**Alkynes**

**Alkynes: General Outline: —**

Alkynes are the open chain, linear unsaturated acyclic hydrocarbons characterized by the presence of a carbon-carbon **triple** bond (). They form a homologous series having general formula . Since, alkenes contain four hydrogens ***fewer*** than the corresponding alkanes (saturated acyclic hydrocarbons); they are also known as **unsaturated aliphatic hydrocarbons**. Alkynes are also called ***acetylenes***, since they are derived from **acetylene**, the simplest alkyne. Alkynes are not easily bent into a ring though a few (e.g. **cyclooctyne** and **cyclononyne**) which are not very stable, have been synthesized. **Cycloalkynes** are rare except when the ring is large.

**Sources and Utility of Alkanes: —**

The chemistry of carbon-carbon **triple** bond () is similar to the carbon-carbon **double** bond. There are, however, some reactions that are specific to the triple bond of the alkynes. Acetylenic , is a reactive functional group. The **unusual acidity** of acetylenic , together with other important reactions of acetylenic triple bond, has helped acetylene to emerge as a powerful tool in **synthetic organic chemistry**.

Alkynes are not common in nature as alkenes, but some natural products (e.g. , , etc.), containing triple bond have been identified. Acetylenic bond is rare in drugs. However, a few drugs of interest (**an analgesic**),(**a birth control pill**), (an **antitumor agent**) have been of interest as **medicinal** interest.

**Nomenclature of Alkynes: —**

In trivial (common) systems, alkynes are considered as derivatives of acetylene. In IUPAC system, the longest continuous chain containing triple bond is chosen and the carbon numbering is given from the end close to the triple bond. The **suffix**used for naming alkyne is instead of of the corresponding alkane. The substituents are named as usual as in alkanes and alkenes. For example,

IUPAC: Ethyne Propyne But-1-yne But-2-yne

Common: Acetylene Methyl acetylene Ethyl acetylene Dimethyl acetylene



**Acidity of Alkynes: —**

Acetylene, (unlike ethyne and ethane), reacts with to form the salt **sodium acetylide** and liberates hydrogen gas ( The reaction of with water, ).

This reaction shows the **acidic character** of **hydrogen** attached to **triple bonded** carbon in alkynes.

A weaker acid is known to be displaced from its salt by a stronger acid. While acetylene displaced from its salt **sodamide** (), water displaces acetylene from its salt, sodium acetylide.



Therefore, ***acetylene is a stronger acid than ammonia, but weaker acid than water*** as apparent from their values.

**The relative acidities of ethane, ethylene and acetylene**: The decreasing order of acidities of these hydrocarbons is:

Conversely, the **decreasing** order of **basic character** of anions resulting from these hydrocarbons should be:



**Explanation**: The above sequence of acidities or basicity order can be well explained in two approaches —

**[1]**In , and the **unshared pair of electrons** occupy an **, and hybrid orbital** respectively. When we proceed along the series**, and , the - character** of the hybrid orbital decreases and the - character increases. Electrons in - orbitals are held **closer to the nucleus** than they are in - orbitals. This means that - electrons have lower energy and **greater stability than - electrons**. In general, **greater is the - character** in the hybrid containing a pair of electrons, the **less basic** is that pair of electron and **higher is the acidity** of its **conjugate** acid. Therefore, the **acetylene should** be the **most acidic** and **ethane least** in the above series.

**[2]**The bonds in acetylene, ethylene and ethane are respectively. In other words, the **- hybridized carbon** would **attract the electron pair** constituting the bond of acetylene **morethan** does the **- hybridized carbon** for the electron pair constituting the bond of ethylene. Similarly, the **- hybridized carbon** in **ethylene** compared to **- hybridized carbon** in **ethane** have greater attraction for electron pair constituting the bond in them. This means that bond in **acetylene** would be **moreionic** than ethylene and bond in **ethylene** would be **more ionic than ethane**. This implies that the hydrogen attached to a **triply bonded** carbon in acetylene have greater tendency to depart as proton () than the hydrogen attached to a doubly bonded carbon in ethylene. On similar ground ethylene tends to depart proton () to a greater extent than the hydrogen attached to a singly bonded carbon in ethane. Hence, **acetylene** is **more acidic than ethylene**, and **ethylene** should be **more acidic** than **ethane**.

