13. ORGANIC CHEMISTRY

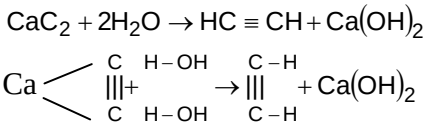
IV) ALKYNES

SYNOPSIS

- Alkynes are commonly known as acetylenes. Acetylene is the simplest and important member of the alkyne series.
- Alkynes contain – C ≡ C –
- General molecular formula of alkynes is C_nH_{2n-2}
- Triple bonded carbons are 'sp' hybridized and greater s – character is associated with it.
- Alkynes will exhibit chain, position and functional isomerism.
- Their functional isomers are alkadienes and cyclo alkenes.
- The minimum number of carbons required to exhibit chain isomerism by an alkyne is five.

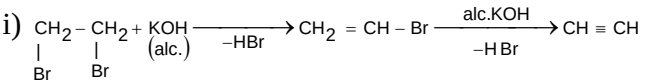
Preparation of Acetylene or ethyne :

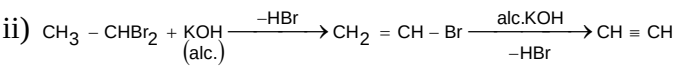
1. Industrial method : **By the hydrolysis of calcium carbide**



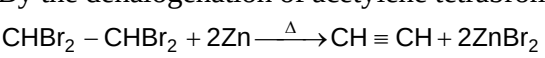
Even, other carbides like, MgC_2, SrC_2, BaC_2 on hydrolysis will give acetylene.

2. By the dehydrohalogenation of gem or vicinal dihalides.

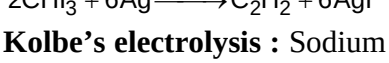




3. By the dehalogenation of acetylene tetrabromide

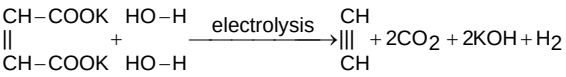


4. Iodoform reacts with silver powder to give acetylene.



5. **Kolbe's electrolysis :** Sodium or potassium salts of unsaturated dicarboxylic acids, on electrolysis will give alkynes.

- Potassium maleate or potassium fumerate on electrolysis gives acetylene



at anode at cathode

Physical properties : Pure acetylene is colorless, odourless gas, presence of impurities such as H_2S, PH_3 will give garlic odour.

- It is sparingly soluble in polar solvents like H_2O, but readily soluble in non – polar solvents like alcohol, ether etc.
- It is less volatile than ethylene and ethane.

Chemical properties : Acetylene undergoes addition reactions because it is unsaturated.

- Acetylene undergoes both electrophilic additions and nucleophilic additions while ethylene undergoes only electrophilic additions.

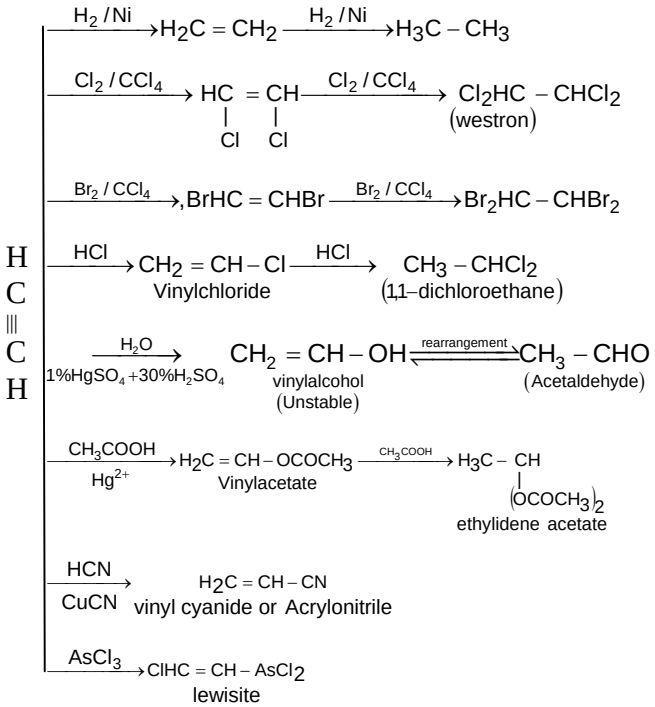
- **Reactivity :** Acetylene is more reactive due to the presence of triple bond or 2 bonds.
- But, acetylene is less reactive than ethylene due to shortening of C – C bond length –electrons are strongly held.

  Reactivity order :

  $$H_2C = CH_2 > HC \equiv CH > H_3C - CH_3$$

I) Addition reactions:

In these additions, two molecules of the reagent will be added to acetylene



Reaction with H_2O and HCN are nucleophilic additions.

II. Oxidation :

i) Acetylene is oxidised to oxalic acid with alkaline $KMnO_4$. Pink colour of $KMnO_4$ is declorised .

$$HC \equiv CH + 4(O) \xrightarrow[OH^-, 25^0C]{KMnO_4} HOOC - COOH$$

ii) Acetylene is oxidised to acetic acid in presence of chromic acid.

$$HC \equiv CH + (O) + H_2O \xrightarrow{\text{chromic acid}} CH_3COOH$$

III. Combustion : Acetylene burns in air to give oxy- acetylene flame, which is used in weldings and cuttings.

$$CH \equiv CH + \frac{5}{2}O_2 \rightarrow 2CO_2 + H_2O + \text{oxyacetylene flame}$$

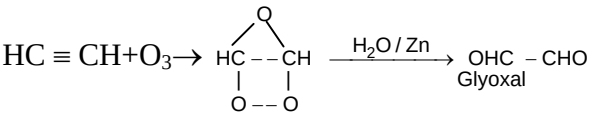
$$C_nH_{2n-2} + \left(\frac{3n-1}{2}\right)O_2 \rightarrow nCO_2 + (n-1)H_2O$$

IV) Polymerisation : Acetylene when passed through red hot iron tubes, it trimerises to give benzene.

$$3C_2H_2 \xrightarrow{\Delta} C_6H_6$$

In the above trimerisation, 3 bonds are broken and 3 bonds are formed.

v) Ozonolysis : Acetylene on addition of ozone, followed by reductive hydrolysis gives glyoxal.



Acetylene ozonide

vi) Acidic nature of alkynes :

- In alkynes, triple bonded carbons are sp hybridised.
- Due to greater s – character (50%), the hydrogens bonded to triple bonded carbons are slightly acidic.
- The hydrogens of acetylene or hydrogens bonded to triple bonded carbon of any other alkyne are acidic hydrogens and they can be easily replaced by metal atoms like Ag, Na, Cu to give corresponding metal acetylides.
- Thus acetylene and terminal alkynes (Alk –1-ene) are acidic. Non – terminal alkynes are not acidic.
- Acetylene is slightly acidic, but less acidic than even H_2O.

a) With Na or $NaNH_2$:

$HC \equiv CH + Na \rightarrow NaC \equiv CH + ½\ H_2$

$HC \equiv CH + 2Na \rightarrow NaC \equiv CNa + H_2$

$HC \equiv CH + NaNH_2 \rightarrow NaC = CH + NH_3$

Sodium acetylides are useful in the preparation of higher alkynes.

i) $HC{\equiv}CNa + CH_3 - Br \rightarrow HC \equiv C - CH_3 + NaBr$
Propyne

ii) $NaC{\equiv}CNa + 2CH_3{-}Br \rightarrow CH_3{-}C{\equiv}C{-}CH_3 + 2NaBr$
2 – Butyne

iii) $HC{\equiv}CNa + C_2H_5 - Br \rightarrow HC \equiv C - C_2H_5 + NaBr$
1 – Butyne

b) with Tollen's reagent (Ammonical silver nitrate):

$HC \equiv CH + 2AgNO_3 + 2NH_4OH \rightarrow AgC \equiv CAg\downarrow + 2NH_4NO_3 + 2H_2O$
Silver acetylide (white ppt)

c) with ammoniacal cuprous chloride :

$HC{\equiv}CH + Cu_2Cl_2 + 2NH_4OH \rightarrow CuC \equiv CCu\downarrow + 2NH_4Cl + 2H_2O$
Cuprous acetylide (red ppt)

The above reactions are substitution reactions.

Uses :

- In oxyacetylene flame used in weldings and cuttings
- In the preparation of compounds like acetaldehyde, aceticacid, ethyl aclcohol, benzene etc.
- In the preparation of industrial solvents like westron and westrasol (1, 1, 2 – trichloro ethene)
- In Hawkers lamp for illumination purposes.