

## 1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 2)
Module Name/Title	Hydrocarbons: Part 3
Module Id	kech_21303
Pre-requisites	Knowledge about hybridization and orbital overlap, sigma and pi bonds, Rules of IUPAC nomenclature, Substitution reactions, Addition reactions
Objectives	After going through this lesson, the learners will be able to: <ul style="list-style-type: none"><li>• Name alkynes according to IUPAC system of nomenclature.</li><li>• Write structures for different isomers possible for alkynes.</li><li>• Understand the structure of triple bond and hybridization involved in alkynes.</li><li>• Write different methods of preparation of alkynes.</li><li>• Explain the various physical and chemical properties of alkynes.</li><li>• Distinguish between alkanes, alkenes and alkynes on the basis of these properties.</li><li>• Appreciate the role of polymerization reaction for industrial applications.</li></ul>
keywords	Triple bond, hybridization, acidity, terminal alkynes, addition, polymerization

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### 1. Introduction

You have studied earlier that hydrocarbons can be classified as saturated and unsaturated. Saturated hydrocarbons are called alkanes whereas alkenes and alkynes are unsaturated hydrocarbons. Alkynes are those hydrocarbons which contain at least one triple bond between two carbon atoms. The number of hydrogen atoms is less in alkynes as compared to alkenes or alkanes. Their general formula is  $C_nH_{2n-2}$ . The first stable member of alkyne series is ethyne which is popularly known as acetylene. Acetylene is used for arc welding purposes in the form of oxyacetylene flame obtained by mixing acetylene with oxygen gas. Alkynes are starting materials for a large number of organic compounds. Hence, it is interesting to study this class of organic compounds.

### 2. Nomenclature and Isomerism

In common system, alkynes are named as derivatives of acetylene. In IUPAC system, 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 triply bonded carbon. Common and IUPAC names of a few members of alkyne series are given in Table given below.

Table 13.2 Common and IUPAC Names of Alkynes ( $C_nH_{2n-2}$ )

Value of n	Formula	Structure	Common name	IUPAC name
2	$C_2H_2$	H-C≡CH	Acetylene	Ethyne
3	$C_3H_4$	CH <sub>3</sub> -C≡CH	Methylacetylene	Propyne
4	$C_4H_6$	CH <sub>3</sub> CH <sub>2</sub> -C≡CH	Ethylacetylene	But-1-yne
4	$C_4H_6$	CH <sub>3</sub> -C≡C-CH <sub>3</sub>	Dimethylacetylene	But-2-yne

You observe from the above table that, ethyne and propyne have got only one structure but there are two possible structures for butyne –

(i) but-1-yne and

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(ii) but-2-yne.

Since these two compounds differ in their structures due to the position of the triple bond, they are known as **position isomers**. Similarly for the next homologue i.e., the next alkyne with molecular formula  $C_5H_8$ , we can arrange five carbon atoms with a continuous chain and with a side chain.

Following are the possible structures :

Structure	IUPAC name
I.    1   2   3   4   5 $HC\equiv C-CH_2-CH_2-CH_3$	Pent-1-yne
II.   1   2   3   4   5 $H_3C-C\equiv C-CH_2-CH_3$	Pent-2-yne
III.  4   3   2   1 $H_3C-CH-C\equiv CH$   $CH_3$	3-Methyl but-1-yne

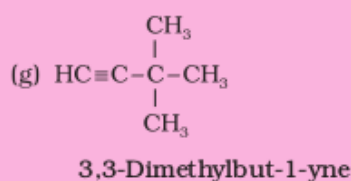
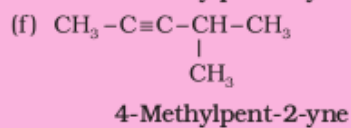
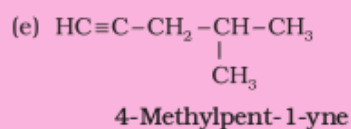
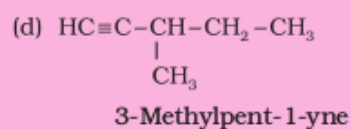
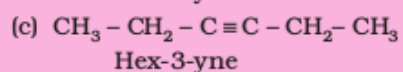
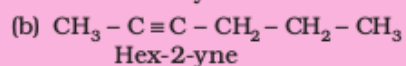
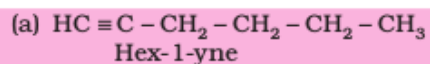
Structures I and II are position isomers and structures I and III as well as II and III are chain isomers.

