacetyl nitrate is $-CH_3$, but other hydrocarbon chains may also be present.

➤ **Formation of PAN:**

The main component of oxidizing smog is ozone, which oxidizes hydrocarbon to produce aldehyde. The aldehyde then reacts with hydroxyl radical to produce acyl radical. The acyl radical reacts with oxygen to produce peroxyacyl radical, which finally reacts with nitrogen peroxide to form peroxyacyl nitrate.

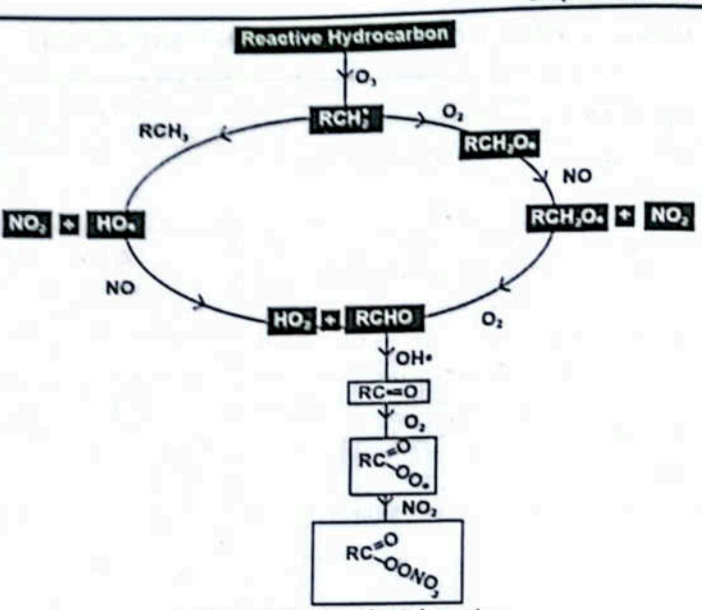


Figure: Mechanism of PAN formation

QUICK CHECK 12.2

a) Draw the structures of the following oxides of nitrogen. Also, briefly explain their bonding.

i) N_2O ii) NO iii) NO_2

Ans.

(i) N_2O (Nitrous oxide / Laughing gas)

Structure:

[N = N = O ⟶ N ≡ N—O]

Dinitrogen Oxide, N_2O (nitrous oxide)

Or :N ≡ N^+ – O^- (linear molecule)

Bonding explanation:

- N_2O is linear, with a triple bond between the two nitrogen atoms and a coordinate bond to oxygen.
- It has resonance forms, and the terminal nitrogen carries a positive charge, while oxygen has a negative charge.

(ii) NO (Nitric oxide)

Structure:

:N = O:

Nitrogen Oxide, NO (nitric oxide)

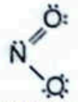
Or N = $O^{\bullet}$ (linear with one unpaired electron)

Bonding explanation:

- NO is a diatomic, linear molecule with a double bond and one unpaired electron, making it a free radical.
- It is paramagnetic due to this lone unpaired electron.

(iii) NO_2 (Nitrogen dioxide)

Structure:



Nitrogen dioxide, NO_2 (nitrogen peroxide)

Or O = N – $O^{\bullet}$ (bent molecule, 134°)

Bonding Explanation:

- NO_2 is angular (bent) and also a free radical with one unpaired electron. It has resonance structures and is paramagnetic due to the unpaired electron.

b) What does PAN stand for? Give its general formula.

Ans.

- PAN stands for Peroxyacetyl Nitrate. It is a toxic compound found in photochemical smog.
- Its general formula is $CH_3C(O)OONO_2$. It irritates eyes and affects plants and human health.

c) Write down the formulas of the compounds responsible for the formation of PAN.

Ans. PAN is formed from the reaction of the following compounds:

- Hydrocarbons (RH) → R – CHO (aldehydes)
- Nitrogen oxides (NO and NO_2)
- Oxygen (O_2) and sunlight

These react to form peroxyacyl radicals and then PAN.

d) If magnesium ribbon is ignited and placed in a jar containing N_2O, it continues to burn brightly, how does the product form in this reaction confirm the structure of N_2O?

Ans. When magnesium burns in N_2O, it produces magnesium oxide (MgO) and nitrogen gas (N_2). This reaction proves N_2O contains oxygen, as the flame is sustained by O release, confirming its structure N ≡ N^+ – O^-.