**The relative acidities of terminal and disubstituted alkynes**:

Terminal alkynes, i.e. alkynes having at least one bond, show an acidic character, but disubstituted alkynes (e.g. dimethyl acetylene) do not show acidic character due to the lack of hydrogen attached to triple bonded carbon. It is reasonable in the light of what we have explained above.

**General Methods of Preparation of Alkynes: —**

Alkynes are best prepared from —

1. **From Alkyl halides ()**: It includes
   1. Dehydrohalogenation of vicinal or geminal dihalides, and
   2. Dehalogenation of tetrahalides.
2. **From Acetylene**: — by alkylation of acetylene (conversion into higher alkynes).

These general synthetic methods of preparative interest are described below with their suitable mechanisms:

**[1] Synthesis of Alkyne by the Dehydrohalogenation Halides: —**

Vicinal as well as geminal dihalides on treatment with **alcoholic potash** (, usually ethanolic) followed by the reaction with **sodamide**undergoes dehydrohalogenation to form alkynes. For example,



In this reaction, instead of using alcoholic , use of **sodamide in liquid ammonia** fives better yield, due to the formation of minimum side products.



**Application**: Since ***vicinal*** dihalides are easily obtained from alkenes, it provides a **route** for the **conversion of an alkene into an alkyne**. For example, conversion of **ethene** to **ethyne**—

Ethene 1, 2- Dibromoethane Ethyne

**[2] Synthesis of Alkyne by the Dehalogenation of Tetrahalides: —**

When a tetrahalo alkane is heated with metallic zinc, all the halogens are taken away by the zinc to form alkanes to yield an alkyne. For example,



[**Note**: This reaction is more suitable for the purification and protection of a triple bond, and not used as preparative method since the starting tetra halides are themselves obtained from alkynes.]

**[3] Synthesis of Alkyne by the Alkylation of Acetylene: —**

The method consists in treating an acetylene containing at least one -atom on triply bonded - atom with sodamide or better with sodium dissolved in liquid , followed by the action with a - alkyl halide to form higher alkynes. For example,



**Alkylation alkynes using Grignard Reagent:** Alternatively, the interaction of acetylenes with a Grignard reagent, , followed by the action of alkyl halides yields higher alkynes (it is an example of **nucleophilic substitution** reaction). Thus—



**General Physical Properties of Alkynes: —**

Important physical properties of alkynes are studied under the following headings —

1. Physical appearance,
2. Boiling point and melting point, and
3. Solubility

**Physical appearance of Alkynes**:

First three members of alkene () are **gases**,

Next eightmembers of alkene () are **liquids**, and

Alkynes containing - atoms or more are **solids** at ordinary temperature.

Except acetylene all alkynes are colourless and odourless.

**Boiling and Melting point trends of Alkynes**:

The melting point, boiling point and densities of alkyne rise gradually with the increase in - content (i.e. molecular weight).

**Solubility and Dipole moments of Alkenes**:

Alkynes are practically insoluble in water, but soluble in non-polar organic solvents like ether, carbon tetrachloride, benzene, petroleum ether, acetone, etc.

In general, the physical properties of alkynes are similar to alkenes and alkanes of similar molecular weights.  **//**

**General Chemical Properties (Reactions) of Alkynes: —**

The most important reactions of alkynes are —

1. Substitution of acetylenic hydrogen in terminal alkynes,
2. Addition reactions,
3. Reduction reactions,
4. Oxidation reactions,
5. Polymerization reactions,
6. Rearrangement reactions, and
7. Miscellaneous reaction.

*Some of the representative reactions are discussed in detailed with appropriate mechanisms*—

1. **Substitution Reactions of Alkynes involving Acetylenic Hydrogen in terminal Alkynes**:

This includes —

1. Formation of metal acetylides,
2. Formation of heavy metal acetylides, and
3. Substitution by halogens.

**These are discussed with representative examples with appropriate mechanisms**—

1. **Formation of Metal(*alkali*) Acetylides**:

Acetylene and terminal alkynes, but not internal alkynes (dialkylacetylenes) react with alkali metals and Grignard reagents to form acetylides due to the acidic character of acetylenic hydrogen. For example,



Acetylenes can be regenerated from the acetylides by the action of water. For example,