### Problem 1

Write structures of different isomers corresponding to the 5th member of alkyne series. Also write IUPAC names of all the isomers. What type of isomerism is exhibited by different pairs of isomers?

### Solution

5th member of alkyne has the molecular formula  $C_6H_{10}$ . The possible isomers are:



Position and chain isomerism shown by different pairs.

### 3. Structure of Triple Bond

Ethyne is the simplest molecule of alkyne series. Structure of ethyne is shown in Fig. 1 below.

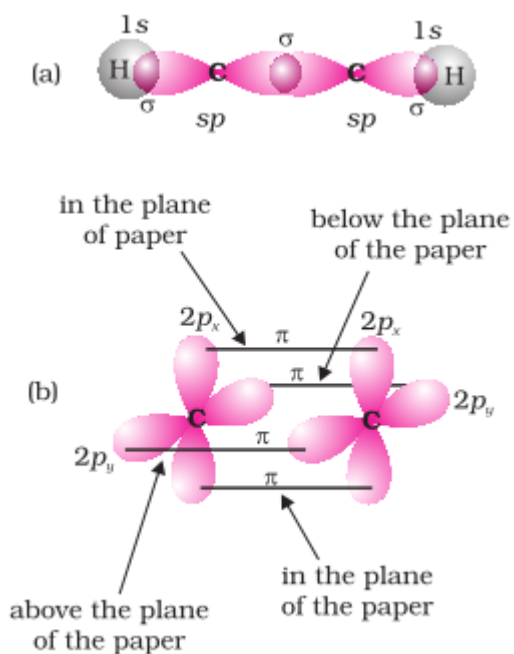


Fig. 1 . Orbital picture of ethyne showing (a) sigma overlaps (b) pi overlaps

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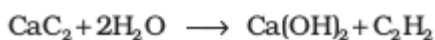
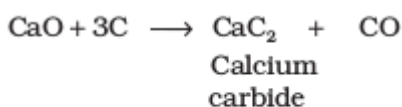
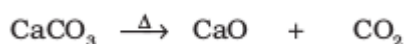
Each carbon atom of ethyne has two  $sp$  hybridised orbitals. Carbon-carbon sigma ( $\sigma$ ) bond is obtained by the head-on overlapping of the two  $sp$  hybridised orbitals of the two carbon atoms. The remaining  $sp$  hybridised orbital of each carbon atom undergoes overlapping along the internuclear axis with the  $1s$  orbital of each of the two hydrogen atoms forming two C-H sigma bonds. H-C-C bond angle is of  $180^\circ$ . Each carbon has two unhybridised  $p$  orbitals which are perpendicular to each other as well as to the plane of the C-C sigma bond. The  $2p$  orbitals of one carbon atom are parallel to the  $2p$  orbitals of the other carbon atom, which undergo lateral or sideways overlapping to form two pi ( $\pi$ ) bonds between two carbon atoms. Thus ethyne molecule consists of one C-C  $\sigma$  bond, two C-H  $\sigma$  bonds and two C-C  $\pi$  bonds. The strength of C $\equiv$ C bond (bond enthalpy  $823 \text{ kJ mol}^{-1}$ ) is more than those of C=C bond (bond enthalpy  $681 \text{ kJ mol}^{-1}$ ) and C-C bond (bond enthalpy  $348 \text{ kJ mol}^{-1}$ ). The C $\equiv$ C bond length is shorter ( $120 \text{ pm}$ ) than those of C=C ( $133 \text{ pm}$ ) and C-C ( $154 \text{ pm}$ ). Electron cloud between two carbon atoms is cylindrically symmetrical about the internuclear axis. Thus, ethyne is a linear molecule.

#### 4. Preparation of Alkynes

##### 1. Specific methods for preparation of ethyne

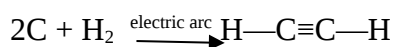
###### (i) From calcium carbide

On industrial scale, ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime with coke. Quick lime can be obtained by heating limestone as shown in the following reactions:



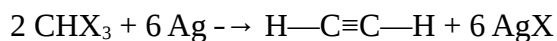
###### (ii) Berthelot's Synthesis

Ethyne is also produced when electric spark is produced between carbon electrodes in the atmosphere of hydrogen gas .

