15 ALKYNES

15.1 Introduction :

Q.1.What are alkynes ?

Ans : *Alkynes are aliphatic unsaturated hydrocarbons containing a carbon-carbon triple bond* (C≡C) *in their molecules.*

e.g. CH ≡CH Acetylene

CH_3–C≡ CH Propyne.

a) General formula of alkynes is C_nH_{2n-2}.

b) Alkynes contain four hydrogen atoms less than corrosponding alkanes & two hydrogen aoms less than corrosponding alkenes.

c) The first member of alkynes is acetylene hence they are called acetylenes.

d) The –C≡C– (functional group in alkynes) is called acetylenic linkage or bond.

15.2 Electronic structure of acetylene

Q.2. Give dash and dot (structures) formulae of i) Acetylene ii) Propylene

Ans: i) Acetylene

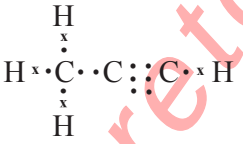
H — C ≡ C — H
Structural formula

H ×• C ⁝⁝ C •× H
Electronic formula

ii) Propylene

CH_3 — C ≡ C — H

(Dash strucutre)



(Dot structure)

(Lewis electron-dot formula)

15.3 Nomenclature of alkynes

a) Derived names : The first member of alkyne series is acetylene.Other members are considered as alkyl derivatives of acetylene, obtained by replacing one or both H — atoms by alkyl groups.

b) IUPAC names : (Rules)

i) Select the longest continuous carbon chain containing triple bond as the parent alkane.

ii) From the name of parent alkane suffix *-ane* is replaced by *-yne* (i.e. alkane → alkyne).

iii) Indicate the position of triple bond by lowest possible number.

iv) Side chains if present are located by proper numbers.

Compound	Derived name	IUPAC name
CH≡CH	Acetylene	Ethyne
H_3C–C≡CH	Methyl acetylene	Propyne
H_3C–CH_2–C≡CH	Ethyl acetylene	But-1-yne
CH_3–C≡C–CH_3	Dimethyl acetylene	But-2-yne
CH_3–C≡C–C_2H_5	Ethyl methyl acetylene	Pent-2-yne
H_3C–CH(–CH_3)–C≡CH	Isopropyl acetylene	3-Methyl-but-1-yne

Q.3. Give the IUPAC names of the following compounds.

Compounds	IUPAC names
i) CH_3–CH_2–CH(CH_3)–C≡CH	3 Methylpent-1-yne
ii) CH_3–C≡C–CH(CH_3)–CH_3	4-Methylpent-2-yne

15.4 General methods of preparation of alkynes

i) By dehydrohalogenation of dihalides

ii) From calcium carbide

iii) From tetrahalides using Zn (dehalogenation)

i) By dehydrohalogenation of dihalides :

Dihaloalkanes :

The derivatives of alkanes obtained by replacing two H atoms by two halogen atoms are called dihaloalkanes.

They are of two types :

i) Geminal dihalides ii) Vicinal dihalides

i) Geminal dihalides : The dihalides in which both the halogen atoms (X-atoms) are attached to the same carbon are called as geminal dihalides.

Their common name is alkylidene dihalide

e.g.

i) CH_2Cl_2
Methylene dichloride
(Dichloromethane)

ii) CH_3– CH(Cl)(Cl)
Ethylidene dichloride.
(1,1– Dichloroethane.)

iii) $CH_3-CH_2-CH(Br)_2$ iv) $CH_3-C(Cl)_2-CH_3$

n-Propylidene dibromide (1,1 - Dibromopropane)

Isopropylidene dichloride. (2,2 - Dichloropropane)

ii) Vicinal dihalides : The dihalides in which the two halogen atoms are attached to adjacent carbon atoms are called vicinal dihalides.

Their common name is alkylene dihalide

e.g. i) $CH_2(Cl)-CH_2(Cl)$ Ethylene dichloride (1,2 – Dichloroethane.)

ii) $CH_3-CH(Cl)-CH_2(Cl)$ Propylene dichloride. (1,2 – Dichloropropane.)

Q.4. What is action of alcoholic KOH on
i) Ethylidene dichloride
ii) Propylene dibromide.

Ans : i) When ethylidene dichloride is boiled with alcoholic caustic potash acetylene is obtained.

$$CH_2(Cl)-CH(Cl)-H + 2KOH \xrightarrow[\text{Alcoholic}]{\Delta} CH \equiv CH + 2KCl + 2H_2O$$

Ethylidene dichloride — Ethyne

ii) When propylene dibromide is boiled with alcoholic caustic potash propyne is obtained.

$$CH_3-CH(Br)-CH_2(Br) + 2KOH \xrightarrow[\text{Alcoholic}]{} CH_3-C\equiv CH + 2KBr + 2H_2O$$

Propylene dibromide — Propyne

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ii) From calcium carbide :

Q.5.How will you prepare acetylene (ethyne) by calcium carbide.

Ans : When calcium carbide reacts with water to form acetylene.

$$C(Ca)\equiv C + 2HOH \longrightarrow CH \equiv CH + Ca(OH)_2$$

Acetylene — Calcium carbide

Q.6. Explain the preparation of acetylene in laboratory.

Ans : In laboratory acetylene is prepared by the action of water on calcium carbide.

$$C(Ca)\equiv C + 2HOH \longrightarrow CH \equiv CH + Ca(OH)_2$$

Acetylene — Calcium carbide

i) The apparatus is flushed with N_2 gas to displace air since acetylene forms explosive mixture with oxygen in air.

ii) Pieces (lumps) of calcium carbide are taken in a conical flask fitted with a dropping funnel and a delivery tube.

iii) Water is then added dropwise on calcium carbide from dropping funnel, when acetylene gas is obtained.

iv) Acetylene contains impurities of hydrogen sulphide, phosphine (PH_3), ammonia etc. It is purified by passing through acidified $CuSO_4$ solution.

v) Pure acetylene is then collected by downward displacement of water.

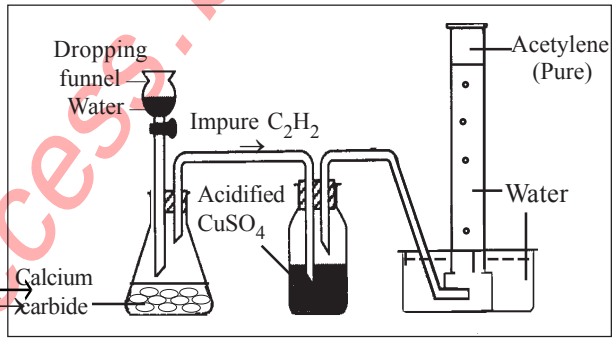

Fig. 15.1 Preparation of Acetylene.

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iii) From tetrahalides using Zn (dehalogenation) :

Q.7.How will you prepare acetylene from ethylene tetrabromide.

Ans : When ethylene tetra bromide reacts with zinc in presence of methyl alcohol to form acetylene

$$H-C(Br)_2-C(Br)_2-H + 2.Zn \xrightarrow[\text{Methanol}]{\Delta} \underset{\text{Acetylene}}{H\text{-}C\equiv C\text{-}H} + 2ZnBr_2$$

(1,1,2,2- tetrabromoethane)

15.5 Chemical Properties of Acetylene

i) Alkynes are highly unsaturated compounds. They contain a triple bond which consists of one sigma (σ) and two pi (π) bonds.

ii) Hence characteristics reactions of alkynes are *addition reactions* (similar to alkenes).

iii) Addition reactions of acetylene occurs in two steps.

In first step, one molecule of reagent is added to form ethylene derivatives. This on addition of second molecule of reagent in second step gives ethane derivative.

iv) Chemical properties of acetylene :

1) Hydrogenation **2) Halogenation**

3) Hydrohalogenation **4) Addition of H_2SO_4**

5) Addition of H_2O **6) Ozonolysis**

7) Formation of benzene

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1) Hydrogenation : Addition of hydrogen

Q.8.Explain the addition of hydrogen on acetylene.

OR

What is the action of hydrogen on acetylene?

Ans : When acetylene upon catalytic hydrogenation gives ethane.

$$\underset{\text{Acetylene}}{CH \equiv CH} + H_2 \xrightarrow[523-573\ K]{Ni} \underset{\text{Ethylene}}{CH_2 = CH_2}$$

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + H_2 \xrightarrow[523-573\ K]{Ni} \underset{\text{Ethane}}{CH_3 - CH_3}$$

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2) Halogenation : Addition of halogens

Q.9.What is the action of chlorine on acetylene?

Ans : When acetylene combines with chlorine in the presence of carbon tetrachloride to form ethylene tetrachloride.

$$\underset{\text{Acetylene}}{CH \equiv CH} + Cl_2 \xrightarrow{Light} \underset{\text{Acetylene dichloride}}{\underset{\text{(trans-1,2-Dichloroethane)}}{\underset{H}{\overset{Cl}{C=C}}\overset{H}{\underset{Cl}{}}}} \xrightarrow{Cl_2}$$

$$\underset{\text{Acetylene tetrachloride}}{\underset{\text{(1,1,2, 2-Dichloroethane)}}{H-\overset{Cl}{\underset{Cl}{C}}-\overset{Cl}{\underset{Cl}{C}}-H}}$$

Q.10. What is action of bromine on ethyne

Ans : Acetylene combines with bromine water to form ethylene tetrabromide.

$$\underset{\text{Acetylene}}{CH \equiv CH} + \underset{\text{aq.}}{Br_2} \xrightarrow{Br_2} \underset{\text{trans-1,2 Dibromoethene}}{\underset{H}{\overset{Br}{C=C}}\overset{H}{\underset{Br}{}}}$$

$$\underset{\text{(1,1,2,2-terabromoethane)}}{H-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}-H}$$

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3) Hydrohalogenation :

Q. 11. Explain Hydrohalogenation of acetylene.

Ans : Addition of halogen acid (HX)

Acetylene combines with two molecules of halogen acid to form first vinyl halide and then ethylidene dihalide.

Addition of second HX molecule takes place according to Markownikoff's rule. Reactivity of the acids is HI > HBr > HCl.

$$\underset{\text{Acetylene}}{CH \equiv CH} + H\text{-}Br \xrightarrow{HBr\ (\text{Markownikoff's add}^n)} \underset{\text{Vinyl bromide}}{CH_2 = \underset{Br}{CH}}$$

$$\xrightarrow{} \underset{\text{Ethylidene dibromide}}{CH_3 - \overset{Br}{\underset{Br}{CH}}}$$

$$\underset{\text{Acetylene}}{CH \equiv CH} + H\text{-}I \rightarrow \underset{\text{Vinyl iodide}}{CH_2 = \underset{I}{CH}} \xrightarrow[(\text{Markownikoff's add}^n)]{HI} \underset{\text{Ethylidene iodide}}{CH_3 - \overset{I}{\underset{I}{CH}}}$$

$CH_2 = CH$ – group is called vinyl group.

Q.12. What is action HBr on acetylene in presence of peroxide.

Ans :Peroxide effect : Acetylene reacts with HBr in presence of peroxide to give antimarkownikoff's addition product 1,2-dibromoethane.

$$\underset{\text{Acetylene}}{CH \equiv CH} + HBr \rightarrow \underset{\text{Vinyl bromide}}{CH_2 = \underset{Br}{CH}} \xrightarrow[peroxide]{HBr} \underset{\text{Ethylene dibromide}}{CH_2 - \underset{Br}{CH_2}}$$

N.B. Peroxide effect is observed only in addition of HBr (and not for HCl or HI)

Q.13. How will you convert acetylene into
i) Ethylidene dibromide &
ii) Ethylene dibromide.

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4) Addition of concentrated H_2SO_4 :

Q.14. Explain addition of concentrated H_2SO_4 on ethyne OR How will you convert acctylene into ethylidene dihydrogen sulphate.

Ans : Acetylene combines with two molecules of H_2SO_4 to form first vinyl hydrogen sulphate and then ethylidene dihydrogen sulphate (a Markownikoff's addition product).

$$CH \equiv CH + HOSO_3H \longrightarrow CH_2 = CH(OSO_3H)$$

Acetylene — Vinyl hydrogen sulphate

$$CH_3 - CH(OSO_3H)_2$$

($HOSO_3H$, Markownikoff's addn) — Ethylidene dihydrogen sulphide

5) Addition of water : Hydration of Acetylene :

Q.15. Explain the addition of water molecule on acetylene.

Ans : When acetylene is passed through dil H_2SO_4 (42%) at 333K in presence of mercuric sulphate catalyst (1%), acetaldehyde is obtained.

The intermediate product vinyl alcohol is quite unstable. It isomerises to give acetaldehyde.

$$CH \equiv CH + HOH \xrightarrow[HgSO_4\ (1\%)\ 333\ K]{dil.\ H_2SO_4} CH_2 = CH(OH)$$

Acetylene — Vinyl alcohol (enol)

$$\xrightarrow{Isomerism} CH_3 - C(H)=O$$

Acetaldehyde

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6) Ozonolysis: Addition of ozone :

Q.16. Explain the ozonolysis of acetylene.

Ans : When ozone is passed through the solution of acetylene in CCl_4 ozonide is formed. This upon hydrolysis by water in presence of zinc gives glyoxal.

$$CH \equiv CH + O_3 \xrightarrow{Ether} H-C(-O-O-)-C-H$$

Acetylene — Acetyleneozonide

$$H-C(-O-O-)-C-H \xrightarrow[H_2O]{Zn} H-C(=O)-C(=O)-H + H_2O_2$$

Acetyleneozonide — Glyoxal

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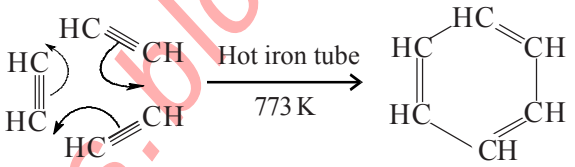
7) Formation of benzene (polymerisation) :

Q.17. Explain the formation of benzene by acetylation.

Ans : When acetylene is passed through red hot iron tube at 773K it polymerisation give benzene.



Acetylene (3 molecules) — Benzene

Q.18. Give the uses of acetylene :

Uses : Acetylene is used .

i) In artificial ripening of fruits.
ii) As illuminant (i.e. for producing light).
iii) In oxyacetylene flame (about 3273 K) used for cutting and welding metals.
iv) In preparation of acetaldehyde, acetic acid, ethyl alcohol etc.
v) In preparation of vinyl chloride which is used to prepare polyvinyl chloride plastic (P.V.C.).
vi) In preparation of acrylonitrile which is used to prepare synthetic rubber.
vii) In preparation of acetylene dichloride and acetylene tetra chloride which are used as solvents.

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