CATALYTIC CONVERTER

- A catalytic converter is a ceramic or metallic monolith with a honeycomb-like structure (as shown in Figure).
- Its inner channels have a layer of alumina to provide a high surface area.
- Noble precious (expensive) metals such as Pt (Platinum), Pd (Palladium), and Rh (Rhodium) are dispersed on the alumina.
- These metals catalyze three redox reactions to remove the half harmful exhaust gases.
- The three-way converter converts harmful CO, NO, and hydrocarbons into CO_2, N_2, and water.
- These precious metals can also be recycled.

Figure: Three-way Catalytic Converter

Reduction: $2NO_{(g)} + 2CO_{(g)} \xrightarrow{Pt/Rd} N_{2(g)} + 2CO_{2(g)}$

Oxidation: $2CO_{(g)} + O_{2(g)} \xrightarrow{Pt/Rh} 2CO_{2(g)}$

$2C_2H_6 + 6O_{2(g)} \xrightarrow{Pt/Rd} 4CO_{2(g)} + 4H_2O_{(g)}$

> **Rack Your Mind!**
>
> **6. What is the primary function of a catalytic converter in an automobile?**
>
> A) Increase engine
> B) Improve fuel efficiency
> C) Reduce harmful emissions
> D) Enhance vehicle speed

> **Rack Your Mind!**
>
> **7. What is catalytic convertor?**

> **Rack Your Mind!**
>
> **8. Which of the following gases are primarily reduced or oxidized by a catalytic converter?**
>
> A) Carbon dioxide, oxygen, and nitrogen
> B) Methane, ammonia, and hydrogen
> C) CO, nitrogen oxides, and hydrocarbons
> D) Sulphur dioxide, ozone, and water vapour

NITRIFICATION AND DENITRIFICATION

- Nitrification and denitrification are the two phases of the nitrogen cycle.
- Nitrification involves the conversion of ammonium (NH_4^{1+}) to nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}), while denitrification involves the conversion of nitrate (NO_3^{1-}) to Nitrogen (N_2).
- These two processes are also involved in the wastewater treatment to remove nitrogen. Some differences between nitrification and denitrification are given in Table.

Table: Differences between Nitrification and Denitrification

Nitrification	Denitrification
In nitrification Ammonia ion (NH_4^{1+}) is converted into nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}).	Nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}) are converted back to N_2 that is released into the atmosphere.
Nitrifying bacteria aerobic conditions, pH 6.5 – 8.0, optimum temperature 20°C – 30°C.	Denitrifying bacteria anaerobic conditions, pH 7.0 – 9.0, optimum temperature 26°C – 38°C.
Plants absorb these nitrites and nitrates for their nutrition as they cannot assimilate nitrogen directly from the atmosphere.	It is important in wastewater treatment and useful for aquatic life, to oxidize NH_4^+ with NO_2^- to form N_2 gas.
Oxidation of nitrogen $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ $2NH_{4(aq)}^{1+} + 3O_{2(aq)} \rightarrow 2NO_{2(aq)}^{1-} + 4H_{(aq)}^+ + 2H_2O_{(l)}$ $2NO_{2(aq)}^{1-} + O_{2(aq)} \rightarrow 2NO_{3(aq)}^{1-}$	Reduction of nitrogen $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$ $2NO_{3(aq)}^{1-} + 10e^- + 12H_{(aq)}^+ \rightarrow N_{2(g)} + 6H_2O_{(l)}$

☑ QUICK CHECK 12.3

a) **Write down the reduction and oxidation reactions that occur in the catalytic converter in the vehicle exhausts.**

Ans. These metals catalyze three redox reactions to remove the half harmful exhaust gases. The three-way converter converts harmful CO, NO, and hydrocarbons into CO_2, N_2, and water. These precious metals can also be recycled.

Reduction: $2NO_{(g)} + 2CO_{(g)} \longrightarrow N_{2(g)} + 2CO_{2(g)}$

Oxidation: $2CO_{(g)} + O_{2(g)} \xrightarrow{Pt/Rh} 2CO_{2(g)}$

$2CH_{4(g)} + 6O_{2(g)} \xrightarrow{Pt/Rd} 4CO_{2(g)} + 4H_2O_{(g)}$

b) **What is the basic principle of catalytic converter? Describe the role of catalyst in the catalytic converter.**

Ans. These metals catalyze three redox reactions to remove the half harmful exhaust gases. The three-way converter converts harmful CO, NO, and hydrocarbons into CO_2, N_2, and water. These precious metals can also be recycled.

c) **Do hybrid and electric cars have catalytic converters? Explain why or why not.**

Ans. **Hybrids:** Yes, because they still use gasoline engines that produce emissions.

Electric cars: No, since they run on batteries and produce no exhaust gases to treat.

SULPHUR

Sulphur is a member of group 16 which is also called the Chalcogen family. Some physical properties of sulphur are listed in Table.

Table: Physical properties of Sulphur

Atomic number	16	Ionic radius	184 pm
Relative atomic mass	32.06 a.m.u.	1st Ionization energy	1000 kJ/mol
Physical appearance	Solid Yellow	Electronegativity	2.5
Electronic configuration	$[Ne]3s^2 3p^4$	Electron affinity	–200 kJ/mol
Melting point	113°C (honey yellow)	Density	$2.07\ g/cm^3$
Boiling point	445°C (dark brown)	Common oxidation states	4+ and 6+
Covalent radius	104 pm	Common Bonding	Covalent bond

Reactivity of Sulphur

Sulphur usually forms single bonds with other sulphur atoms instead of double bonds due to poor overlapping of the orbitals. As a result, it forms larger molecules and structures through a process called catenation. S_8 is a crown-like molecule, as shown in Figure 12.7.

Oxidation States of Sulphur

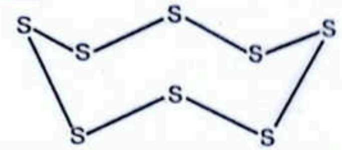


Figure: Cyclo-octasulphur, (S_8) crown molecule

Sulphur exhibits oxidation states of –2, 0, +2, +4, and +6. The electronic configuration of sulphur is depicted in Figure, where the oxidation state is determined by the number of unpaired electrons. Under standard conditions, sulphur and oxygen react to produce Sulphur dioxide (SO_2) in which sulphur has an oxidation state of +4. However, to form sulphur trioxide (SO_3) with an oxidation state of +6, high energy is required.

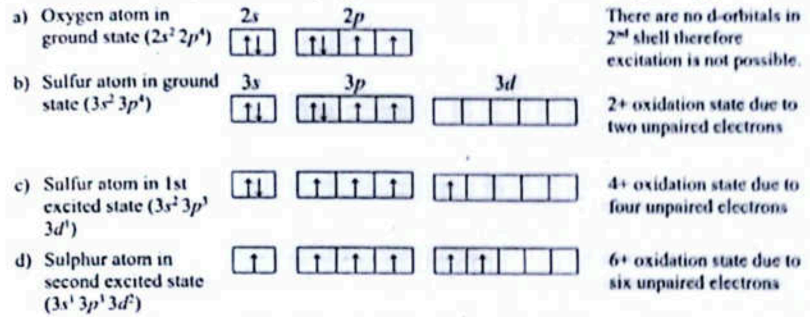


Figure: Electronic configurations of sulphur for attaining different oxidation states

STABILITY OF OXIDATION STATES OF SULPHUR

Sulphur displays a range of oxidation states, principally from -2 to +6. The stability of these states is influe[illegible] by the factors like pH, temperature, nature of the compound and the chemical environment.

pH

In general, under acidic conditions, reduced forms (like H2S, -2 oxidation state) are more stable, while under basic or neutral conditions, oxidized forms (like SO_4^{2-}, +6 oxidation state) become more stable in water.

Thermodynamics and Kinetics

Although Sulphur (+6), as in SO_3, is thermodynamically the most stable, kinetic limitations can prevent it from forming readily at standard temperatures, making Sulphur (+4), as in SO_2, the more frequent form.

Nature of the Compound

The stability of Sulphur's oxidation state can be affected by the elements it is bonded to, and the overall chemical environment. In acidic environment SO_4^{2-} is kinetically stable due to strong O-S bonds.

Catalyst

A catalyst can also enhance the rate of formation of a specific oxidation state, for example vanadium in the contact process increases the rate of formation of SO_3.