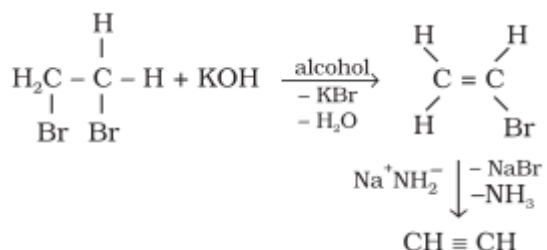


###### (iii) From haloforms

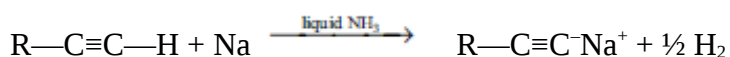
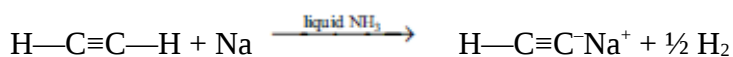
Ethyne can also be obtained by the reaction of haloforms with silver metal.



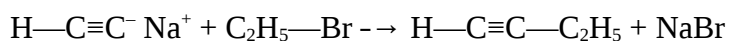
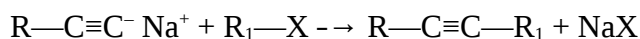
**2. From vicinal dihalides :** Vicinal dihalides on treatment with alcoholic *potassium hydroxide* undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form vinyl halide (alkenyl halide) which on further treatment with sodamide gives alkyne.



**3. From smaller alkynes :** Terminal alkynes on treatment with sodium metal in liquid ammonia give the sodium salts. Such as acetylene reacts to give sodium Ethynide (also known as sodium acetylide).



These sodium salts react with primary alkyl halides to form higher alkynes



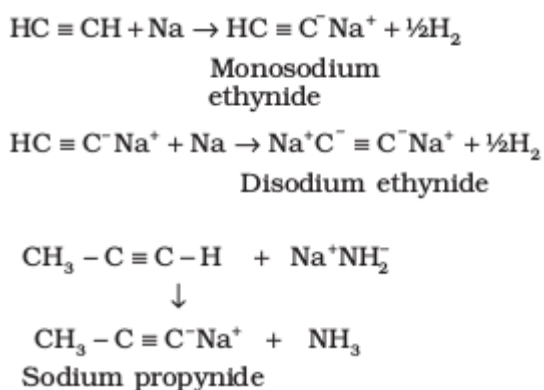
## 5. Physical Properties of Alkynes

Physical properties of alkynes follow the same trend as in alkenes and alkanes. First three members are gases, the next eight are liquids and the higher ones are solids. All alkynes are colourless. Ethyne has a characteristic odour. Other members are odourless. Alkynes are weakly polar in nature. They are lighter than water and immiscible with water but soluble in organic solvents like ether, carbon tetrachloride and benzene. Their melting point, boiling point and density increase with increase in molar mass.

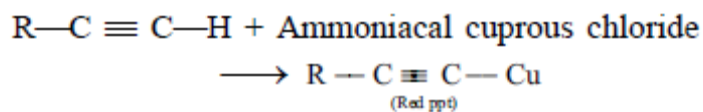
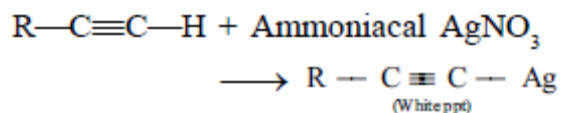
## 6. Chemical Properties of Alkynes

Alkynes show acidic nature, addition reactions and polymerisation reactions as explained below. The other reactions include oxidation and reduction.

**A. Acidic character of alkyne:** Sodium metal and sodamide ( $\text{NaNH}_2$ ) are strong bases. They react with ethyne to form sodium acetylide with the liberation of hydrogen gas as has been shown above in the preparation of higher alkynes. These reactions have not been observed in case of ethene and ethane thus indicating that ethyne is acidic in nature in comparison to ethene and ethane. This happens because the hydrogen atoms in ethyne are attached to  $sp$  hybridised carbon atoms whereas they are attached to  $sp^2$  hybridised carbon atoms in ethene and  $sp^3$  hybridised carbons in ethane. Due to the maximum percentage of  $s$  character (50%), the  $sp$  hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity; hence, these attract the shared electron pair of the C-H bond of ethyne to a greater extent than that of the  $sp^2$  hybridised orbitals of carbon in ethene and the  $sp^3$  hybridised orbital of carbon in ethane. Thus in ethyne, hydrogen atoms can be liberated as protons more easily as compared to ethene and ethane. Hence, hydrogen atoms of ethyne attached to triply bonded carbon atom are acidic in nature. You may note that only the hydrogen atoms attached to the triply bonded carbons are acidic and not all the hydrogen atoms of alkynes.



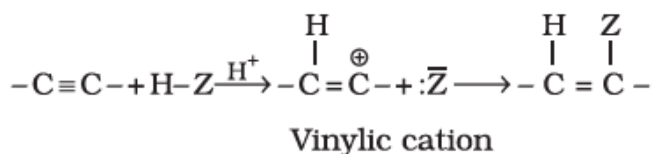
Due to the acidic nature of hydrogen atoms attached to triply bonded carbon atoms, they also react with certain heavy metal ions, e.g.,  $\text{Ag}^+$  and  $\text{Cu}^+$  to form insoluble acetylides which are obtained as precipitates. These reaction will be shown by terminal alkynes only and hence can be used to differentiate from nonterminal alkynes.



These reactions are not shown by alkenes and alkanes, hence are also used to distinguish terminal alkynes from alkenes and alkanes. Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour :

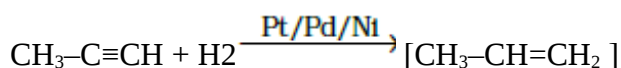
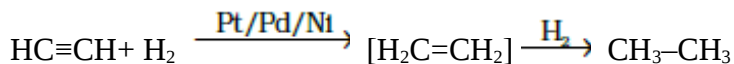
- (i)  $\text{HC}\equiv\text{CH} > \text{H}_2\text{C}=\text{CH}_2 > \text{CH}_3-\text{CH}_3$   
 (ii)  $\text{HC}\equiv\text{CH} > \text{CH}_3-\text{C}\equiv\text{CH} \gg \text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$

**B. Addition reactions:** Alkynes contain a triple bond, so they add up two molecules of hydrogen, halogen, hydrogen halides etc. Formation of the addition product takes place according to the following steps.



The addition product formed depends upon stability of vinylic cation. Addition in unsymmetrical alkynes takes place according to Markovnikov rule. Majority of the reactions of alkynes are the examples of electrophilic addition reactions. A few addition reactions are given below:

**(i) Addition of hydrogen**



Propyne

Propene

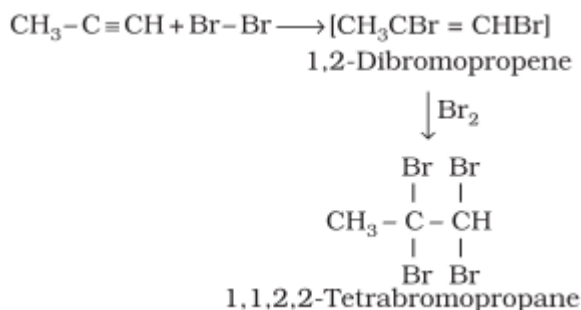


Propane



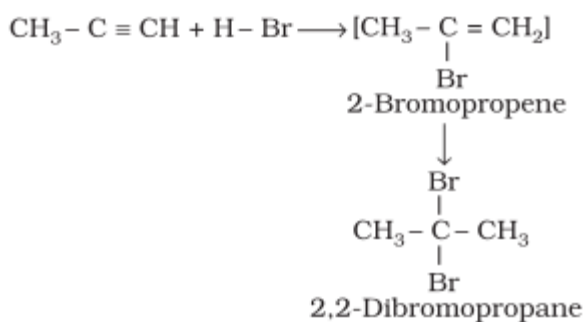
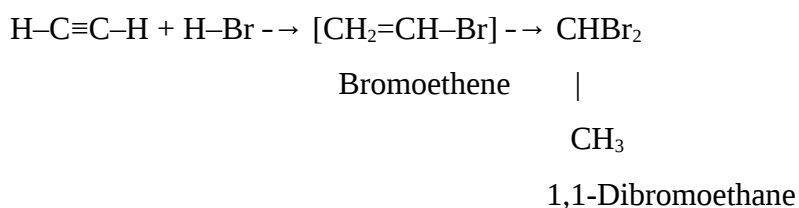
## (ii) Addition of halogens

When a solution of bromine is added to any alkyne, two moles of bromine add up to form a tetrabromo derivative. Reddish orange colour of the solution of bromine in carbon tetrachloride is decolourised. This can also be used as a test for unsaturation.



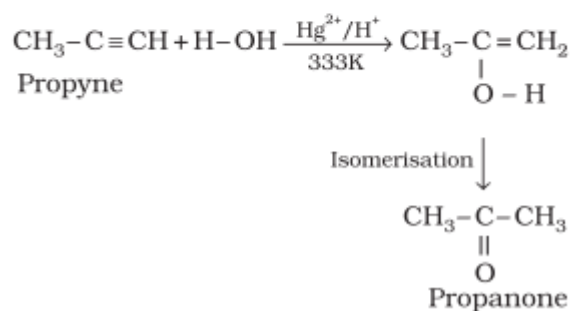
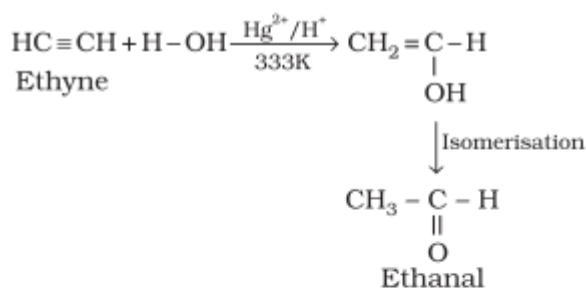
## (iii) Addition of hydrogen halides

Two molecules of hydrogen halides (HCl, HBr, HI) add to alkynes to form *gem* dihalides (in which two halogens are attached to the same carbon atom)



## (iv) Addition of water

Like alkanes and alkenes, alkynes are also immiscible and do not react with water. However, one molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333 K to form carbonyl compounds. For example ethyne gives ethanal whereas propyne gives propanone. The addition of water molecule follows Markovnikov's rule.



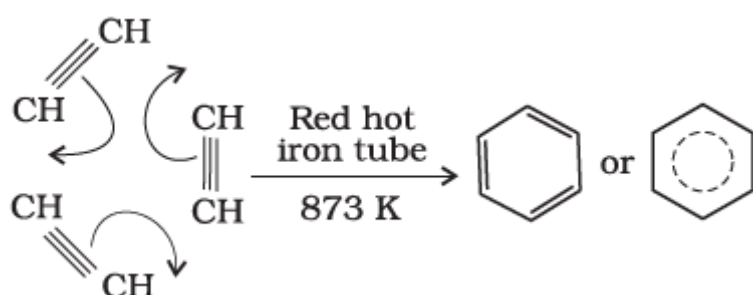
### (v) Polymerisation

**(a) Linear polymerisation:** Under suitable conditions, linear polymerisation of ethyne takes place to produce polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of

$(\text{CH}=\text{CH}-\text{CH}=\text{CH})$  and can be represented

as  $-(\text{CH}=\text{CH}-\text{CH}=\text{CH})_n-$ . Under special conditions, this polymer conducts electricity. Thin film of polyacetylene can be used as electrodes in batteries. These films are good conductors, lighter and cheaper than the metal conductors.

**(b) Cyclic polymerisation:** Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene, which is the starting molecule for the preparation of derivatives of benzene, dyes, drugs and large number of other organic compounds. This is the best route for entering from aliphatic to aromatic compounds.



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## 7. Summary

Alkynes are unsaturated compounds containing one or more triple bonds. Each triple bond contains one sigma bond formed by head-on overlapping between the two sp hybridized orbitals of the two carbon atoms and two pi bonds formed by the sideways overlapping of the two unhybridized p orbitals of each carbon atom forming the triple bond. The smallest alkyne, ethyne is industrially prepared by the treatment of calcium carbide with water. Other alkynes can be obtained from ethyne and also by the elimination reactions. The hydrogen atoms attached to the triply bonded carbons in alkynes are acidic in nature and thus can be used to distinguish between terminal and non-terminal alkynes. Alkynes like alkenes mainly undergo electrophilic addition reactions. They also undergo linear polymerisation to form industrially important products and cyclic polymerization to form benzene.