1. **Formation of Heavy Metal Acetylides**:

Acetylene and terminal alkynes react with heavy metal ions like ( in and ammonical ) to form insoluble acetylides also known as heavy metal acetylides. Internal alkynes, which do not contain any acidic hydrogen, do not form these heavy metal acetylides. Acetylene also reacts with lithium (2 moles)to form dilithium acetylides as shown below:



**Analytical Application**: The heavy metal acetylides are bonded more covalently than alkali metal acetylides. Hence, these are ***much less basic and less nucleophilic***. Thus, we can **distinguish** between a **terminal alkyne** and an **internal alkyne** by simply adding silver or copper (I) reagents. Formation of white or reddish precipitate indicates a terminal alkyne.

**Importance**: The reaction of heavy metal ions provides the basis of —

1. A **diagnostic test** for acetylene or terminal alkynes,
2. The **purification of acetylenes** (the acetylenes are readily decomposed by dilute mineral acids to regenerate acetylenes),
3. Separation of **alkynes from alkenes and alkanes**,and
4. **Acetylides**, being typical **nucleophile**, react with alkyl halides to form **higher alkynes**. For example,



1. **Substitution of terminal acidic hydrogens of acetylenes by Halogens**:

Acetylenic hydrogen can be replaced by halogen when treated with **sodium hypohalides ()**, or with the reaction of iodine in ammonia. For example,



1. **Addition Reactions of Alkynes**:

This includes both the Electrophilic and Nucleophilic addition reactions.

**General Approach for Electrophilic Addition reactions in Alkynes**:

Electrophilic addition reactions in alkynes are ***slower*** than alkenes. Many such additions require a ***catalyst*** like **mercuric ion** (). Possibly, the bridged cation intermediate formed here a **highlystrained** system and hence **less stable** than the bridged cation intermediate formed in the case of alkenes.



Another way to look at this ***lower reactivity of alkynes*** is that the triply bonded carbons are **- hybridized** and **- electrons are more tightly held**by such - nuclei, hence are **less available** for combination with the **electrophiles** (**).** These **steric** and **electronic** factors can explain the **lower rate of electrophilic addition** in alkynes than alkenes.

Some Important and representative**Electrophilic Addition** reactions of alkynes are —

1. Addition of Halogens,
2. Addition of Hydrogen Halides (),
3. Hydroboration-Oxidation, and
4. Addition of hypohalous acid.

**General Approach for Nucleophilic Addition reactions in Alkynes**:

We know that triple bond has a **reduced reactivity** towards **electrophiles**. Therefore, it is logical to assume that such triple bond should also be susceptible to nucleophilic attack and this is actually so. These **nucleophilic additions** are generally catalysed by **heavy metal ion**(say) which form a short of - complex with alkynes and lowers the electron-density around the triple bond to facilitate the attack by **nucleophiles**.



Important and representative**Nucleophilic Addition** reactions of alkynes are —

1. Hydration (addition of water),
2. Addition of Acetic acid (**vinylation**),
3. Addition of Alcohols,and
4. Addition of .

**All these Electrophilic & Nucleophilic Addition reactions of Alkynes are discussed with representative examples and appropriate mechanisms**—

1. **Electrophilic addition of Halogens ()to Alkynes**:

Alkynes add to bromine to yield tetrabromo alkane, through dibromoalkene intermediate. Addition is **stereoselective** (Stereoselective reaction is one in which only one **major stereospecific** product is given by the reaction). The major product corresponds to **- addition** of - atoms.



For example,



**Mechanism**: The reaction proceeds through the formation of cyclic bromonium ion involving three steps.



The fact that - dibromoalkene formed in step (2) is - suggest that the ***cationic intermediate*** formed in step (2) has a ***cyclic*** structure.

1. **Electrophilic addition of Halogen halides () to Alkynes**:

Hydrogen halides add to alkynes to give dihaloalkanes via haloalkenes. The reaction is **catalysed by light or mercury salts** and the addition follow ***Markownikoff addition***. Thus, the addition of at both stages is **regioselective** with internal alkynes (-2-) a mixture of products results. The ***order of reactivity*** of haloacids is:



For example,



**Mechanism**: The reaction proceeds through cyclic intermediate with subsequent attack by as shown below:



With , alkynes also give **- