# Organic Chemistry

## Introduction to Organic Chemistry

Organic compounds are vital for sustaining life on earth and include complex molecules such as the genetic information-bearing deoxyribonucleic acid (DNA) and proteins that constitute essential components of our blood, skin, and muscles. Organic chemicals are used to synthesise materials such as clothing, fuels, polymers, dyes, and medicines.

Around the year 1780, scientists began to distinguish organic compounds obtained from plants and animals and inorganic compounds prepared from mineral sources. A Swedish chemist, Berzelius, proposed that a ‘vital force’ was responsible for the formation of organic compounds. However, this notion was rejected in 1828 when F.

Wohler synthesised an organic compound (urea) from an inorganic compound (ammonium cyanate). The pioneering synthesis of acetic acid by Kolbe (1845) and that of methane by Berthelot (1856) showed conclusively that organic compounds could be synthesised from inorganic sources in the laboratory.

As we know that carbon has a unique tendency of catenation, it binds with itself via a series of covalent bonds. This is the basis of organic chemistry.

The number of carbon compounds is so vast that there is one branch of chemistry dedicated only to the study of carbon and its compounds. This branch is known as **organic chemistry.**

Organic chemistry is a discipline within chemistry, which involves scientific study of structure, properties, composition, reactions, and synthesis of compounds containing carbon. These compounds can also contain nitrogen, sulphur, and halogens. The source of these organic compounds is widely spread in nature. Sources of some of the important organic compounds are given in the table below:

| Source | Organic Compound Obtained From Source |
|---|---|
| Plants | Sugar, starch, cellulose, drugs |
| Animals | Urea, proteins, fats |
| Coal | Benzene, toluene, naphthalene, dyes, drugs, perfumes |
| Petroleum | Gasoline, fuel gases, petrol, naphtha |
| Fermentation | Ethyl alcohol, acetic acid |
| Wood | Methyl alcohol, acetone |

### How carbon binds with itself?

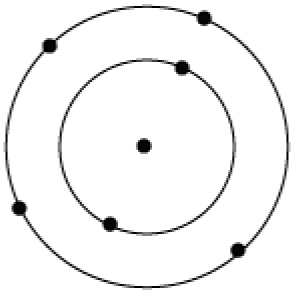
Carbon is a major part of all living things. In the air, it is present as carbon dioxide and comprises around 0.03% of the total atmosphere.

Carbon exhibits two important properties − catenation & tetravalency.

Carbon can combine with other atoms of carbon to form long chains and rings. These chains and rings are not only long but also very stable. This is because carbon can form strong single, double, and triple bonds with other atoms of carbon.

Carbon is a non-metal having the symbol '**C**' and atomic number **six**. Since the atomic number of carbon is six, its electronic configuration is 2, 4. This means that carbon contains two electrons in K-shell and 4 electrons in L-shell (outermost shell). Hence, it has four electrons in its valence shell.

Since carbon has four electrons in its valence shell, it requires four more electrons to complete its octet. Therefore, it is a tetravalent element.



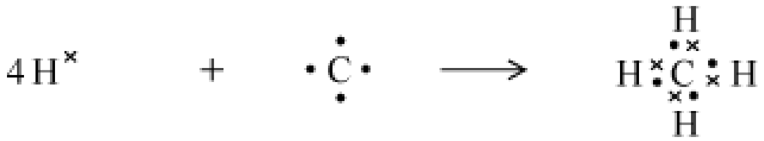
In order to complete its octet i.e., to attain the noble gas configuration and to stabilise itself, carbon can:

- Either lose four electrons to form $\mathbf{C^{4+}}$ or gain four electrons to form $\mathbf{C^{4-}}$. This, however, requires a lot of energy and would make the system unstable.
- Therefore, carbon completes its octet by sharing its four electrons with the other carbon atoms or with atoms of other elements.

**The bonds that are formed by sharing electrons are known as covalent bonds. Covalently bonded molecules have strong intermolecular forces, but intramolecular forces are weak.**

Carbon has four valence electrons and requires four more electrons to complete its octet. Therefore, it is capable of bonding with four other atoms of carbon or atoms of other elements having a valency of 1.

For example, the simplest molecule (methane) can be formed with hydrogen (H) atoms that have only one electron in their K-shell. To attain the noble gas configuration, carbon combines with four hydrogen atoms as shown in the figure.



**Characteristics of organic compounds:** Organic compounds show the following characteristics.

- They are compounds of carbon.
- They can exist in all three states i.e., solid, liquid, and gas.
- They are covalent compounds.
- They are soluble in organic solvents.
- They are poor conductors of electricity.
- They are volatile and flammable.

**Classification of organic compounds:** Organic compounds can be classified into the following categories:

**On the basis of structure**

- Open chain or aliphatic compounds.
- Closed chain or cyclic compounds.

**On the basis of ring system**

- Carbocyclic or homocyclic compounds have a ring comprising only of carbon atoms.
- Heterocyclic compounds contain other elements besides carbon in the ring.

## Organic Compounds - Shapes and Structures

- A Swedish chemist named Berzilius proposed the vital force theory, according to which a vital force existing in living organisms is responsible for the formation of oranic compounds.

  However, this was proved to be incorrect when F. Wohler, a German chemist synthesised urea- an organic compound from ammonium cyanate, an inorganic compound.

- **Shape of carbon compounds**

  $CH_4 \longrightarrow sp^3$ hybridised carbon
  Methane
  $C_2H_4 \longrightarrow sp^2$ hybridised carbon
  Ethene
  $C_2H_2 \longrightarrow sp$ hybridised carbon
  Ethyne

- *sp* orbital has 50% '*s*' character. Thus, an *sp* hybridised carbon is more electronegative than an $sp^2$ (33% s character) or $sp^3$ (25% s-character) hybridised carbon.

- Hybridisation influences the bond length and bond enthalpy.

**Some Characteristic Features of π-Bonds**

- Parallel orientation of two *p*-orbitals on adjacent atoms is necessary for a proper sideways overlap to form π-bond.

- Rotation about C = C double bond is restricted.

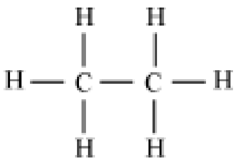
- Electron charge cloud of π-bond is located above and below the plane of bonding atoms.

- Electrons are easily available to attacking reagents.

**Structural Representations of Organic Compounds**

- **Complete Structural Formula**

Examples:

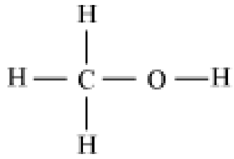


$$H_3C-CH_3 \quad (\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{H})$$

Ethane

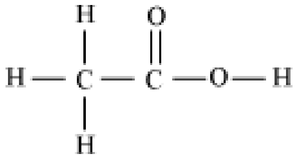
$H-C\equiv C-H$

Ethyne



$$\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{O}-\text{H}$$

Methanol



$$\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-\text{H}$$

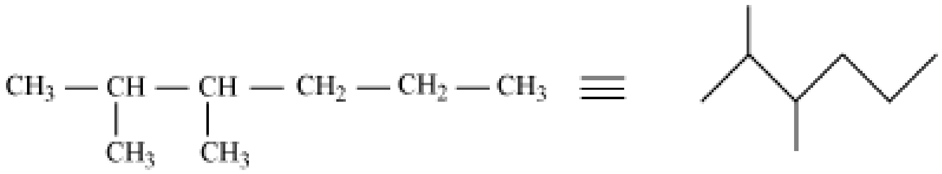
Acetic acid

- **Condensed Structural Formula**

  (Structural formula obtained by omitting some or all of the dashes representing covalent bonds and then using a subscript to indicate the number of identical groups attached to an atom)

| $CH_3CH_3$ | $HC\equiv CH$ | $CH_3OH$ | $CH_3COOH$ |
|---|---|---|---|
| Ethane | Ethyne | Methanol | Acetic acid |

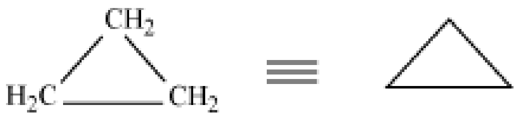
- **Bond-Line Structural Formula**
- Only lines are used to represent the structure of organic compound.
- Carbon and hydrogen atoms are not shown.
- Lines representing the C − C bonds are drawn in a *zig-zag* fashion.
- For example − bone-line formula of 2,3-dimethylhexane can be represented as

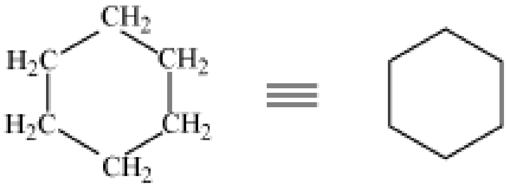


$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3 \equiv$$

(Terminals represent methyl groups)

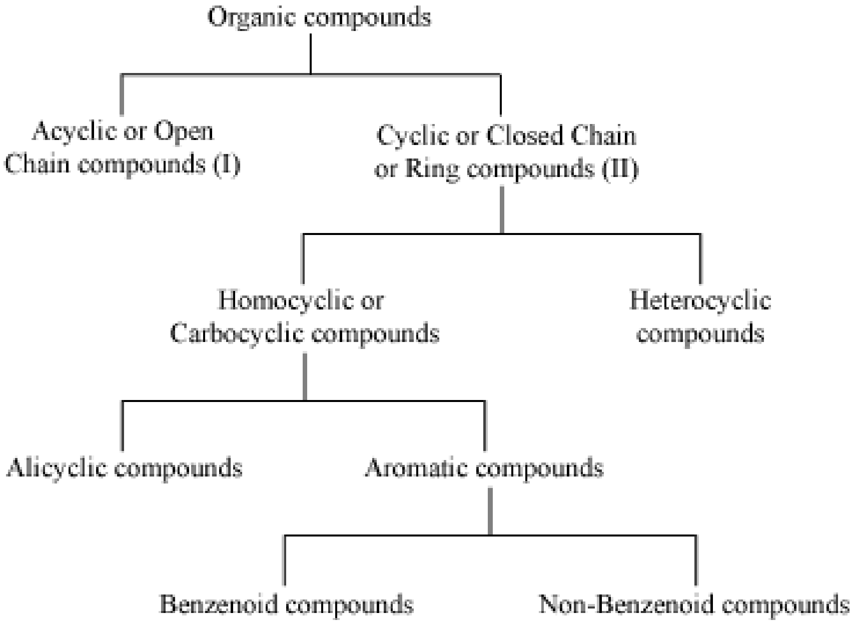
- In cyclic compounds,





To test your knowledge of this concept, solve the following puzzle.

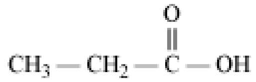
## Classification of Organic Compounds



(I) Acyclic or open chain compounds consist of straight or branched chain compounds.

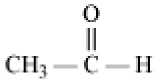
$CH_3CH_3$

Ethane



$CH_3-CH_2-C(=O)-OH$

Propanoic acid



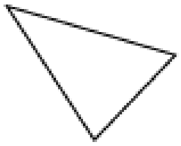
$CH_3-C(=O)-H$

Acetaldehyde

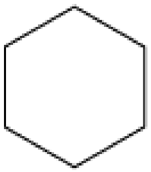
$CH_3-CH=CH_2$

Propene

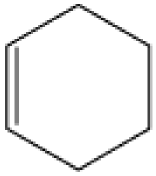
(II) Alicyclic or closed chain or ring compounds contain carbon atoms joined in the form of a ring (homocyclic). In some rings (heterocyclic), atoms other than carbon are present.



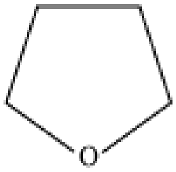
Cyclopropane



Cyclohexane



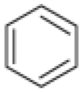
Cyclohexene



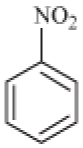
Tetrahydrofuran

### Aromatic Compounds

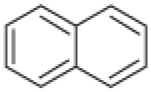
- Benzenoid aromatic compounds (include benzene and other related compounds)



Benzene

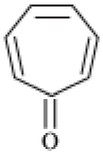


Nitrobenzene



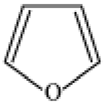
Naphthalene

- Non-benzenoid compounds (do not contain benzene ring)

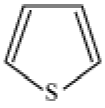


Tropolone

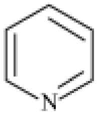
- Heterocyclic aromatic compounds



Furan



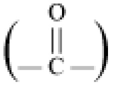
Thiophene



Pyridine

### Functional Group

- An atom or group of atoms joined in a specific manner which is responsible for the characteristic chemical properties of the organic compound.

