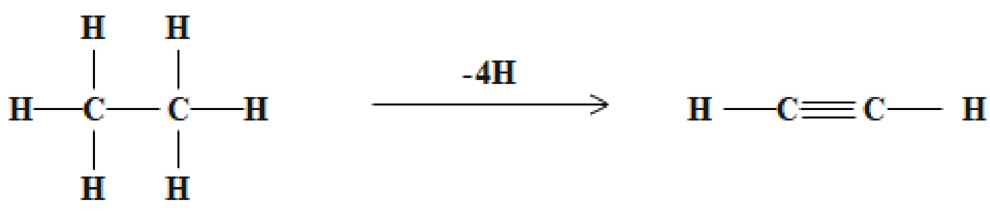
# Alkynes

Alkynes are unsaturated hydrocarbon compound whose molecule contains at least one carbon- carbon triple bond between two carbon atoms. They have the general formula $C_nH_{2n-2}$ where n=2,3 4…

They contains four hydrogen atoms less than the corresponding alkanes and are thus characterized by the presence of a triple bond in the molecule.




Ethane Ethyne

The first and the most important member of alkyne is acetylene or ethyne($HC \equiv CH$) and hence they are also called Acetylenes and the triple bonded linkage is often called Acetylenic linkage.

## Homologous series:-

Alkynes have the general formula $CnH2n_{-2}$ . Different members of the series can be obtained by putting the value of n where n=2,3 4…

$CH\equiv CH$ Ethyne

$CH_3$-$C\equiv CH$ Propyne

$CH_3$-$CH_2$-$C\equiv CH$ Butyne-1

$CH_3$-$CH_2$-$CH_2$-$C\equiv CH$ Pentyne-1

$CH_3$- $CH_2$-$CH_2$-$CH_2$-$C\equiv CH$ Hexyne-1

$CH_3$- $CH_2$-$CH_2$-$CH_2$-$CH_2$-$C\equiv CH$ Heptyne-1

## Nomenclature

| Structure | IUPAC name | Common name |
|---|---|---|
| $HC \equiv CH$ | Ethyne | Acetylene |
| $CH_3-C \equiv CH$ | Propyne | Allylene or Methylacetylene |
| $CH_3-CH_2-C \equiv CH$ | But-1-yne | Ethylacetylene |
| $CH_3-C \equiv C-CH_3$ | But-2-yne | Crotonylene or Dimethyl acetylene |

# General method of preparation:-

## 1. From calcium carbide:-

(Laboratory preparation of Ethyne (Acetylene) :-

Theory:-

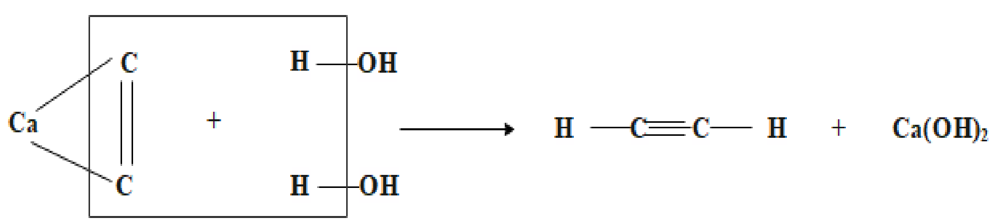
Acetylene gas is prepared in the laboratory by the action of water on calcium carbide. When water is poured over calcium carbide acetylene gas is obtained which can be collected in gas jar by downward displacement of water.

Reaction involved:-

$CaC_2 + 2H_2O \rightarrow H - C \equiv C - H + Ca(OH)_2$

Calcium carbide    acetylene gas    calcium hydroxide

or



Calcium carbide    Ethyne

Figure:-

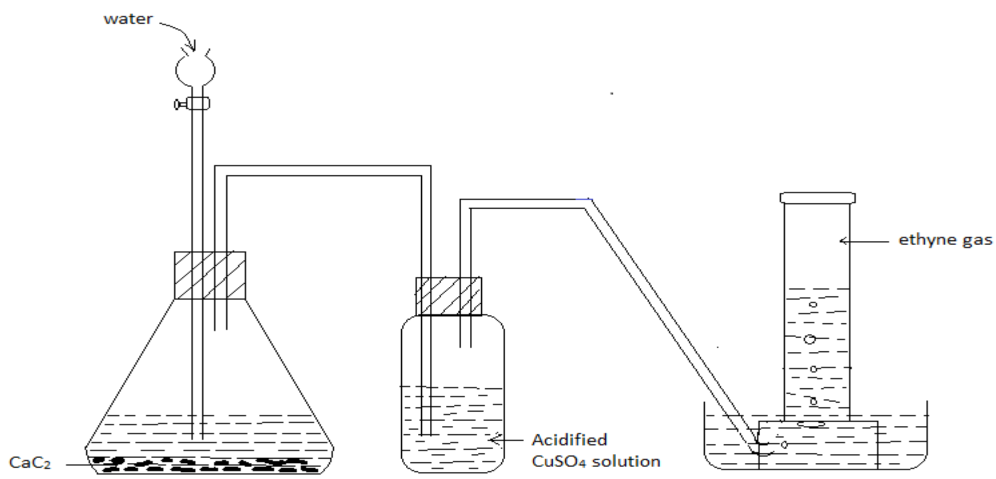



Fig. Laboratory preparation of ethyne gas.

## Procedure:-

A layer of small lumps of calcium carbide is taken in a conical flask which is fitted with a thistle funnel having a rubber stopper and a delivery tube whose other end is introduced in a wash bottle containing acidified copper sulphate solution with some suspension of bleaching powder in water.

The wash bottle is again fitted with a delivery tube whose other end is introduced into a water filled inverted gas jar over water trough.

Water is allowed to fall on calcium carbide dropwise through dropping funnel .On the contact of water with calcium carbide, reaction takes place and acetylene (ethyne) gas is produced. Thus obtained acetylene gas is impure and may be contaminated with hydrogen sulphide gas, phosphine gas ammonia and arsenic gas which may be produced due to the action of water on calcium sulphide and calcium phosphide respectively present as impurities in calcium carbide.

$CaS + 2H_2O \rightarrow H_2S\uparrow + Ca(OH)_2$

Calcium sulphide hydrogen sulphide

$Ca_3P_2 + 2H_2O \rightarrow PH_3\uparrow + Ca(OH)_2$

Calcium phosphide phosphine

Thus acetylene gas produced is freed from these impurities by bubbling the gas an acidic solution of copper sulphate in wash bottle and a suspension of bleaching powder in water.

$CuSO_4 + H_2S \rightarrow CuS\downarrow + H_2SO_4$

Copper sulphide

$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2\downarrow + H_2SO_4$

Copper phosphide

$4NH_3 + CuSO_4 \rightarrow Cu(NH_3)SO_4$

Tetra-amine copper sulphate

Pure acetylene gas is then collected by downward displacement of water over water trough. The first gas coming out mixed with air inside the delivery tube and should be rejected. When a test tube full of gas burns quietly the gas is collected in jars.

**There should be no flame in the vicinity of the generator as acetylene forms an explosive mixture with air.**

In this way pure acetylene gas is prepared in the laboratory.

# Note:-

When aluminium carbide is treated with water methane gas is produced.

$$Al_4C_3 + 12H_2O \rightarrow 3CH_4\uparrow + 4Al(OH)_3$$

**Aluminum carbide** **Methane**

Hydrochloric acid can be used instead of water.

$$Al_4C_3 + 12HCl \rightarrow 3CH_4\uparrow + 4AlCl_{3u}$$

**Aluminum carbide** **Methane**

Likewise hydrolysis of beryllium carbide also produce methane gas.

$$Be_2C + 4H_2O \rightarrow CH_4\uparrow + 2Be(OH)_2$$

**Beryllium carbide** **Methane**

These two carbides (Aluminium carbide and beryllium carbide) are also called **Methanides** since these carbides produces **methane gas .**
**Thus from these carbides methane gas can be prepared in the laboratory.**

But magnesium carbide undergo hydrolysis with water to produce propyne gas.

$$Mg_2C_3 + 4H_2O \rightarrow CH_3-C\equiv CH\uparrow + 2Mg(OH)_2$$

**Magnesium carbide** **propyne**

## 2. By dehydrhalogenation of dihaloalkane:-

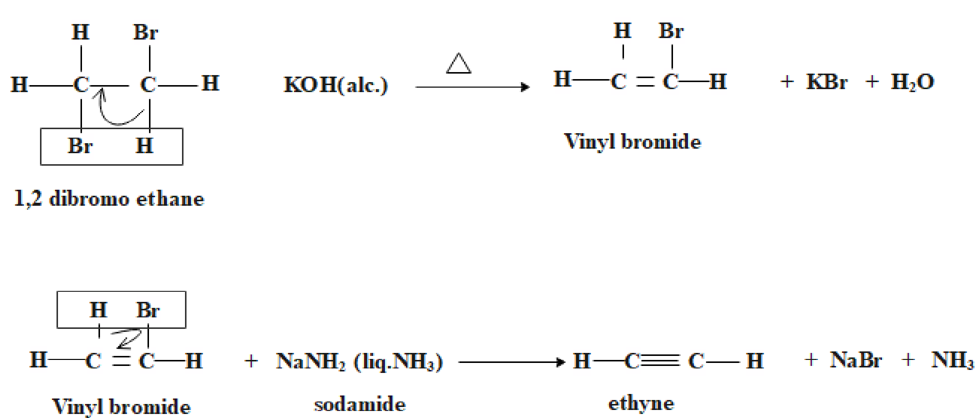
Compounds containing two halogen atoms on two adjacent carbon atoms are called vicinal dihalide.

Vicinal dihaloalkane like 1,2 dibromo ethane when boiled with alcoholic solution of alkali like alc.KOH, undergo dehydrohalogenation (i.e. removal of hydrogen and halogen from two adjacent carbon atoms ) to give bromo ethene (vinyl bromide) which undergo futher dehydrohalogenation in presence of stronger base soda-amide ($NaNH_2$) in presence of liquid ammonia to produce alkyne (ethyne).

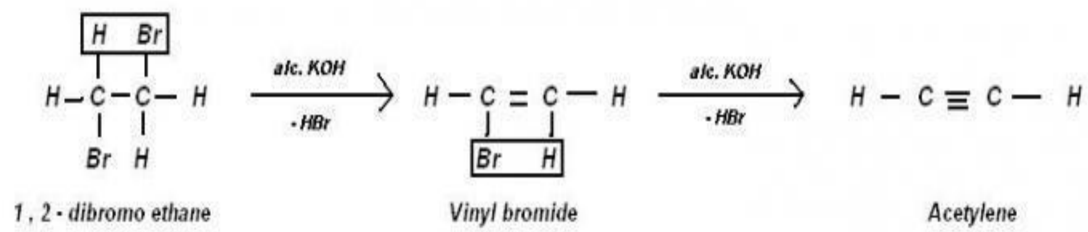
$$\underset{\text{1,2 dibromo ethane}}{CH_2Br-CH_2Br} + KOH(alc.) \xrightarrow{\triangle} \underset{\text{Vinyl bromide}}{CH_2=CH-Br} + KBr + H_2O$$

$$\underset{\text{Vinyl bromide}}{CH_2=CH-Br} + NaNH_2\ (liq.NH_3) \longrightarrow \underset{\text{ethyne}}{H-C\equiv C-H} + NaBr + NH_3$$

OR



Ethyne can also be obtained by dehydrohalogenation of vicinal dibromo ethane with alc. KOH in two steps via the formation of vinyl bromide in first step which again undergo dehydrohalogenation to produce ethyne. But vinyl bromide formed in first step is less reactive, the second step does not proceed easily with alcoholic KOH to give better yield.

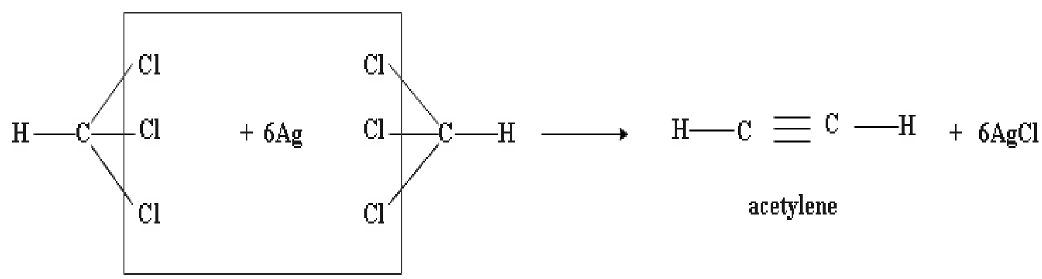


## 3. From haloform like chloroform of iodoform :-

When haloform like chloroform or iodoform is heated with silver powder it undergo dehalogenation to produce acetylene gas.

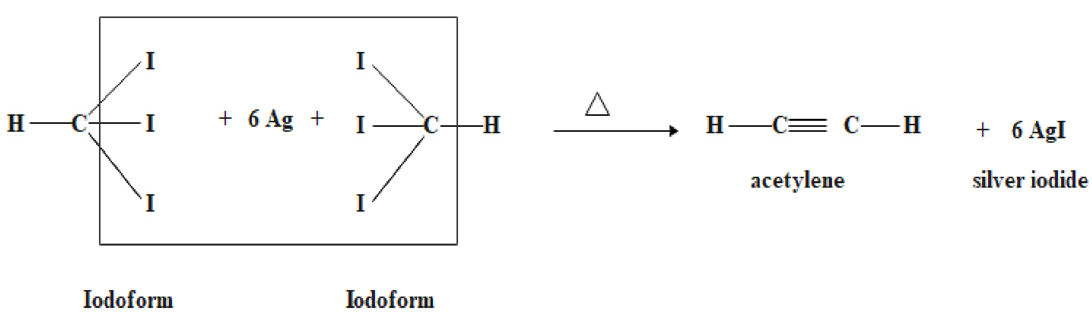
$$2CHCl_3 + 6Ag \xrightarrow{\Delta} H-C\equiv C-H + 6AgCl$$

Or




$$2CHI_3 + 6Ag \xrightarrow{\Delta} H-C\equiv C-H + 6AgI$$

or



## 4. From carbon and hydrogen:-

( By Berthelot's synthesis)

When electric spark is applied between two carbon electrodes in an atmosphere of hydrogen in a fused silica tube ethyne gas or acetylene gas is produced.

This method is called Berthelot's method.

$$2C + H_2 \xrightarrow[\Delta]{\text{electric spark}} \underset{\text{Acetylene}}{HC \equiv CH}$$

Pure acetylene gas cannot be obtained by this method because acetylene thus obtained is mixed with some amount of methane and ethylene gas.

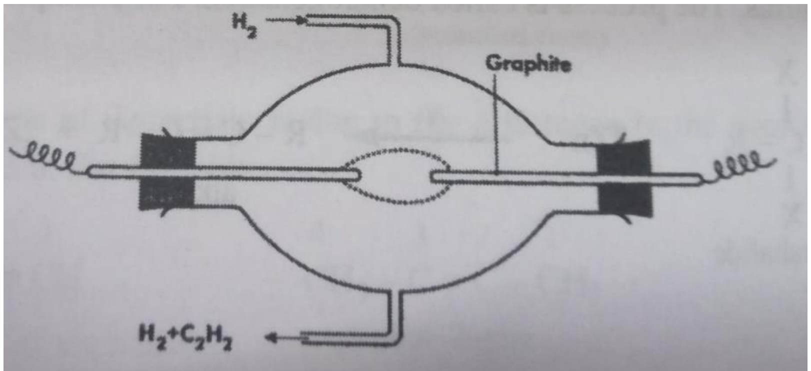
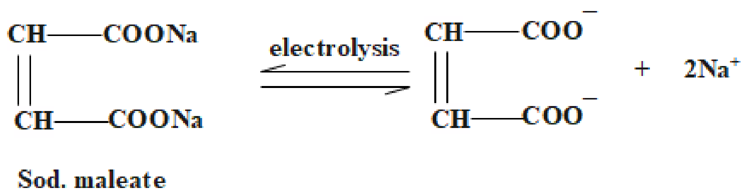



Fig: Berthelot's synthesis of ethyne

# 5. From Kolb's electrolytic process:-

Electrolysis of Aqueous solution of sodium salt of maleic acid gives acetylene gas at anode.

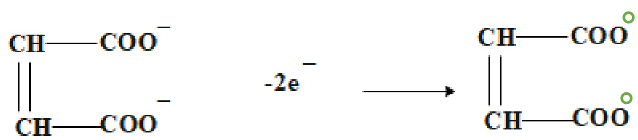
First sodium salt of maleic acid undergoes ionization as follows-

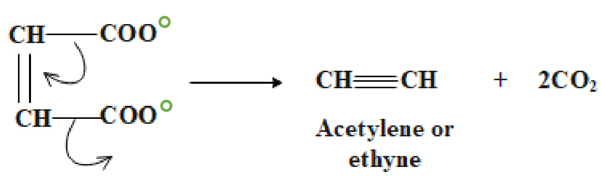



At the same time water gets ionized as

$2H_2O \rightarrow 2H^+ + 2OH^-$

At anode-




The mixture of ethyne and $CO_2$ liberated is passed through KOH or NaOH solution to absorb $CO_2$ gas.

At cathode-

$2H^+ + 2e^- \rightarrow H_2$

$2Na^+ + 2OH^- \rightarrow 2NaOH$

## Properties:-

## Physical properties:-

1. The first three lower members of alkynes like acetylene, allylene and crotonylene are gaseous.

   The homology from carbon 5 to 15 ($C_5H_8$ to $C_{15}H_{28}$) are liquids and still higher members are solid.
2. They are all colourless and odourless except acetylene which has garlic odour when impure owing to the presence of traces of phosphine and hydrogen sulphide .When pure it has ethereal odour.
3. They are only slightly soluble in water, dissolves readily in organic solvents like acetone ethyl alcohol and benzene.
4. The boiling point, melting point and specific gravity shows a regular increase with the increase in molecular mass.

   Acetylene has M.pt.—81.8℃ and B.pt.-83.4℃
5. Acetylene is somewhat poisonous and produces general anesthesia when inhaled.
6. Acetylene under suitable condition decomposes with great het and the sudden increase in volume casing explosion. So liquid acetylene is highly explosive.

## Chemical properties:-

Acetylene contains carbon-carbon triple bond and is more unsaturated than alkene. Among three bonds one is strong $\sigma$ bond and two weak π bonds forming cloud of π electrons above and below the $\sigma$ bond. These π electron cloud is easily attacked by electrophiles. Thus it resembles with olefin and give addition reaction, oxidation reaction and also polymerization reaction.

Besides, alkynes also give substitution reaction because acetylinic hydrogen is weakly acidic and thus can be replaced.

Thus overall reactions of alkynes can be grouped into following four groups-

1. Addition reactions
2. Polymerization reaction
3. Oxidation reactions
4. Substitution reactions

## 1. Addition reactions:-

Alkynes contains two π covalent bonds. Therefore these hydrocarbon adds two molecules of many substances in two steps and give a saturated compound. For example alkynes add hydrogen, halogen, halo acids etc. in two steps.

In first step, it gives a compound containing carbon-carbon double bond which undergo further addition of same molecule in same condition to give saturated compound.

## a. Addition of Hydrogen (Hydrogenation):-

When acetylene gas is heated with hydrogen in the presence of finely divided nickel or platinum catalyst at 250-300℃, it adds a molecule of hydrogen by breaking one of the π bond to give alkene which again adds another molecule of hydrogen in same condition to give saturated hydrocarbon or alkane.

$$\underset{\text{Ethyne (acetylene)}}{CH \equiv CH} + H_2 \xrightarrow[250-300^\circ C]{\text{nickel}} \underset{\text{ethene (ethylene)}}{CH_2 = CH_2} \xrightarrow[250-300^\circ C]{\text{nickel/H2}} \underset{\text{ethane}}{CH_3 - CH_3}$$

$$\underset{\text{Propyne}}{CH_3 - C \equiv CH} + H_2 \xrightarrow[250-300^\circ C]{\text{nickel}} \underset{\text{Propene}}{CH_3 - CH = CH_2} + H_2 \xrightarrow[250-300^\circ C]{\text{nickel}} \underset{\text{Propane}}{CH_3\text{-}CH_2\text{-}CH_3}$$

$$\underset{\text{But-2-yne}}{CH_3\text{-}C \equiv C - CH_3} + H_2 \xrightarrow[250-300^\circ C]{\text{nickel}} \underset{\text{But-2-ene}}{CH_3\text{-}CH{=}CH\text{-}CH_3} + H_2 \xrightarrow[250-300^\circ C]{\text{nickel}} \underset{\text{Butane}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3}$$

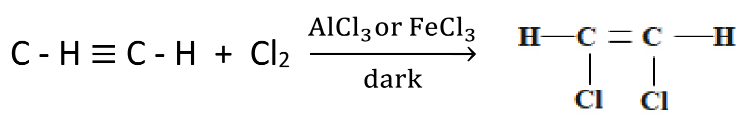
However, in presence of Lindler,s catalyst (Palladium in $BaSO_4$) with calculated amount of hydrogen, acetylene produces ethylene by partial hydrogenation.

$$\underset{\text{acetylene}}{HC \equiv CH} + H_2 \xrightarrow[\text{250-300°C partially poisoned by S}]{\substack{\text{Pd /BaSO4} \\ \text{(Lindler's catalyst)}}} \underset{\text{ethylene}}{CH_2 = CH_2}$$

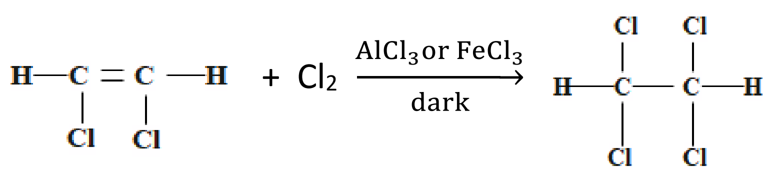
# b. Addition Halogens (Halogenetion):-

Chlorine, or bromine reacts with alkyne like ethyne in presence of $AlX_3$ or $FeX_3$ as catalyst to give addition product .Acetylene combines more easily with chlorine than bromine or iodine since reactivity of halogens for this reaction follows following order $Cl_2 > Br_2 > I_2$

Acetylene give addition products like di and tetra halogen derivatives with gaseous chlorine or bromine in dark.



ethyne 1,2 dichloroethene



1,1,2,2,tetrachloroethane

Acetylene explodes if mixed with chlorine in day light or direct sunlight giving carbon and hydrogen chloride gas.

$$CH \equiv CH + Cl_2 \xrightarrow{\text{light}} 2C + 2HCl$$

The addition of $Br_2$ takes similar to that of chlorine, when liquid bromine is treated with ethyne gas.

$$C\text{-}H \equiv C\text{-}H + Br_2 \xrightarrow[\text{dark}]{AlBr_3 \text{ or } FeBr_3} CHBr{=}CHBr$$

1,2 dibromoethene

$$CHBr{=}CHBr + Br_2 \xrightarrow[\text{dark}]{AlBr_3 \text{ or } FeBr_3} CHBr_2 - CHBr_2$$

1,2 dibromoethene 1,1,2,2-tetra bromoethane

In this reaction the brown colour of bromine gets discharged thus, this reaction is used **as the test of unsaturation.**

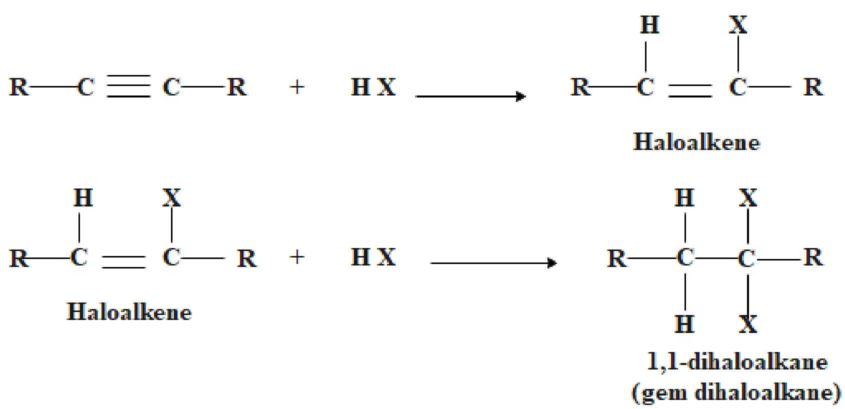
The addition of iodine is very slow and needs some special condition to give addition reaction.

## c. Addition of hydrogen halides( Hydrohalogenetion):-

Alkynes reacts with hydrogen halides in two steps.

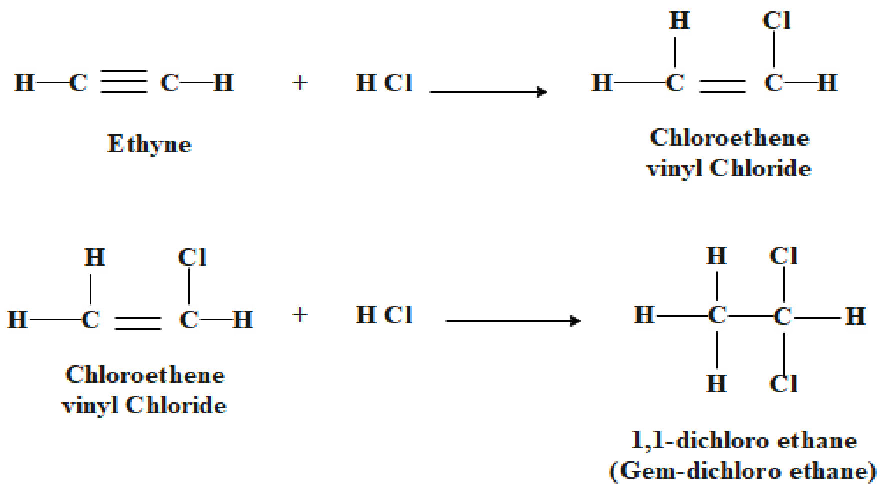
In first step it adds one molecule of hydrogen halide to give haloalkene which again adds another molecule of hydrogen halide to give gem-dihalide.

Symmetrical alkene reacts with hydrogen halide to give haloalkene in first step which further reacts with hydrogen halide following Markonikov's rule.

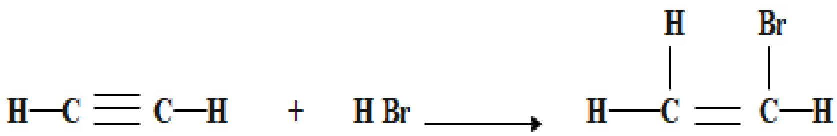


For example acetylene reacts with hydrogen halide like HCl, HBr or HI to give vinyl halide . Vinyl halide adds up one more molecule of hydrogen halide and this addition of hydrogen halide to vinyl halide takes place according to the Markonikov's rule to give 1,1-dihaloethane( gem dihaloalkane)

Addition of HCl→

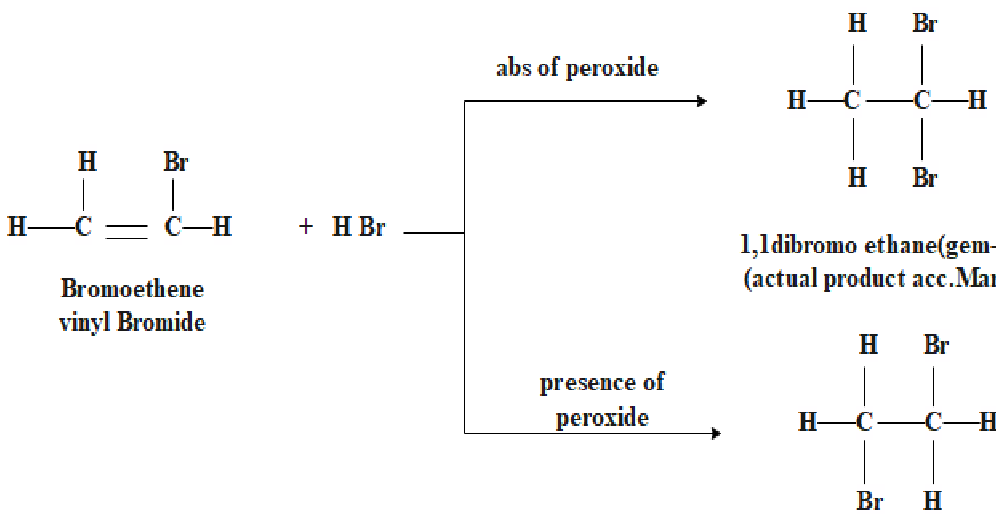


Addition of HBr→



Ethyne

Bromoethene
vinyl Bromide




Bromoethene
vinyl Bromide

1,1dibromo ethane(gem- dibrormethane)
(actual product acc.Markonokov's rule)

1,2 dibromo ethane (vic-dibromoethane)
(Actual product according to
anti-Markonikov's rule)

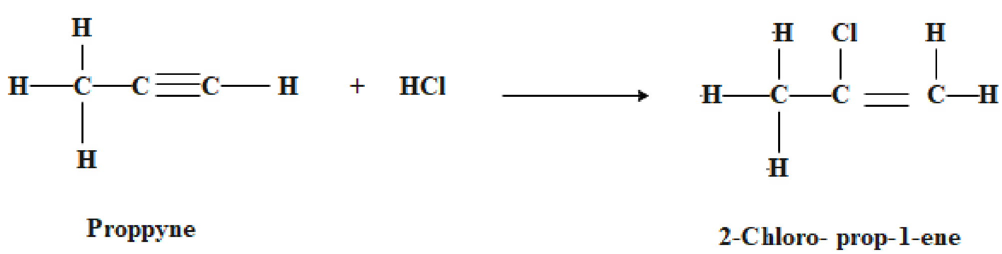
The addition of halogen acids to unsymmetrical alkyne takes place according to the Markonikov's rule in both the steps.

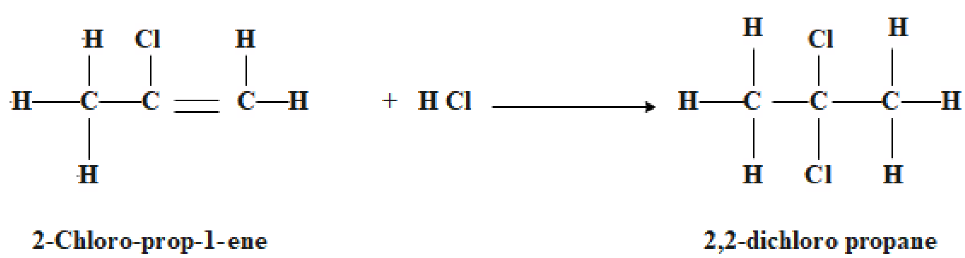
For example-

Addiion of HCl→

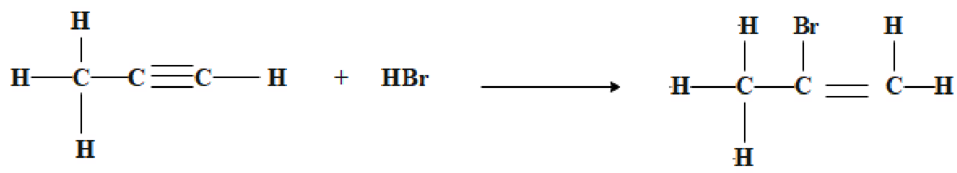
$CH_3 - C \equiv CH$ + HCl → $CH_3 - C\,Cl = CH_2$ + HCl → $CH_3 - CCl_2 - CH_3$

Propyne 2-chloro propene 2,2-dichloroparpane

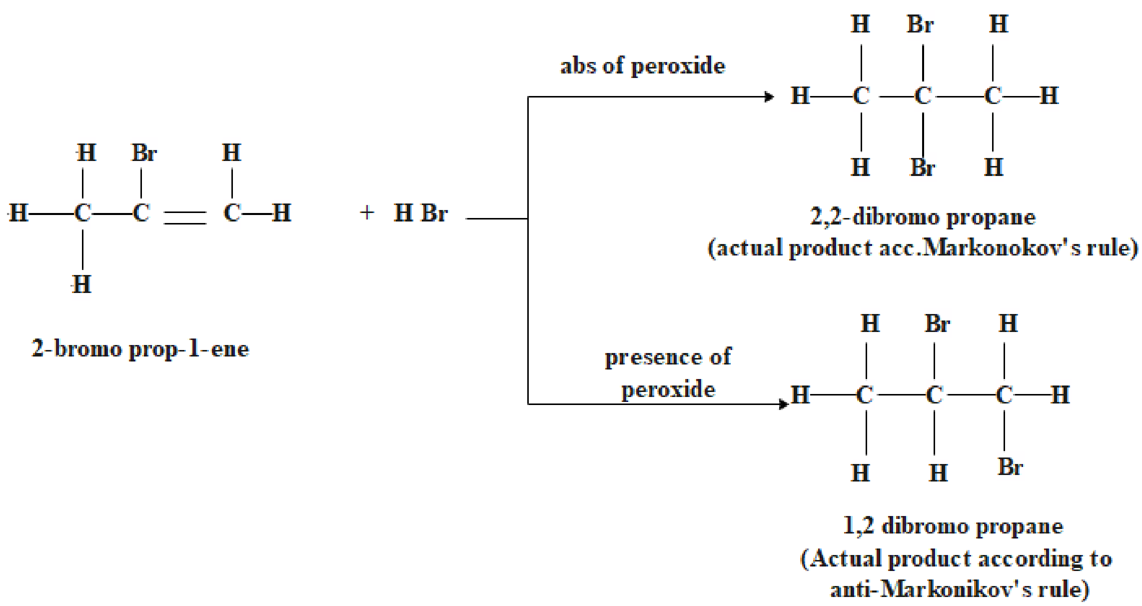




Addition of HBr→



2-bromo prop-1-ene



## d. Addition of water ( Catalytic hydration ):-

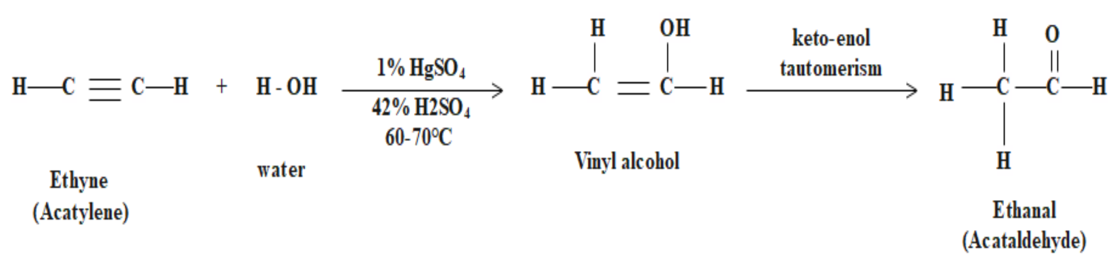
When alkynes are heated with water in presence of mercuric sulphate ($1\%$ $HgSO_4$) and sulphuric acid ($42\%$ $H_2SO_4$), at 60-70°C alkynes add a molecule of water across carbon-carbon triple bond to give an unsaturated alcohol (alkenol), which being unstable undergo intermolecular rearrangement to give carbonyl compound (aldehyde or ketone) depending upon the alkyne used.

This process of rearrangement is called tautomerization. And the reaction is called catalytic hydration.

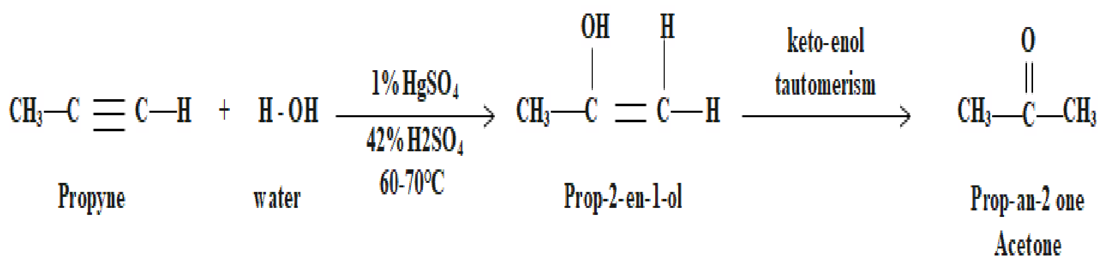
All alkynes on reacting with water produces ketone except the first member ethyne which give aldehyde.

Example:-

When acetylene (ethyne) gas is heated with water in presence of 1% $HgSO_4$ and 42% $H_2SO_4$ at 60-70°C , water molecule is added over carbon-carbon triple bond of acetylene to give vinyl alcohol (unsaturated alcohol) which being unstable undergo rearrangement ( tautomerize) to give acetaldehyde (ethanal).

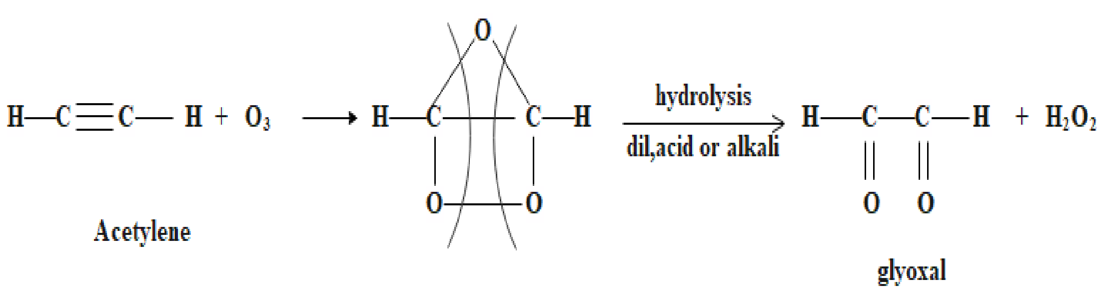


When higher alkynes except acetylene like Propyne gives is hydrated produces ketone.




## e. Addition of Ozone (Ozonolysis):-

Acetylene adds up a molecule of ozone across carbon-carbon triple bond to form an intermediate ring compound ozonoid which when subjected to hydrolysis with boiling water in the presence of catalyst dilute acid or dilute alkali then breaking of ozonoid takes place yielding glyoxal ( 1,2 ethane- di-al)



## 2. Polymerization reaction:-

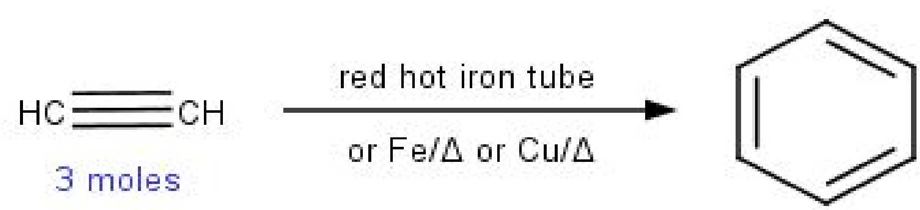
Acetylene undergo polymerization under different condition.

a. When acetylene gas is passed through a solution of ammonical cupric chloride, adds on to itself to form a polymer (a simple dimer) vinyl acetylene.

$$CH \equiv CH + CH \equiv CH \xrightarrow{CuCl_2/NH_4OH} CH_2 = CH - C \equiv CH$$

Vinyl acetylene

b. When acetylene gas is passed through a red hot copper tube or iron tube heated up 400-600℃ three molecules of acetylene undergo trimerization to form a trimer benzene, an aromatic hydrocarbon compound. Benzene was prepared for the first time by Berthelot in 1870 by this method.

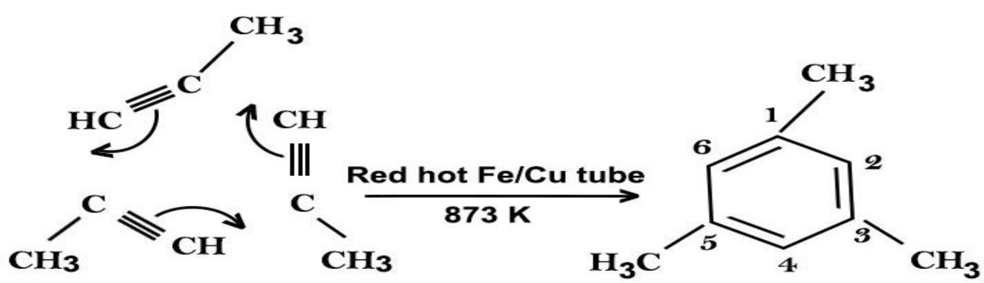



This reaction is useful to convert aliphatic hydrocarbon compound to aromatic hydrocarbon.

Similarly, when propyne gas is passed through red hot iron tube three molecules of it undergo trimerization to give tri-methyl benzene.


1, 3, 5 trimethylbenzene

Or




1,3,5 trimethylbenzene

# 3. Oxidation reaction:-

## a. Combustion:-

When acetylene gas is burnt in oxygen it undergo full combustion and burns explosively producing carbon dioxide and water (steam). The reaction is purely exothermic and produces heat energy up to 3000℃. Thus a mixture of acetylene and oxygen is used for the production of oxy-acetylene flame used for welding.

$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$ + heat energy.

## b. Oxidation with alkaline $KMnO_4$:-

### (Bayer's test or test of unsaturation)-

The alkaline solution of cold and dilute potassium permanganate is also called Bayer' reagent. It is an oxidizing agent.

When unsaturated compound like alkyne is treated with Bayer's reagent is the pink colour of Bayer's reagent is discharged due to the formation of acid. Such a test of unsaturated compound with alkaline $KMNO_4$ is called Bayer's test.

Alkyne like ethyne with Bayer's reagent give oxalic acid.

The reaction undergoes by following steps-

$$C - H \equiv C - H \; + \; 2[O] \xrightarrow[<30℃]{KMNO_4/OH-} CHO = CHO$$

1, 2 ethenedial

Thus formed ethenedial undergo further oxidation under same condition to give 1, 2 ethane dioic acid (Oxalic acid).

$$\underset{\text{1, 2 ethenedial}}{CHO = CHO} \; + 2[O] \xrightarrow[<30℃]{KMNO_4/OH-} \underset{\text{1, 2 ethane dioic acid (Oxalic acid)}}{COOH - COOH}$$

Similarly propyne reacts with Bayer's reagent to give ethanoic acid

$$\underset{\text{Propyne}}{CH_3 - C \equiv CH} \; + \; 4[O] \xrightarrow[<30℃]{KMNO_4/OH-} \underset{\text{Ethanoic acid}}{CH_3 - COOH} \; + \; CO_2$$

## c. Oxidation with acidified $K_2Cr_2O_7$:-

Acetylene gas is passed through acidified solution of potassium dichromate the orange colour of the solution gets discharged due to the redox reaction and the formation of ethanoic acid.

$$C - H \equiv C - H \; + \; [O] \; + H_2O \xrightarrow{\text{acidified } K_2Cr_2O_7} \underset{\text{Ethanoic acid}}{CH_3 - COOH}$$

## 4. Substitution reaction (Showing acidic nature of acetylene):-

The acidic nature of hydrocarbon is the tendency of the molecule to lose proton ($H^+$)

Hydrogen becomes more and more positive as we pass along the series Ethane < Ethene < Ethyne.

That means the hydrogen atom linked to the triply bonded carbon atom is the most positive and can be lost as a proton under suitable condition.

Thus acetylene shows acidic character.

The acidic character of acetylene can be explained on the basis of the hybridization of carbon orbitals.

The carbon atom in acetylene ($CH \equiv CH$) is SP hybridized, in ethene ($CH_2=CH_2$) it is $SP^2$ hybridized and in ethane ($CH_3$ -$CH_3$) carbon atom is $SP^3$ hybridized.

The percentage of S character in SP hybridized orbital is 50%, the percentage of S character in $SP^2$ hybridized orbital is 33.33% and that in $SP^3$ hybridized orbital is onlt 25%.

A hybrid orbital having greater percentage of S character will tend to keep the shared electron closer to the nucleus i.e. electronegativity of carbon atom increases with the increase of percentage of S character in itd hybrid orbital and it becomes easy for hydrogen to liberate as a proton ($H^+$).

Hence ethyne is more acidic than ethene which in turn more acidic than ethane.

Due to is acidic nature, acetylene forms metallic salts with active metals like sodium and with active metals like ammonical cuprous chloride and ammonical silver nitrate.

The metallic salts obtained are called **Acetylides.**

a. Reaction with sodium:-

Acetylene reacts with sodium in presence of liquid ammonia to form sodium acetylide.

$$2CH\equiv CH \; + \; 2Na \xrightarrow{Liq.NH_3} 2CH\equiv CNa \; + \; H_2$$

monosodium acetylide

$$2CH\equiv CNa \; + 2Na \xrightarrow{Liq.NH_3} 2NaC\equiv CNa \; + H_2$$

disodium acetalide

b. Reaction with ammonical Cuprous Chloride solution:-

When acetylene gas is passed over ammonical Cuprous Chloride, a red precipitation of Copper acetylide is formed.

$$CH\equiv CH \; + \; Cu_2Cl_2 \; + 2NH_4OH \rightarrow CuC\equiv CCu\downarrow + 2NH_4Cl \; + \; 2H_2O$$

Copper acetylide
Red ppt.

Copper acetylide on treating with dilute HCl regenerates the acetylene gas.

$$CuC\equiv CCu \; + \; 2HCl \rightarrow HC\equiv CH \; + Cu_2Cl_2$$

c. Reaction with ammonical silver nitrate solution:-

When acetylene gas is passed over ammonical silver nitrate solution, a white precipitation of silver acetylide is formed.

$CH\equiv CH + 2AgNO_3 + 2NH_4OH \rightarrow AgC\equiv CAg\downarrow + 2NH_4NO_3 + 2N_2O$

Silver acetylide

White ppt.

These silver and copper acetylides are used for the purification of acetylene gas. When silver or copper acetylides are treated with mineral acid pure acetylene gas is obtained.

$AgC\equiv CAg + 2HNO_3 \rightarrow H-C\equiv C-H \quad 2AgNO_3$

$CuC\equiv CCu + 2HCl \rightarrow HC\equiv CH + Cu_2Cl_2$

NOTE:-

Only terminal alkynes with acidic proton (i.e.alkyne in which hydrogen is bonded to triply bonded carbon like in ethyne) can react with sodium, ammonical silver nitrate solution and with ammonical cuprous chloride to form corresponding acetylides.

Non-terminal alkynes with no acidic proton do not respond to any of these reagents.

$H-C\equiv C-H + 2Na \rightarrow 2NaC\equiv CNa + H_2$

$CH_3-C\equiv C-H + 2Na \rightarrow 2CH_3-C\equiv C-Na$

$CH_3-C\equiv C-CH_3 + 2Na \rightarrow$ No rxn.

$CH_3-C\equiv C-CH_3 + AgNO_3 + NH_4OH \rightarrow$ No rxn.

$CH_3-C\equiv C-CH_3 + Cu_2Cl_2 + NH_4OH \rightarrow$ No rxn.

Uses:-

1. Acetylene gas is used for the artificial ripening of fruits.
2. Used for the production of oxyacetylene flame for welding and cutting of iron.
3. Used for making acetylene lamps for illumination as acetylene burns with bright light.
4. Uesd in preparing plastics, synthetic rubber, synthetic fibres called orlon.
5. Used as starting material for the production of acstaldehydes, acetic acid , ethyl alcohol etc.