- Examples: Hydroxyl group (− OH), carboxylic acid group (− COOH), aldehyde group (−CHO), ether group (−O−), ketone group  $\left(-\overset{O}{\overset{\|}{C}}-\right)$, etc.

### Homologous Series

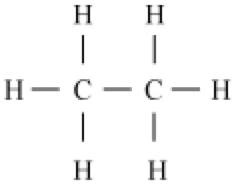
- A group or a series of organic compounds each containing a characteristic functional group.
- The members of the series are called homologues.
- Successive members differ from each other in a molecular formula by a $-CH_2$ unit.
- Alkanes, alkenes, alkynes, alkanoic acids, amines, etc. represent homologous series.

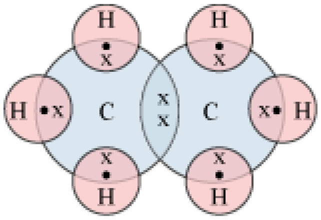
## Saturated and Unsaturated Compounds

### Saturated compounds:

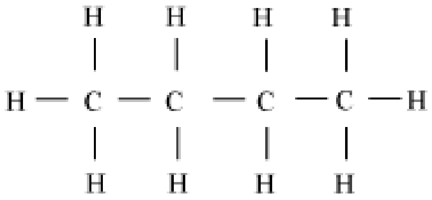
- The compounds of carbon having only single bonds between the carbon atoms are called saturated compounds.

For example, a molecule of ethane ($C_2H_6$) contains one single bond between the carbon atoms.





Similarly, butane ($C_4H_{10}$) can exist in two different structures, **I** and **II**. Both these structures contain three single bonds between the carbon atoms.



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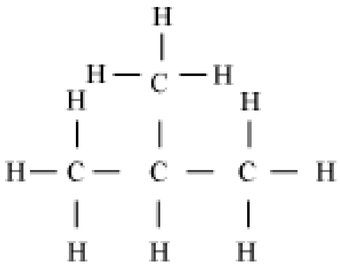
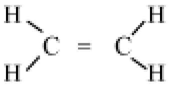


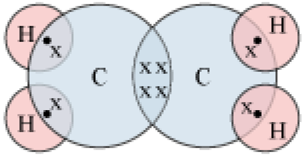
II

**Unsaturated compounds:**

- The compounds of carbon having double and triple bonds between the carbon atoms are called unsaturated compounds.

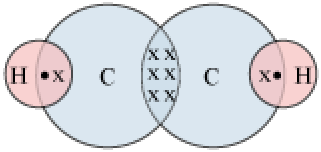
For example, ethene is an unsaturated compound containing one double bond between the carbon atoms.





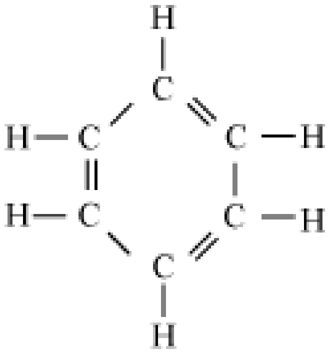
Similarly, ethyne is an unsaturated compound containing one triple bond between the carbon atoms.

$$H-C\equiv C-H$$



**The chains, branches, and rings that carbon forms by forming bonds with it can be saturated as well as unsaturated.**

For example, benzene is a six-member ring that contains three double bonds. Thus, it is an unsaturated hydrocarbon

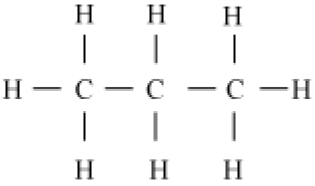


## Organic compounds and Homologous Compounds

The number of carbon compounds is so vast that there is one branch of chemistry dedicated only to the study of carbon and its compounds. This branch is known as **organic chemistry.**

**The compounds of carbon having only single bonds between the carbon atoms are called saturated compounds and those that contain a double or a triple bond between any two carbon atoms are known as unsaturated compounds.**

For example, a molecule of propane ($C_3H_8$) contains two single bonds between the carbon atoms.



There are two main groups of hydrocarbons:

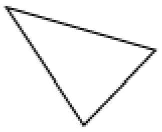
**Aliphatic hydrocarbons:**

- They are derived from fossil fuels.
- They are those hydrocarbons which possess straight chain or branched chain structures.
- They are grouped as:
- Alkanes: The general formula of alkanes is $C_nH_{(2n+2)}$, n = number of carbon atoms.
- They contain only single bonds between all the carbon atoms present in a given molecule of an alkane.
- For example, methane ($CH_4$), ethane ($C_2H_6$) etc.
- Alkenes: The general formula of alkenes is $C_nH_{2n}$, where n = number of carbon atoms
- They contain at least one carbon − carbon double bond.
- For example, ethene ($C_2H_4$), propene ($C_3H_6$) etc.

- Alkynes: The general formula of alkynes is $C_nH_{(2n-2)}$, where n = number of carbon atoms
- They contain at least one carbon-carbon triple bond.
- For example, ethyne ($C_2H_2$), propyne ($C_3H_4$) etc.

**Alicyclic saturated hydrocarbons:**

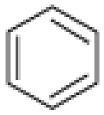
- They are those saturated hydrocarbons in which the carbon atoms form a ring.
- Their general formula is similar to that of alkenes ($C_nH_{2n}$).
- For example, cyclopropane



Cyclopropane

**Aromatic hydrocarbons:**

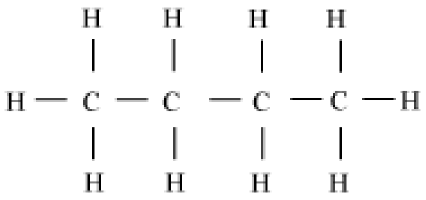
- Members of this group have a characteristic odour.
- First recognised aromatic hydrocarbon is Benzene ($C_6H_6$)



Benzene

- Benzene is a good organic solvent, which is used in the preparation of dyes, medicines, perfumes etc.

Consider, a molecule of butane ($C_4H_{10}$) contains three single bonds between the carbon atoms.



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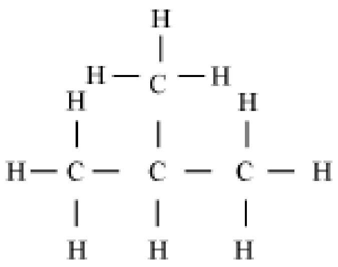


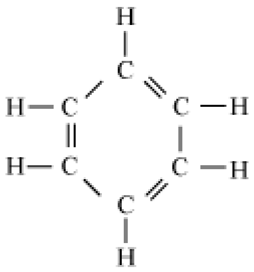
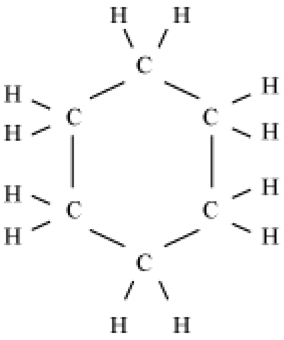
II

You must have noticed that these structures have carbon atoms linked to each other in a repeated manner. Such structures are called **Chain structures** and compounds exhibiting such structures are known as **aliphatic compounds**.

**Do you observe anything in the structure of butane?** The carbon atoms can be linked in two different ways (**I** and **II**). While **I** is a chain structure, **II** is a branched structure. Both have the same chemical formula, but they differ in their structures. Such compounds are called **Structural isomers.**

Carbon atoms in a molecule cannot only be linked in a chain or branch form, but these can also be arranged in a ring. For example, benzene, cyclohexane etc.

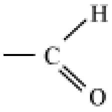
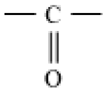
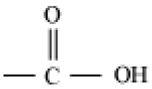
Benzene is a six-member ring that contains three double bonds. Thus, it is an unsaturated hydrocarbon. On the other hand, cyclohexane has only single bonds. Hence, it is a saturated compound.

|  |  |
|---|---|
| **Structure of benzene** | **Structure of cyclohexane** |

However, the organic compounds which contain at least one benzene ring are known as **aromatic compounds**. For example, benzene, toluene, xylenes etc.

Carbon not only bonds to carbon and hydrogen, but it can also bond to other atoms like halogens (Br, Cl, I, F), nitrogen, oxygen etc. Sometimes, the hydrogen attached to a carbon in a hydrocarbon can also be replaced by another atom. In such cases, the replacing atom is called a **heteroatom**. A single atom or a group of atoms, which on bonding with a hydrocarbon, modifies the properties of the compound, is referred to as a **functional group**.

| **Heteroatom** | **Functional group** | **Formula of functional group** |
|---|---|---|

| | | |
|---|---|---|
| Cl/Br | Halo- (Chloro / bromo) | —Cl, —Br (substitutes for hydrogen atom) |
| Oxygen | Alcohol | $-OH$ |
| | Aldehyde |  |
| | Ketone |  $-\underset{\underset{O}{\Vert}}{C}-$ |
| | Carboxylic acid |  $-\overset{\overset{O}{\Vert}}{C}-OH$ |

Thus, we see that carbon atoms can be linked to each other, or to hydrogen atoms, or to functional groups. In addition, the functional groups can change their properties.

However, it was noticed that the properties of $CH_3OH$, $C_2H_5OH$, and $C_3H_7OH$ are very similar. **Can you tell why?** This is because they form a part of the Homologous series.

Organic compounds that have similar general formula belong to a series called **homologous series**. The chemical properties of the compounds in the series are the same because of the presence of the same functional group. Therefore, the organic compounds containing same functional group are tested using same identification tests.

On the other hand, the organic compounds with different functional groups will have different physical and chemical properties, hence different identification tests are needed to identify them.

Alkanes, alkenes, and alkynes form such series in which members differ in mass by 14 atomic mass units. For example, the alkane homologous series contains methane ($CH_4$), ethane ($C_2H_6$), propane ($C_3H_8$), butane ($C_4H_{10}$), and pentane ($C_5H_{12}$) as its members. Each member differs from the previous one by a $CH_2$ group (or 14 atomic mass units).

Let us see the first four members of the alkane family.

| Name | Molecular Formula |
|---|---|
| Methane | $CH_4$ |
| Ethane | $CH_3CH_3$ |
| Propane | $CH_3CH_2CH_3$ |
| Butane | $CH_3CH_2CH_2CH_3$ |

Thus, it is seen that any two consecutive members differ by a common difference of $CH_2$ group. Hence, any two consecutive members differ in mass by 14 units.

Similarly, in alcohol homologous series, we have methanol ($CH_3OH$), ethanol ($C_2H_5OH$), isopropanol ($C_3H_7OH$), and butanol ($C_4H_9OH$).

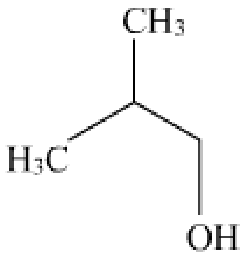
Organic compounds show an interesting phenomenon called **STRUCTURAL ISOMERISM**. This phenomenon is shown by organic compounds with same molecular formula but different structural formula. These compounds are called **ISOMERS**. They have different properties from one another.

Structural isomerism arises due to the difference in the arrangement of atoms within the molecule. Types of isomerism:

**a) Chain/ skeletal/ nuclear isomerism**:

- In this type, there is a difference in the structure of the carbon chain that forms the nucleus of the molecule. For example:

*n*-butyl alcohol



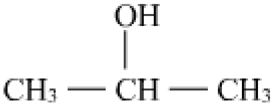
Isobutyl alcohol

**b) Position isomerism:**

- It arises due to the difference in the position of the functional group, the carbon-carbon multiple bonds or the substituent group. For example:

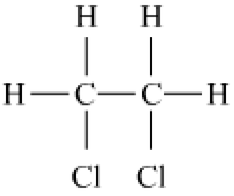
$CH_3 - CH_2 - CH_2 - OH$

*n*-propyl alcohol



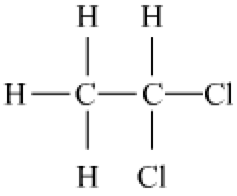
$$\begin{array}{c} \quad\; OH \\ \quad\; | \\ CH_3 - CH - CH_3 \end{array}$$

Isopropyl alcohol



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & Cl & & Cl & & \end{array}$$

1, 2-dichloroethane



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & Cl \\ & & | & & | & & \\ & & H & & Cl & & \end{array}$$

1, 1-dichloroethane

**c) Functional group isomerism:**

- It arises by virtue of the presence of different functional groups. For example:

$CH_3CH_2OCH_2CH_3$ diethyl ether

$CH_3CH_2CH_2CH_2OH$ *n*-butyl alcohol

**d) Metamerism:**

- In this type, there is a difference in the number of carbon atoms on either side of the functional group. For example:

$CH_3 - O - C_3H_7$ methyl propyl ether

$CH_3\,CH_2 - O - CH_2\,CH_3$ diethyl ether

## IUPAC Nomenclature of Carbon Compounds

Earlier, various organic compounds were known by their common names. However, the number of organic compounds increased at such a rapid pace that it became important to devise a method to name them scientifically to allow the scientists in every part of the world to understand their molecular formula. Hence, the **International Union of Pure and Applied Chemistry (IUPAC)** devised rules to name organic compounds.

In this system of nomenclature, the names are correlated with the structures such that the learner can deduce the structure from the name. However, before the IUPAC system of nomenclature, organic compounds were assigned trivial or common names based on their origin or certain properties. For instance, citric acid is named so because it is found in citrus fruits. Also, the acid found in red ant is named formic acid since the Latin word for ant is '*formica*'.

**Common or trivial names of some organic compounds**

| **Compound** | **Common name** |
|---|---|
| $CH_3COOH$ | Acetic acid |
| $CHCl_3$ | Chloroform |
| $CH_3COCH_3$ | Acetone |
| $(CH_3)_2CHCH_3$ | Isobutane |
| $C_6H_6$ | Benzene |

The naming of various compounds of carbon can be done as follows:

1. **The longest continuous chain of carbon atoms should be identified first.** This chain may or may not be a straight chain.

The base name of an organic compound depends upon the number of carbon atoms present in the chain. A compound having only one carbon atom starts with ‘meth-’, two carbon atoms start with ‘eth-’, and so on. The list of base names for one to ten carbon atoms is given in the following table.

| **Number of carbon atoms** | **Base or root name** |
|---|---|
| 1 | Meth- |
| 2 | Eth- |
| 3 | Prop- |
| 4 | But- |
| 5 | Pent- |
| 6 | Hex- |
| 7 | Hept- |
| 8 | Oct- |
| 9 | Non- |
| 10 | Dec- |

**Base names according to the number of C atoms**

**2. The presence of a functional group is indicated by adding either a suffix or prefix to the base or root name.**

If a hydrocarbon contains no double or triple bonds i.e., the hydrocarbon is saturated, then it is known as **alkane** and the suffix **‘-ane’** is added to the base word.

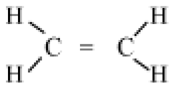
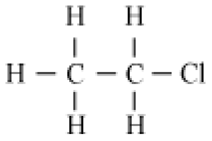
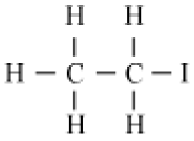
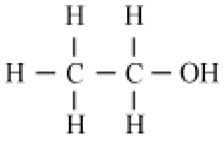
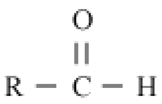
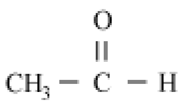
Therefore, $CH_4$ becomes methane and $CH_3CH_3$ become ethane.

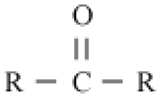
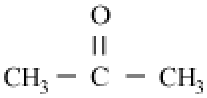
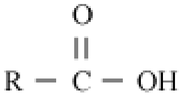
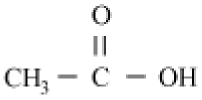
If a compound contains one or more double bonds, then it is known as **alkene** and the suffix ‘-**ene’ i**s used.

If a compound contains one or more triple bonds, then it is called **alkyne** and the suffix **‘-yne’** is used.

Similarly, the presence of other functional groups is indicated by adding different suffixes or prefixes to the root word. The following table shows the list of functional groups along with the suffixes/prefixes used to indicate their presence.

**Prefixes/suffixes used to indicate different functional groups**

| **Functional group** | **General formula** | **Prefix/Suffix** | **Example** |
|---|---|---|---|
| Double bond | R=R | -ene | <br>Ethene |
| Triple bond | $R\equiv R$ | -yne | $H-C\equiv C-H$<br>Ethyne |
| Halogens | R–X<br>where, X = Cl, I, etc. | Halo- | <br>$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-Cl$<br>Chloroethane<br><br>$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-I$<br>Iodoethane |
| Alcohol | R–OH | -ol | <br>$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$<br>Ethanol |
| Aldehyde | <br>$R-\overset{O}{\overset{\parallel}{C}}-H$ | -al | <br>$CH_3-\overset{O}{\overset{\parallel}{C}}-H$<br>Ethanal |

| | | | |
|---|---|---|---|
| Ketone |  $R-\overset{\overset{O}{\|}}{C}-R$ | -one |  $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ Propanone |
| Carboxylic acid |  $R-\overset{\overset{O}{\|}}{C}-OH$ | -oic acid |  $CH_3-\overset{\overset{O}{\|}}{C}-OH$<br>Ethanoic acid |

If the last letter of a hydrocarbon is ‘e’ as in alkanes, then ‘e’ is deleted when the suffix for the functional group is added. For example, ‘e’ of pentane is deleted when the suffix ‘-one’ for the ketone group is added. Thus, we obtain pentanone from pentane and not pentaneone.

Hence, the name of each compound in a homologous series is based on the name of the basic carbon chain, modified by a prefix or a suffix, indicating the nature of the functional group.

Let us name a few compounds using IUPAC nomenclature.

**Functional groups:**

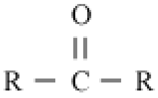
Functional groups are structural units within organic compounds that are defined by specific bonding arrangements between specific atoms.

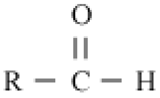
**Alcohol**

If one hydrogen atom of an alkane is displaced by hydroxyl group(-OH), then alcohol compound is obtained. General formula of alcohol is $C_nH_{2n+1}OH$. Hence, it is represented as R-OH where R stands for alkyl group.

**Aldehyde and Ketone**

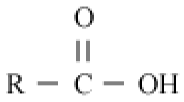
These are the functional groups containing carbonyl group. The carbon atom of carbonyl group is attached with one alkyl group and one hydrogen atom in case of aldehyde whereas, in case of a ketone carbon atom of carbonyl compound is attached with carbon atoms of two alkyl groups.


$R-\overset{\overset{O}{\|}}{C}-R$


$R-\overset{\overset{O}{\|}}{C}-H$

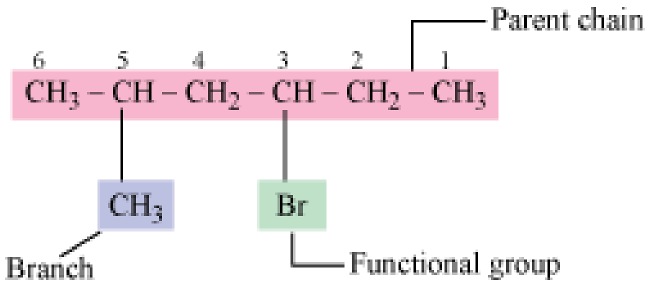
**Carboxylic acid**

Compounds having -COOH functional group are called carboxylic acid compounds.

Some of them are ethanoic acid and propanoic acid. Carboxylic acid containing compounds have "oic" suffix. The general formula of carboxylic acid is  $R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$.

A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it. See the example given below.

Let us try to name the following compounds.



**Step − I**: **Select the longest carbon chain.**

The longest possible chain of carbon atoms is picked and the compound is named as a derivative of this alkane.

**Step − II**: **Assign the lowest number to the side chain.**

The carbon chain selected is numbered from the end nearest to the side chain or the substituent so as to give the lowest number to the side chain.

**Step-III: Arrangement of prefixes**

In case more than one group is attached to the chain, these should be arranged alphabetically. Each substituent group is located on the parent chain by placing before it the number of carbon atom to which it is attached.

**Step-IV: Lowest number for functional group**

In case some functional group is present in the chain, the lowest number is given to it. The lowest number is given in the following order of preference:

To the principle functional group of the compound

To the double or triple bond

To the substituent atoms or groups designated by prefixes

Therefore, the IUPAC name of the above organic compound is 3-Bromo-5-methylhexane.

Conversely, using the IUPAC of an organic compound, it's structure can be determined. The following rules help in accomplishing the task:

**Step − I**: Identify the root word. It forms the carbon skeleton in the structure.

**Step − II**: Write the number of carbon atoms as per the root word and number them from any end.

**Step − III**: As per the suffix in the name, ascertain the type of bond present in the compound. If any multiple bond is present, place it between the carbon atoms as stated in the IUPAC name.

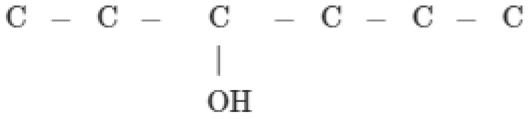
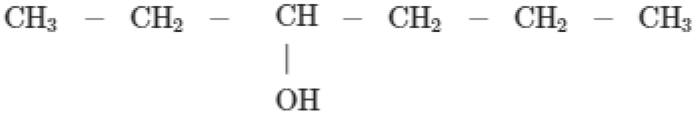
**Step − IV**: Place the substituents at the carbon atoms mentioned in the IUPAC name.

**Step − V**: Place the functional group at the designated carbon atom.

**Step − VI**: Complete the valencies of the remaining carbon atoms by attaching hydrogen atoms.

For example, consider the given IUPAC name of an organic compound:

Hexan-3-ol

| **Step** | **Rule** | **Structure** |
|---|---|---|
| I and II | Root word: Hexan<br>Carbon skeleton: 6 carbon atoms | C−C−C−C−C−C |
| III | Use suffix to identify type of bonds: All single bonds | C−C−C−C−C−C |
| IV | Place of substituents: No substituents | C−C−C−C−C−C |
| V | Place of functional group: At third carbon atom |  $C - C - \underset{\underset{OH}{\vert}}{C} - C - C - C$ |
| VI | Completion of valencies |  $CH_3 - CH_2 - \underset{\underset{OH}{\vert}}{CH} - CH_2 - CH_2 - CH_3$ |

## Preparation and Properties of Alkanes

**Alkanes**: As we already know, alkanes are the saturated hydrocarbons with all the valencies of the carbon atoms satisfied, having a general formula $C_nH_{2n+2}$ . The main source of alkanes is natural gas and petroleum. The following table gives the sources of some of the important alkanes:

| **Occurrence of Methane and Ethane** |
|---|
| Methane is the main constituent of marsh gas.<br>Methane is exhaled by animals that feed on food containing cellulose.<br>Methane is found in the intestinal gas of humans and animals.<br>Methane is found in cavities in coal.<br>Ethane occurs along with methane. |

### Preparation

- **From Unsaturated Hydrocarbons**

$$\underset{\text{Ethene}}{CH_2=CH_2}+H_2\xrightarrow{Pt/Pd/Ni}\underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{Propyne}}{CH_3-C\equiv C-H}+2H_2\xrightarrow{Pt/Pd/Ni}\underset{\text{Propane}}{CH_3-CH_2-CH_3}$$

- The process is called hydrogenation.
- Metals (Pt, Pd, and Ni) adsorb dihydrogen on their surfaces and activate H − H bond.
- **From Alkyl Halides**
- Reduction of alkyl halides (except fluorides) with zinc and hydrochloric acid

$$\underset{\text{Chloromethane}}{CH_3-Cl}+H_2\xrightarrow{Zn/HCl}\underset{\text{Methane}}{CH_4}+HCl$$

$$\underset{\text{1-Chloropropane}}{CH_3-CH_2-CH_2-Cl}+H_2\xrightarrow{Zn/HCl}\underset{\text{Propane}}{CH_3CH_2CH_3}+HCl$$

- **Wurtz reaction** − Alkyl halides on treatment with sodium in presence of dry ether give higher alkanes (containing an even number of carbon atoms).

$$CH_3Br \quad + \quad 2Na \quad + \quad BrCH_3 \xrightarrow{\text{dry ether}} CH_3-CH_3 \quad + \quad 2NaBr$$

Bromomethane Ethane

- **From Carboxylic Acids**
- **Decarboxylation** (i.e., elimination of $CO_2$) of sodium salts of carboxylic acids on heating with soda lime (mixture of NaOH and CaO) gives alkane. The alkanes thus obtained contain one carbon atom less than the carboxylic acid.

$$CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Sodium ethanoate Methane

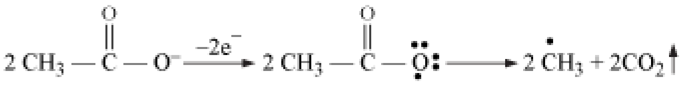
- **Kolbe's Electrolysis Method**

Electrolysis of an aqueous solution of sodium or potassium salt of a carboxylic acid gives alkane (containing an even number of carbon atoms) at the anode.

$$2CH_3CO\overset{-}{O}\overset{+}{N}a + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

Sodium acetate

**At Anode**



$$2\,CH_3-\overset{\overset{O}{\|}}{C}-O^- \xrightarrow{-2e^-} 2\,CH_3-\overset{\overset{O}{\|}}{C}-\ddot{\underset{\bullet}{O}}: \longrightarrow 2\,\dot{C}H_3 + 2CO_2\uparrow$$

Acetate ion Acetate free radical Methyl free radical

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3\uparrow$$

**At Cathode**

$$2H_2O + e^- \longrightarrow \overset{-}{O}H + \dot{H}$$

$$2\dot{H} \longrightarrow H_2\uparrow$$

**Important Note:** Methane cannot be prepared by this method.

**Physical Properties of Alkanes**

- Non-polar molecules
- Due to weak forces, members from $C_1$ to $C_4$ are gases, $C_5$ to $C_{17}$ are liquids, and those containing 18 carbon atoms or more are solids at 298 K.
- Colourless and odourless
- Soluble in non-polar solvents
- Hydrophobic in nature
- Boiling point increases with the increase in molecular mass.

**Question: Pentane having a continuous chain of five carbon atoms has a boiling point of 309.1 K whereas 2,2-dimethylpropane boils at 282.5 K though they have same molecular mass. Why?**

**Answer:**

When the number of branched chains increases, the molecule attains the shape of a sphere, which results in a smaller area of contact. As a result of this, there are weak intermolecular forces between spherical molecules which can be overcome at low temperatures. Hence the boiling point of pentane is higher than that of 2,2-dimethylpropane.

**Chemical properties of alkanes**

- **Combustion**

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta_c H^\ominus = -890\,\text{kJ mol}^{-1}$$

In general for alkanes,

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right) O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

Methane and ethane undergo complete combustion due to low carbon content and thus burn with a blue non-sooty flame.

- **Controlled Oxidation**

- Yield a variety of products on heating with regulated supply of air or dioxygen at high pressure and in the presence of suitable catalysts

$$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} \underset{\text{Methanol}}{2CH_3OH}$$

$$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} \underset{\text{Methanal}}{HCHO} + H_2O$$

$$2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} \underset{\text{Ethanoic acid}}{2CH_3COOH} + 2H_2O$$

$$2\,C_2H_6 + O_2 \xrightarrow[\text{Cu Tube, 475 K}]{\text{120 atm}} \underset{\text{Ethanol}}{2\,C_2H_5\,OH}$$

$$C_2H_6 + O_2 \xrightarrow{MoO} \underset{\text{Acetaldehyde}}{CH_3\,CHO} + H_2O$$

$$C_2H_5\,OH + O_2 \xrightarrow[300\,^\circ C]{Pt} \underset{\text{Ethanoic acid}}{CH_3\,COOH} + H_2O$$

Generally, alkanes resist oxidation. However, alkanes having tertiary H atom can be oxidized to corresponding alcohols by acidified $KMnO_4$ or acidified $K_2Cr_2O_7$.

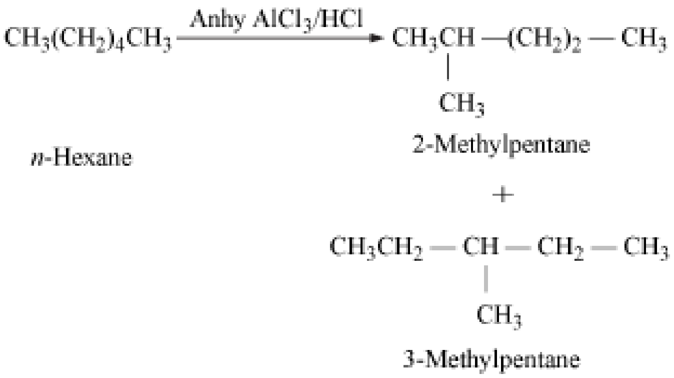
$$\underset{\text{2-Methylpropane}}{(CH_3)_3CH} \xrightarrow{KMnO_4} (CH_3)_3COH$$

- When methane and ethane are burnt in a limited supply of oxygen with no catalyst they form carbon monoxide and water. Further decreased amount of oxygen produces **soot** that is used in the manufacturing of printing inks and tyres.

$$2\,CH_4 + 3\,O_2 \longrightarrow 2\,CO + 4\,H_2O$$
$$2\,C_2H_6 + 5\,O_2 \longrightarrow 4\,CO + 6\,H_2O$$
$$CH_4 + O_2 \longrightarrow \underset{\text{Soot}}{C} + 2\,H_2O$$

- **Isomerisation**

On heating in the presence of anhydrous $AlCl_3$ and HCl gas, *n*-alkanes isomerise to branched-chain alkanes.



$$CH_3(CH_2)_4CH_3 \xrightarrow{\text{Anhy } AlCl_3/HCl} CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2)_2-CH_3 + CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

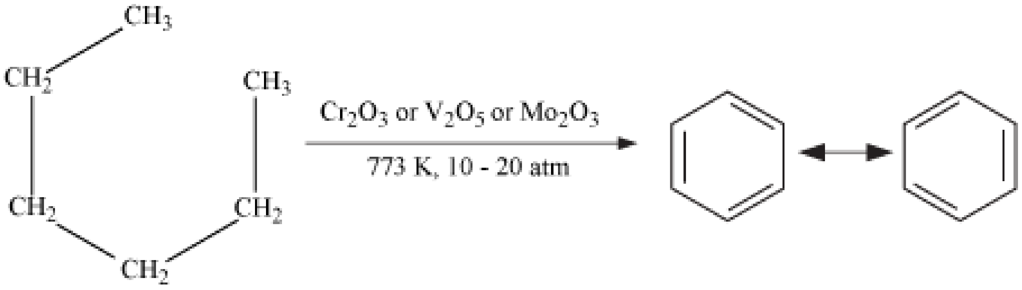
n-Hexane

2-Methylpentane

3-Methylpentane

- **Aromatization (or Reforming)**

  Heating *n*-alkanes (with six or more carbon atoms) to 773 K at 10−20 atmospheric pressure in the presence of the oxides of V, Mo, or Cr supported over alumina produces benzene and it's homologues.

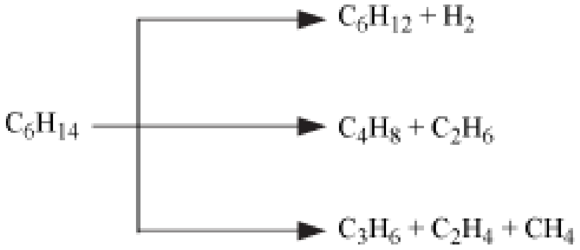


- **Reaction with Steam**

  $$CH_4 + H_2O \xrightarrow[1273K]{Ni} CO + 3H_2$$

- **Pyrolysis or Cracking**

  On heating to a higher temperature, higher alkanes decompose into lower alkanes or alkenes.



$$\underset{\text{Dodecane}}{C_{12}H_{26}} \xrightarrow[973K]{Pt/Pd/Ni} \underset{\text{Heptane}}{C_7H_{16}} + \underset{\text{Pentene}}{C_5H_{10}} + \text{Other products}$$

- **Substitution Reactions**
- Undergo substitution reactions in which one or more hydrogen atoms of alkanes are substituted (replaced) by halogens, nitro group, and sulphonic group
- Example − Halogenation, which takes place either at high temperature or in the presence of UV light (or sunlight)

$$CH_4 + Cl_2 \xrightarrow{hv} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{hv} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{hv} \underset{\text{Trichloromethane}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{hv} \underset{\text{Tetrachloromethane}}{CCl_4} + HCl$$

- Rate of reaction of alkanes with halogens is $F_2 > Cl_2 > Br_2 > I_2$
- Rate of replacement of hydrogens of alkanes is 3° > 2° > 1°
- Mechanism of halogenation (free radical mechanism)

(i) Initiation

$$Cl-Cl \xrightarrow[\text{homolysis}]{hv} \dot{C}l + \dot{C}l$$

Chlorine free radicals

(ii) Propagation

$$\mathrm{CH_4 + C\dot{l} \xrightarrow{h\nu} \dot{C}H_3 + HCl}$$

$$\mathrm{\dot{C}H_3 + Cl-Cl \longrightarrow CH_3-Cl + \underset{\text{Chlorine free radical}}{C\dot{l}}}$$

$$\mathrm{CH_3Cl + C\dot{l} \longrightarrow \dot{C}H_2Cl + HCl}$$

$$\mathrm{\dot{C}H_2Cl + Cl-Cl \longrightarrow CH_2Cl_2 + C\dot{l}}$$

(iii) Termination

$$\mathrm{C\dot{l} + C\dot{l} \longrightarrow Cl-Cl}$$

$$\mathrm{\dot{C}H_3 + \dot{C}H_3 \longrightarrow H_3C-CH_3}$$

$$\mathrm{\dot{C}H_3 + C\dot{l} \longrightarrow H_3C-Cl}$$

**Uses of Some Important Alkanes: Methane and Ethane**

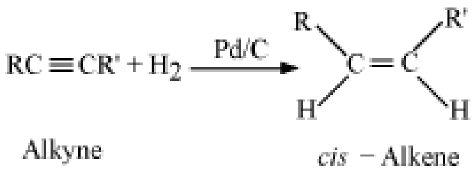
| Methane | Ethane |
|---|---|
| Source of CO and $H_2O$<br>Preparation of acetylene, formaldehyde, methanol, chloromethane and tetrachloromethane<br>Domestic fuel | Preparation of ethene, ethanol, ethanal, ethanoic acid<br>Preparation of a useful solvent in dry cleaning (tetraethyllead-1,1,1,-trichloroethane)<br>Fuel |

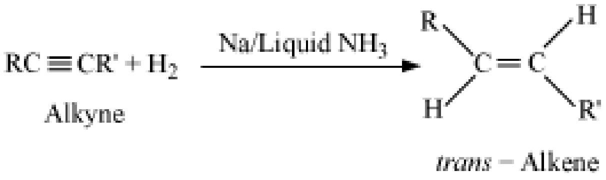
## Preparation and Properties of Alkenes

**Alkenes** : We have studied that alkenes are unstaturated hydrocarbons containing carbon-carbon double bonds with general formula $C_nH_{2n}$ . They are reactive in nature, so they are hardly found in free state.

**Preparation**

- **From alkynes**: Partial reduction of an alkyne in the presence of partially deactivated palladised charcoal (known as Lindlar’s catalyst), or in the presence of sodium, in liquid $NH_3$.





- **From Alkyl Halides**: On heating alkyl halides (R − X) with alcoholic potassium hydroxide

- The reaction is known as dehydrohalogenation.
- It is an example of β-elimination (H atom is eliminated from the β carbon atom).
- The rate of reaction depends upon both the nature of halogen atom and the alkyl group. For halogens, the rate of reaction decreases in the order

  Iodine > Bromine > Chlorine

  while for alkyl groups, the rate of reaction decreases in the order

  Tertiary > Secondary > Primary (for alkyl groups)

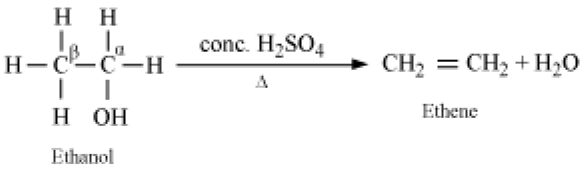
- **From Vicinal Dihalides**: On treatment with zinc metal, vicinal dihalides (dihalides − with two halogen atoms attached to two adjacent carbon atoms) give alkenes.

  $$CH_2Br - CH_2Br + Zn \longrightarrow CH_2 = CH_2 + ZnBr_2$$

  $$CH_3CHBr - CH_2Br + Zn \longrightarrow CH_3CH = CH_2 + ZnBr_2$$

  → This reaction is called dehalogenation.

- **From Alcohols by Acidic Dehydration:**



- **From Alcohols by Dehydration using $Al_2O_3$ as catalyst**

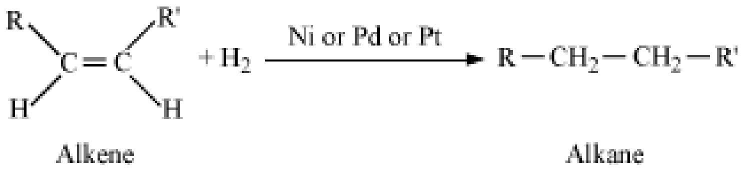
$$C_2H_5OH \xrightarrow[300\,^{\circ}C]{Al_2O_3} C_2H_4 + H_2O$$

**Physical Properties of Alkenes**

- First three members are gases; the next fourteen are liquids; and the higher ones are solids.
- Ethene is a colourless gas, with a faint sweet smell.
- All the alkenes are colourless, odourless, insoluble in water and fairly soluble in non-polar solvents.
- Boiling point of alkenes increases regularly with increase in size.
- Boiling points of straight chain alkenes are higher than those of isomeric branched-chain compounds.

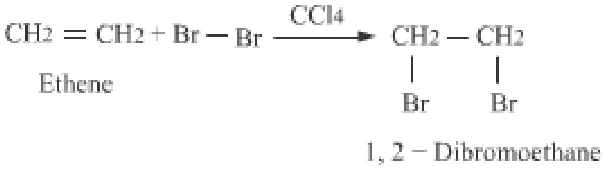
**Chemical Properties of Alkenes**

- **Addition of hydrogen:**

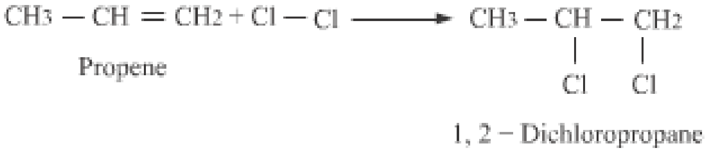


- **Addition of halogens:**

  Bromine and chlorine react with alkene to form vicinal dihalides (iodine does not undergo addition reaction under normal conditions).



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



$$CH_3 - CH = CH_2 + Cl - Cl \longrightarrow CH_3 - \underset{Cl}{CH} - \underset{Cl}{CH_2}$$

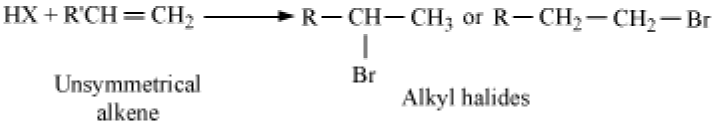
**Addition of hydrogen halides:** (HX; X = Cl, Br, I)

- Addition of hydrogen halides to alkenes is an electrophilic addition reaction which results in the formation of alkyl halides.
- Order of reactivity of hydrogen halides is HI > HBr > HCl

**Addition of hydrogen halides to symmetrical alkenes**

$$HX + \underset{\text{Symmetrical alkene}}{CH_2 = CH_2} \longrightarrow CH_3 - CH_2 - Br$$

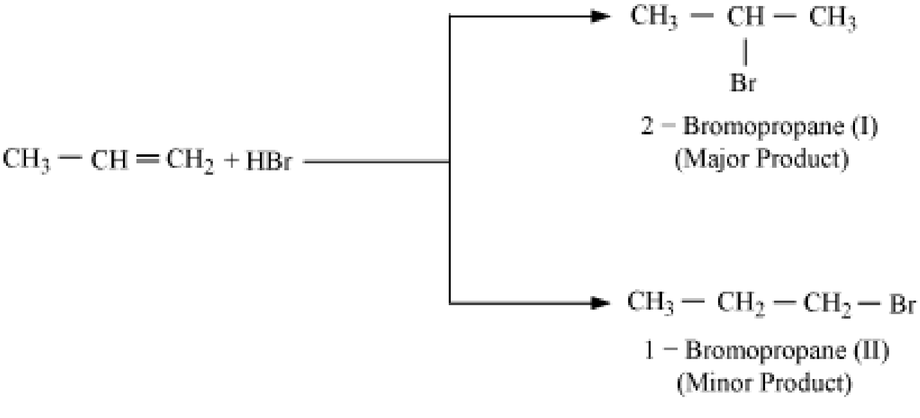
**Addition of hydrogen halides to unsymmetrical alkenes**



$$HX + R'CH = CH_2 \longrightarrow R - \underset{Br}{CH} - CH_3 \text{ or } R - CH_2 - CH_2 - Br$$

Addition of hydrogen halides to unsymmetrical alkenes follows Markovnikov's rule.

**Markovnikov's Rule**

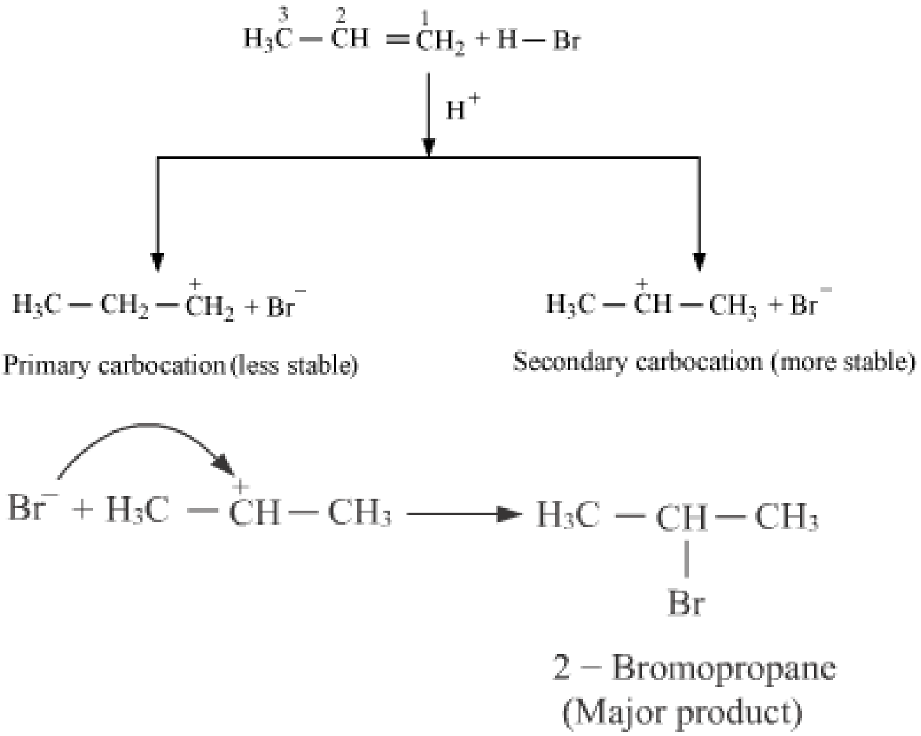


$$CH_3 - CH = CH_2 + HBr \longrightarrow CH_3 - \underset{Br}{CH} - CH_3 \quad \text{or} \quad CH_3 - CH_2 - CH_2 - Br$$

- Negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms.

  I is the major product.

- **Mechanism:**



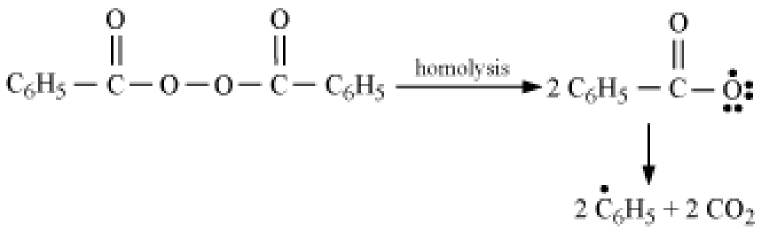
**Anti-Markovnikov's Addition (Or Peroxide Effect or Kharash Effect)**

- Addition of HBr to unsymmetrical alkenes in the presence of peroxide gives a product contrary to Markonikov's rule.

$$CH_3-CH=CH_2+HBr\xrightarrow{(C_6H_5CO)_2O_2}CH_3-CH_2-CH_2-Br$$

1-Bromopropane

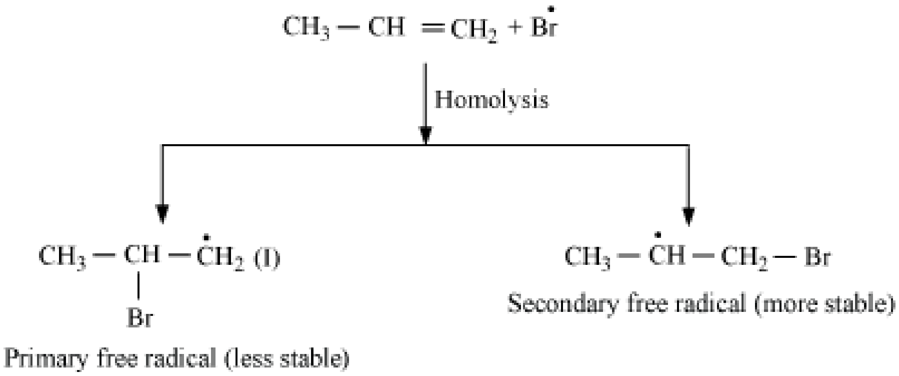
- **Mechanism:**

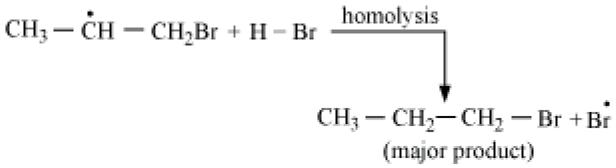


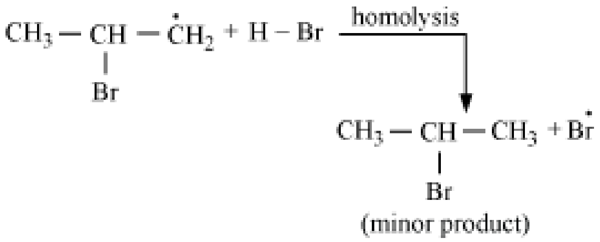
$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5\xrightarrow{\text{homolysis}}2\,C_6H_5-\overset{\overset{O}{\|}}{C}-\dot{\ddot{O}}\!:$$

$$\downarrow$$

$$2\,\dot{C}_6H_5+2\,CO_2$$

- $\dot{C}_6H_5 + H-Br \xrightarrow{\text{homolysis}} C_6H_6 + \dot{B}r$
- 

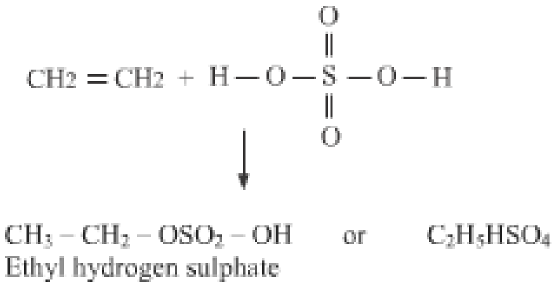
- 

- 

- Peroxide effect is observed only with HBr, and not with HCl and HI
- Reason:
- HCl bond is stronger (430.5 kJ/mol) and is not cleaved by the free radicals.
- HI bond is weaker and the iodine free radicals combine to form iodine molecules, instead of adding to the double bond.

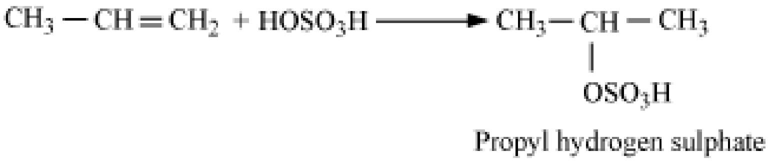
**Some Other Chemical Properties of Alkenes**

- **Addition of $H_2SO_4$** ( In accordance with Markovnikov's rule)



$$CH_2=CH_2 + H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-H \longrightarrow CH_3-CH_2-OSO_2-OH \text{ or } C_2H_5HSO_4$$

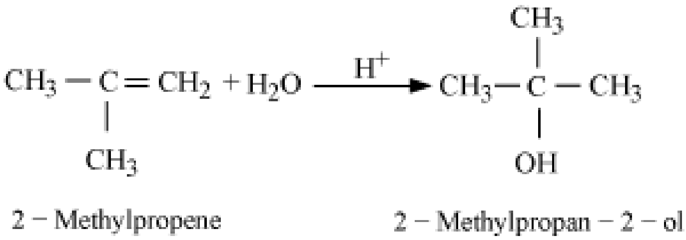
Ethyl hydrogen sulphate



$$CH_3-CH=CH_2 + HOSO_3H \longrightarrow CH_3-\underset{\underset{OSO_3H}{|}}{CH}-CH_3$$

Propyl hydrogen sulphate

- **Addition of water** (In accordance with Markovnikov's rule)



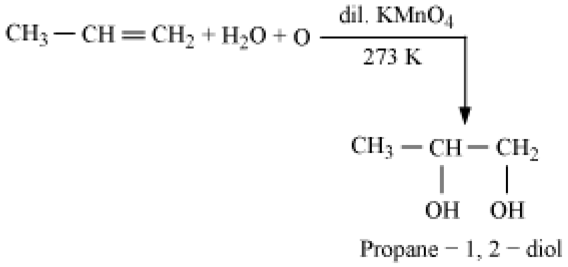
$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + H_2O \xrightarrow{H^+} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$$

2 − Methylpropene        2 − Methylpropan − 2 − ol

- **Oxidation**

- With a cold, dilute, aqueous solution of $KMnO_4$ (Baeyer's reagent), alkenes are oxidised to give vicinal glycols.

$$H_2C=CH_2 + H-O-H + [O] \xrightarrow[KMnO_4]{H^+} \underset{\text{Ethane–1,2–diol}}{OH-H_2C-CH_2-OH}$$



$$CH_3-CH=CH_2 + H_2O + O \xrightarrow[273\text{ K}]{\text{dil. }KMnO_4} CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$$

Propane − 1, 2 − diol

- Acidic $KMnO_4$ or acidic $K_2Cr_2O_7$ oxidises alkenes to give ketones or acids (depending upon the nature of alkenes).

$$(CH_3)_2C=CH_2 \xrightarrow{KMnO_4/H^+} (CH_3)_2C=O + CO_2 + H_2O$$

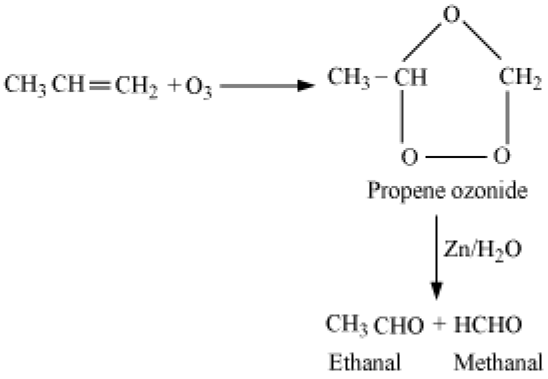
2-Methylpropene Propan-2-one

$$CH_3-CH=CH-CH_3 \xrightarrow{KMnO_4/H^+} 2CH_3COOH$$

But-2-ene Ethanoic acid

- **Ozonolysis**

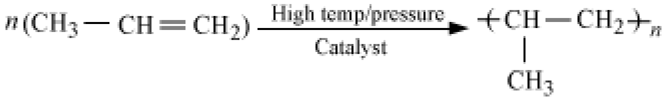
$$H_2C=CH_2 + H-O-H + [O] \xrightarrow[KMnO_4]{H^+} \underset{\text{Ethane}-1,2-\text{diol}}{OH-H_2C-CH_2-OH}$$



- **Polymerisation**

$$n(CH_2=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp/pressure}} \left(CH_2-CH_2\right)_n$$

Polythene (Polymer)



$$n(CH_3-CH=CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp/pressure}} \left(\underset{\substack{|\\CH_3}}{CH}-CH_2\right)_n$$

Polypropene (Polymer)

- **Combustion**

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O + \text{Heat}$$

**Uses:** Some of the common uses of ethene are as follows:

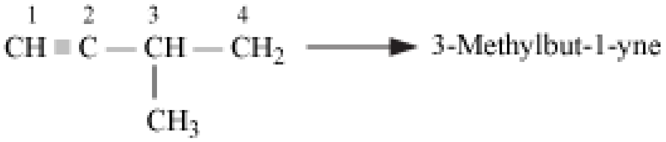
- Manufacture of polyethene
- Making ethanol which is required for making cosmetics and toileteries
- Ripening of fruits
- Manufacture of raw material for detergents (epoxyethane)
- Producing oxy-ethylene flame (used for cutting and welding purposes)

- Manufacture of synthetic chemicals

## Alkynes

- The general formula is $CnH_{2n-2}$ .
- Contain at least one triple bond between two carbon atoms
- In IUPAC nomenclature:
- They are named as derivatives of the corresponding alkanes replacing ‘ane’ by the suffix ‘yne’.
- The position of the triple bond is indicated by the first the triply bonded carbon.

$$H_3\overset{1}{C}-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{C}H_2-\overset{5}{C}H_3 \longrightarrow \text{Pent}-2-\text{yne}$$

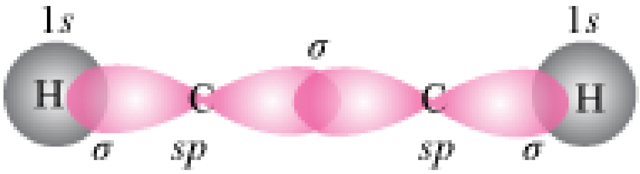


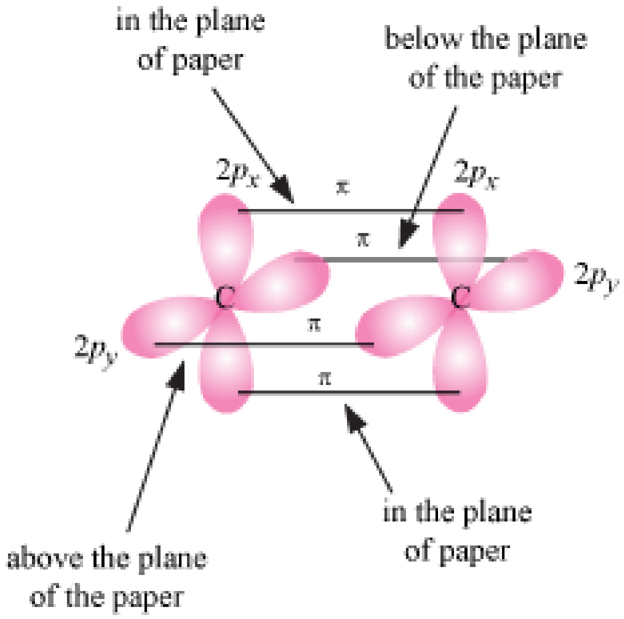
$$\overset{1}{CH}\equiv\overset{2}{C}-\underset{\displaystyle CH_3}{\overset{3}{CH}}-\overset{4}{CH_2} \longrightarrow \text{3-Methylbut-1-yne}$$

- But-2-yne and but-1-yne differ in their structures due to the position of the triple bond. Hence, they are known as **position isomers.**

| $CH_3-C\equiv C-CH_3$ | $CH_3-CH_2-C\equiv CH$ |
|---|---|
| But-2-yne | But-1-yne |

### Structure of Triple Bond (Ethyne)





- Each carbon atom of ethyne has two *sp* hybridised orbitals.

- C − C sigma bond is formed by head-on overlapping of two *sp* hybridised orbitals of the two C atoms.

- 2*p* orbitals of one carbon atom undergo lateral or sideways overlapping with 2*p* orbitals of other carbon atoms to form two *pi* (π) bonds.

- H − C − C bond angle is 180°.

- C ≡ C bond enthalpy = 823 kJ $mol^{-1}$

- C ≡ C bond length is 120 pm, which is shorter than those of C = C (133 pm) and C − C (154 pm) bonds.

### Preparation of Ethynes

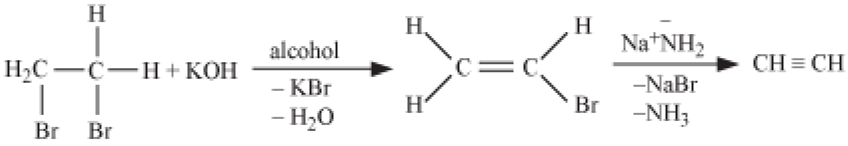
- **From calcium carbide ($CaC_2$)** − Ethyne is prepared by treating calcium carbide (which is obtained by heating quick lime with coke) with water.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + 3C \longrightarrow \underset{\substack{\text{Calcium}\\ \text{carbide}}}{CaC_2} + CO$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

- **From vicinal dihalides**



**Physical Properties of Alkynes**

- First three members are gases; the next eight are liquids; and the higher ones are solids.
- Colourless, odourless (except ethyne)
- Weakly polar in nature
- Lighter than water; immiscible with water, but soluble in organic solvents such as ethers, $CCl_4$, benzene, etc.
- Melting point, boiling point, and density increase with the increase in molar mass.

**Chemical Properties of Alkynes**

- Hydrogen atoms of ethyne (or any other alkyne), attached to the triply bonded carbon atom, are acidic in nature.

$$HC\equiv CH + Na \longrightarrow HC\equiv C^{-}Na^{+} + \frac{1}{2}H_2$$

Monosodium
ethynide

$$HC\equiv C^{-}Na^{+} + Na \longrightarrow N\overset{+}{a}\overset{-}{C}\equiv\overset{-}{C}N\overset{+}{a} + \frac{1}{2}H_2$$

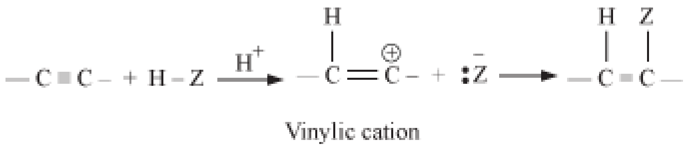
Disodium
ethynide

$$CH_3-C\equiv C-H + \overset{+}{N}aN\overset{-}{H}_2 \longrightarrow CH_3-C\equiv\overset{-}{C}\overset{+}{N}a + NH_3$$

Sodamide
(base)

Sodium propynide

- **Addition Reactions of Alkynes**



$$-C\equiv C- + H-Z \xrightarrow{H^+} -\overset{H}{\overset{|}{C}}=\overset{\oplus}{C}- + :\overset{-}{Z} \longrightarrow -\overset{H}{\overset{|}{C}}=\overset{Z}{\overset{|}{C}}-$$

- In unsymmetrical alkynes, addition takes place according to

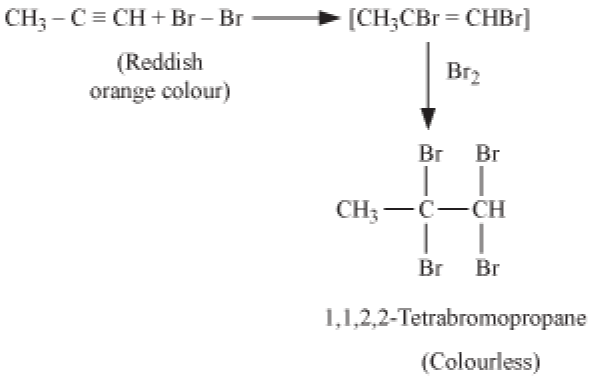
  Markovnikov’s rule.

- **Addition of dihydrogen**

$$H-C\equiv C-H \xrightarrow{Pt/Pd/Ni} [H_2C=CH_2] \xrightarrow{H_2} CH_3-CH_3$$

$$CH_3-C\equiv CH \xrightarrow[Pt/Pd/Ni]{H_2} [CH_3-CH=CH_2] \xrightarrow{H_2} CH_3-CH_2-CH_3$$

- **Addition of halogens**

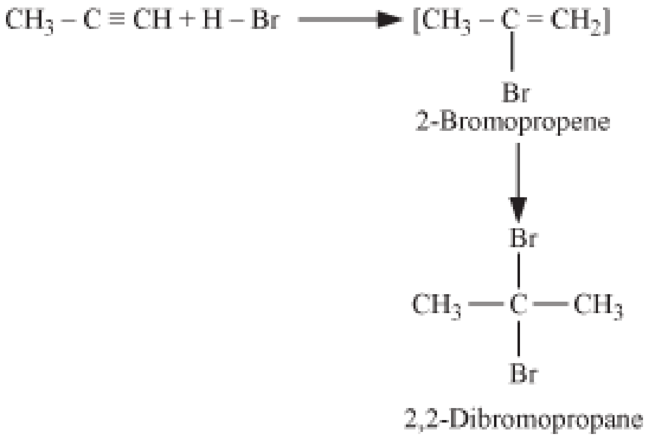


-

- It is used as a test for unsaturation.

- **Addition of hydrogen halides (HX; X = Cl, Br, I)**

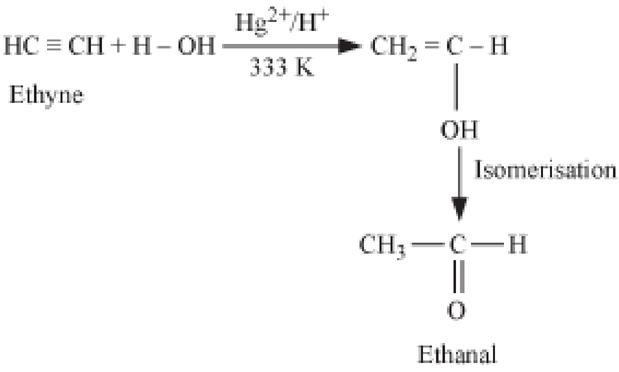
  HX adds to alkynes to form gem halides (in which two halogens are attached to the same carbon atom).



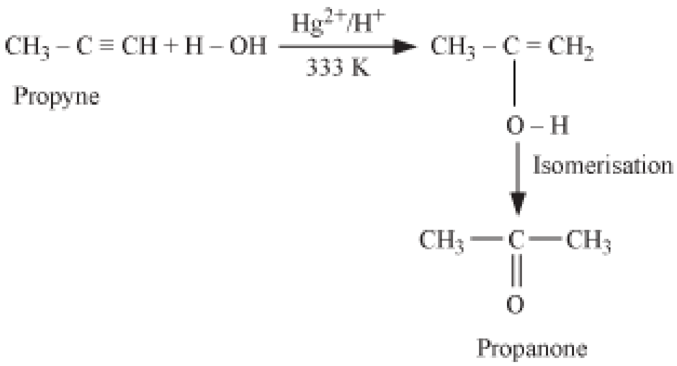
$$CH_3-C\equiv CH + H-Br \longrightarrow [CH_3-C(Br)=CH_2] \longrightarrow CH_3-CBr_2-CH_3$$

- **Addition of water**

  Generally, these do not react with water. However, on warming alkynes with mercuric sulphate and dilute sulphuric acid at 333 K, one molecule of water adds to them to form carbonyl compounds.



$$HC\equiv CH + H-OH \xrightarrow[333\ K]{Hg^{2+}/H^{+}} CH_2=C(OH)-H \xrightarrow{\text{Isomerisation}} CH_3-C(=O)-H$$



$$CH_3-C\equiv CH + H-OH \xrightarrow[333\ K]{Hg^{2+}/H^{+}} CH_3-C(O-H)=CH_2 \xrightarrow{\text{Isomerisation}} CH_3-C(=O)-CH_3$$

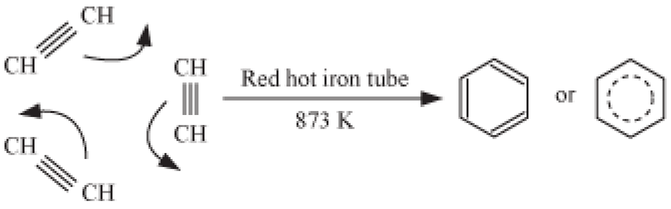
- **Polymerisation**

- **Linear polymerisation −** Polyacetytene or polyethyne is produced by linear polymerisation of ethene.

Repeating units − CH = CH − CH = CH

Represented as – $-\!(CH=CH-CH=CH)\!-_n$

- **Cyclic polymerisation**

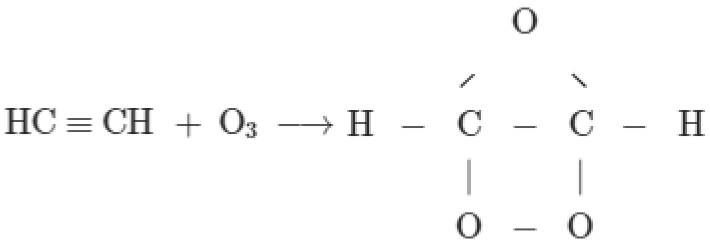


- **Oxidation**

  - **Oxidation**

$$2\,HC\equiv CH + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + \text{Heat}$$

  - **Ozonolysis**



$$HC\equiv CH + O_3 \longrightarrow H-\overset{\diagup\,O\,\diagdown}{C-C}-H \quad (\text{with } C-O-O-C \text{ bridge})$$

Uses: Some of the uses of ethyne are as follows:

- Oxy-acetylene welding at very high temperatures
- Illuminant in oxy-acetylene lamp
- Ripening and preservation of fruits
- Manufacture of several products like polymers. artificial rubber, oxalic acid, acetaldehyde, acetic acid, etc.

**Test to Distinguish between Alkanes, Alkenes and Alkynes**

| **Hydrocarbon** | **Reagents** | | | |
|---|---|---|---|---|
| | **$Br_2$ in $CCl_4$** | **Alk. $KMnO_4$** | **Ammoniacal cuprous chloride** | **Ammoniacal silver nitrate** |
| **Alkanes** | No change | No change | No change | No change |
| **Alkenes** | | | No change | No change |

| | | | | |
|---|---|---|---|---|
| **Alkynes** | Decolourisation of $Br_2$ solution | Decolourisation of $KMnO_4$ solution | Red precipitate is formed | White precipitate is formed |

## Some Commercially Important Alcohols

### Classification of Alcohols

- On the basis of the number of − OH groups:
- One −OH group: Monohydric alcohol, for example, methanol ($CH_3OH$)
- Two −OH groups: Dihydric alcohol, for example, glycol ($OH-CH_2CH_2-OH$)
- Three −OH groups: Trihydric alcohol, for example, glycerol ($HO-CH_2-CH(OH)-CH_2-OH$)

### Methanol ($CH_3OH$)

- Known as wood spirit
- Preparation
- Earlier produced by destructive distillation of wood
- Nowadays, it is produced by catalytic hydrogenation of carbon monoxide

$$CO + 2H_2 \xrightarrow[200-300\text{ atm},\ 573-673\text{ K}]{ZnO-Cr_2O_3} CH_3OH$$

- **Properties**
  - Colourless liquid
  - Boiling point = 337 K
  - Highly poisonous − Small quantities cause blindness and large quantities cause even death.
- **Uses**
  - As a solvent in paints and varnishes
  - In the preparation of formaldehyde (HCHO)

### Ethanol or Ethyl alcohol, $CH_3CH_2OH$

Ethanol is commonly known as alcohol. It is an active ingredient of all alcoholic beverages, namely beer, wine, whisky, rum etc.It is also referred to as spirit of wine It is also present in digestive and cough syrups. It is a neutral compound and has no effect on litmus paper.

In industries, ethanol is produced by the fermentation of sugar and hence known as grain alcohol. Intake of even a small quantity of pure ethanol can be lethal. If ethanol is consumed regularly for a very long time, then it can lead to many health problems and can also prove fatal.

**Do You Know:**

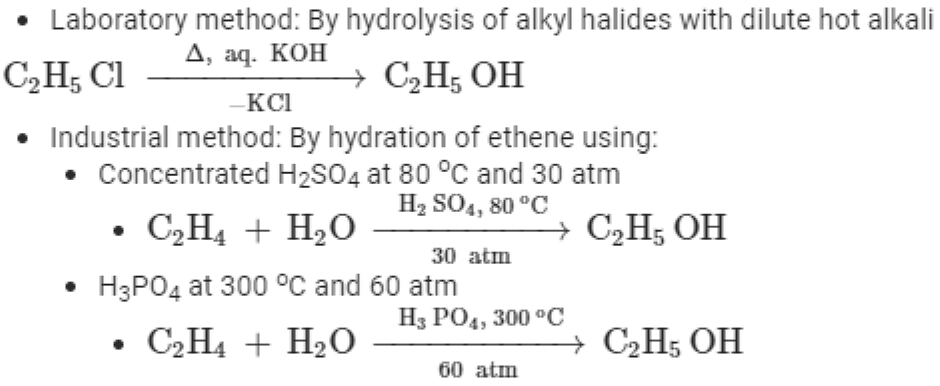
Ethanol is usually obtained from sugarcane. Sugarcane contains a large amount of sucrose. When molasses (a concentrated and dark liquid formed by boiling sugarcane juice) is fermented, ethanol is obtained.

**Preparation of Ethanol:**

- **Industrial preparation of ethanol by fermentation method:**

Sugarcane juice, juice of fruits or grapes, molasses undergoes fermentation reaction in presence of invertase enzyme to form glucose and fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$



- Laboratory method: By hydrolysis of alkyl halides with dilute hot alkali

$$\mathrm{C_2H_5\,Cl} \xrightarrow[-\mathrm{KCl}]{\Delta,\ \mathrm{aq.\ KOH}} \mathrm{C_2H_5\,OH}$$

- Industrial method: By hydration of ethene using:
  - Concentrated $H_2SO_4$ at 80 °C and 30 atm
    - $\mathrm{C_2H_4} + \mathrm{H_2O} \xrightarrow[30\ \mathrm{atm}]{\mathrm{H_2\,SO_4},\ 80\,^\circ\mathrm{C}} \mathrm{C_2H_5\,OH}$
  - $H_3PO_4$ at 300 °C and 60 atm
    - $\mathrm{C_2H_4} + \mathrm{H_2O} \xrightarrow[60\ \mathrm{atm}]{\mathrm{H_3\,PO_4},\ 300\,^\circ\mathrm{C}} \mathrm{C_2H_5\,OH}$

**Physical properties:**

**1.** It is a colourless liquid at room temperature, having a pleasant odour and inflammable toxic liquid.

**2.** It is completely miscible with water in all proportions and in organic solvents as well.

**3.** It is a very good organic solvent. Therefore, it is used in a lot of medicines, syrups, and tonics.

**4.** It is lighter than water.

**5.** Its consumption affects brain, liver and kidney.

**Chemical properties:**

**1. Reaction with sodium:** Ethanol reacts with sodium to produce hydrogen gas. Sodium ethoxide is also obtained in the reaction.

$$\underset{\text{Ethanol}}{2CH_3CH_2OH} + \underset{\text{Sodium}}{2Na} \rightarrow \underset{\text{Sodium ethoxide}}{2CH_3CH_2O^-Na^+} + \underset{\text{Hydrogen}}{H_2}$$

**2. Dehydration reaction:** When ethanol is heated with concentrated sulphuric acid, it loses one water molecule and gives ethene as a product.

$$\underset{\text{Ethanol}}{2CH_3CH_2OH} \xrightarrow[\text{Conc.sulphuric acid}]{\Delta} \underset{\text{Ethene}}{2CH_2=CH_2} + \underset{\text{Water}}{2H_2O}$$

**This reaction is known as dehydration reaction**. In a chemical reaction, a substance is said to be dehydrated if it loses one or more water molecules. In this reaction, concentrated sulphuric acid acts as a dehydrating agent and removes water molecules from ethanol.

**3. Combustion reaction:** Combustion of alcohol results in the formation of carbon dioxide and water along with a large amount of heat and light energy.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Oxygen}}{3\,O_2} \rightarrow \underset{\text{Carbon dioxide}}{2\,CO_2} + \underset{\text{Water}}{3\,H_2O} + \text{Heat} + \text{Light}$$

**Do You Know:**

As a large amount of energy is obtained when alcohol burns, it is used as an additive to petrol in some countries.

It burns to give only carbon dioxide and water. Thus, it is a clean fuel. It does not give out poisonous gases such as sulphur dioxide and nitrogen dioxide. Coal and petroleum contain nitrogen and sulphur, which causes pollution. Hence, they are not clean fuels.

**4. Oxidation with acidified $K_2Cr_2O_7$.** Alcohols are oxidised by oxidising agent to aldehydes. Further oxidation results in the conversion of the respective aldehydes to corresponding carboxylic acids.

$$CH_3OH \xrightarrow[K_2Cr_2O_7]{[O]} HCHO + H_2O \xrightarrow[K_2Cr_2O_7]{[O]} HCOOH$$

$$C_2H_5OH \xrightarrow[K_2Cr_2O_7]{[O]} CH_3CHO + H_2O \xrightarrow[K_2Cr_2O_7]{[O]} CH_3COOH$$

**5. Esterification reaction.** This reaction results in the formation of fruity smelling esters by the combination of alcohol and carboxylic acids in the presence of concentrated $H_2SO_4$.

$$CH_3OH + CH_3COOH \xrightarrow{\text{conc. } H_2SO_4} CH_3COOCH_3 + H_2O$$

$$C_2H_5OH + CH_3COOH \xrightarrow{\text{conc. } H_2SO_4} CH_3COOC_2H_5 + H_2O$$

**6. Reaction with phosphorous halide.** alkyl halides are formed in this reaction.

$$3\ CH_3OH + PCl_3 \longrightarrow 3\ CH_3Cl + H_3PO_3$$

$$3\ C_2H_5OH + PCl_3 \longrightarrow 3\ C_2H_5Cl + H_3PO_3$$

**Uses**

- As a solvent in manufacture of paint and a number of carbon compounds
- Denaturation of alcohol − Commercial alcohol becomes unfit for drinking by mixing some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). This is known as **denaturation** of alcohol.

**Commercially Important Forms of Ethanol**

- Denatured alcohol:
- Addition of poisonous substances like pyridine, methyl alcohol to pure ethanol for making it unfit for consumption
- Also called methylated spirit
- Contains 5% methyl alcohol
- Used for industrial purposes
- Spurious alcohol:
- Illicit liquor prepared by improper distillation
- Contains large portions of methanol
- Fatal for human consumption
- Used as a solvent for paints and varnishes

## Properties and Reactions of Ethanoic Acid

Carboxylic acids are carbon compounds containing carboxyl functional group −COOH. The carboxyl group is named so because it consists of a carbonyl group attached to a hydroxyl group. Examples of carboxylic acid include methanoic acid (HCOOH), ethanoic acid ($CH_3COOH$), propanoic acid ($C_2H_5COOH$), etc.

## Classification of Carboxylic Acids

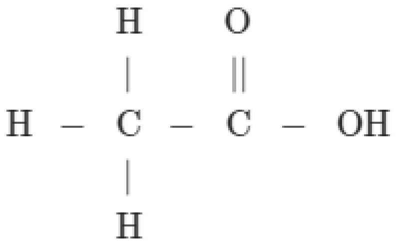
- On the basis of number of −COOH groups
- One −COOH group: Monocarboxylic acid, for example, HCOOH, $CH_3COOH$, etc.
- Two −COOH groups: Dicarboxylic acid, for example, HOOC−COOH, etc.

Now, let us discuss an industrially important carboxylic acid.

## Acetic Acid

Acetic acid is the common name of ethanoic acid ($CH_3COOH$). Its dilute solution in water is known as vinegar, which is used for preserving food. Only 5-8 % solution of ethanoic acid is called vinegar, which is used as a preservative in pickles and salads**.** It is a weak acid in nature and turns blue litmus paper red.

## Structure of acetic acid



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{O} & & \\ & & | & & \| & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{OH} \\ & & | & & & & \\ & & \mathrm{H} & & & & \end{array}$$

## Preparation of acetic acid

- **Laboratory preparation**: By oxidation of ethanol or ethanal (acetaldehyde) using acidified potassium dichromate solution

- $\underset{\text{Ethanol}}{CH_3\,CH_2\,OH} \xrightarrow{[O]} \underset{\text{Ethanal}}{CH_3\,CHO} \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3\,COOH}$

- **Industrial preparation**:
  - From acetylene using concentrated $H_2SO_4$ and $HgSO_4$
    - $\underset{\text{Ethene (Acetylene)}}{C_2H_2} + H_2O \xrightarrow[60\,^\circ C]{40\%\ H_2SO_4,\ 1\%\ HgSO_4} \underset{\text{Ethanal (Acetaldehyde)}}{CH_3\,CHO}$

    $\underset{\text{Ethanal (Acetaldehyde)}}{2\ CH_3\,CHO} + O_2 \xrightarrow[\text{Manganous acetate}]{\Delta} \underset{\text{Ethanoic acid (Acetic acid)}}{2\ CH_3\,COOH}$
  - From catalytic oxidation of ethanol over platinum rod
    - $\underset{\text{Ethanol}}{C_2H_5\,OH} + O_2 \xrightarrow[Pt]{300\,^\circ C} \underset{\text{Ethanoic acid (Acetic acid)}}{CH_3\,COOH} + H_2O$

**Physical properties**

- It is a colourless, pungent smelling liquid.

- The melting point of ethanoic acid is 290 K. This is below room temperature. Thus, it freezes during winters. It looks similar to ice when it freezes. Therefore, it is also known as glacial acetic acid.

- It boils at a temperature of 118 $^oC$.

- It is miscible with water, alcohol and ether in all proportions. It is hygroscopic in nature.

**Chemical properties**

- **Acidic nature**: Acetic acid is a weak acid. The following reactions prove the acidic nature of acidic acid.

- It turns blue litmus red.

- It reacts with active metals such as Zn and Mg to evolve hydrogen gas.

- $\underset{\text{Ethanoic acid (Acetic acid)}}{2\ CH_3\,COOH} + Zn \longrightarrow \underset{\text{Zinc acetate}}{(CH_3\,COO)_2\,Zn} + H_2\,(\uparrow)$

- **Reaction with alcohol or esterification reaction**: The reaction of a carboxylic acid with an alcohol to form an ester is known as **esterification reaction**.

**Curiosity Corner**

Esters are sweet smelling organic compounds. As esters are volatile and pleasant to smell, they are generally used for making perfumes. They are also used as flavouring agents because of their fruity smell.

When ethanoic acid reacts with ethanol in the presence of an acid, ethyl ethanoate is formed.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{\text{Acid}} \underset{\text{Ethyl ethanoate}}{CH_3COOCH_2CH_3} + \underset{\text{Water}}{H_2O}$$

Esters react in the presence of an acid or a base to give back alcohol and sodium salt of carboxylic acid as:

$$\underset{\text{Ethyl ethanoate}}{CH_3\,COOC_2\,H_5} \xrightarrow{\text{NaOH}} \underset{\text{Ethanol}}{C_2H_5\,OH} + \underset{\text{Sodium salt of ethanoic acid}}{CH_3\,COONa}$$

**This reaction is used in the preparation of soaps and is known as saponification reaction.**

- **Reaction with a base:**

  We know that an acid and a base react to form salt and water. Similarly, ethanoic acid reacts with sodium hydroxide to form a salt, sodium ethanoate, and water. Sodium ethanoate is commonly known as sodium acetate.

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Sodium hydroxide}}{NaOH} \rightarrow \underset{\text{Sodium ethanoate}}{CH_3COONa} + \underset{\text{Water}}{H_2O}$$

- **Reaction with carbonates and hydrogen carbonate:**

  Carbonates and bicarbonates are also basic in nature and react with ethanoic acid to form salt and water. Carbon dioxide is also formed in the reaction. The chemical equations involved are given as:

$$\underset{\text{Ethanoic acid}}{2CH_3COOH} + \underset{\text{Sodium carbonate}}{Na_2CO_3} \rightarrow \underset{\text{Sodium ethanoate}}{2CH_3COONa} + \underset{\text{Water}}{H_2O} + \underset{\text{Carbon dioxide}}{CO_2}$$

$$\underset{\text{Ethanoic acid}}{CH_3\,COOH} + \underset{\text{Sodium bicarbonate}}{NaHCO_3} \rightarrow \underset{\text{Sodium Ethanoate}}{CH_3\,COONa} + \underset{\text{Water}}{H_2O} + \underset{\text{Carbon dioxide}}{CO_2}$$

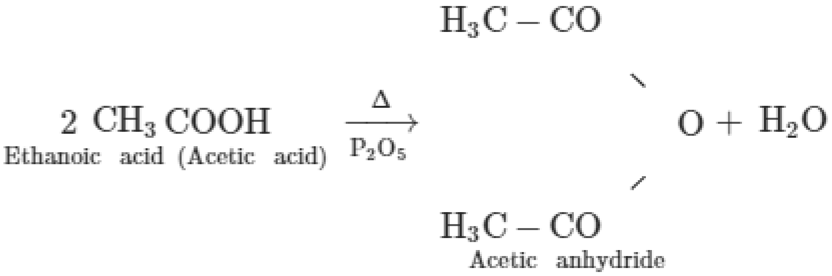
Sodium ethanoate is produced in the reaction. It is commonly known as sodium acetate.

- **Reaction with phosphorous pentachloride**

  Acetic acid reacts with phosphorous chloride to form an acid derivative i.e. acetylchloride.

- **Reaction with phosphorous pentoxide**

  Acetic acid forms another acid derivative when heated with phosphorous pentoxide. The acid derivative is acetic acid anhydride formed after removal of a water molecule from acid by phosphorous pentoxide.



$$\underset{\text{Ethanoic acid (Acetic acid)}}{2\ CH_3COOH} \xrightarrow[P_2O_5]{\Delta} \underset{\text{Acetic anhydride}}{\begin{array}{l} H_3C-CO \\ \quad\quad\quad\quad \searrow \\ \quad\quad\quad\quad\quad O \\ \quad\quad\quad\quad \nearrow \\ H_3C-CO \end{array}} + H_2O$$

- **Reaction with strong reducing agent**

  Acetic acid gets reduced to ethanol by reaction with a strong reducing agent such as $LiAlH_4$.

$$\underset{\text{Ethanoic acid (Acetic acid)}}{CH_3COOH} + \underset{\text{Provided by } LiAlH_4}{4[H]} \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + H_2O$$

### Tests for Acetic acid

| Reagent | Observation |
|---|---|
| $Na_2CO_3$ or $NaHCO_3$ | Evolution of gas that turns lime water milky. The gas is $CO_2$ . |
| $C_2H_5OH$ + Conc. $H_2SO_4$ | Fruity smell of ester |
| Neutral $FeCl_3$ solution | Wine red colouration |

### Uses of acetic acid

Some uses of acetic acid are:

- In the manufacture of vinegar for preserving foods
- In the manufacture of cellulose acetate for photographic film
- As organic solvent
- In the production of polyethylene terephthalate used in soft drink bottles
- In the manufacture of polyvinyl acetate for synthetic fibres and fabric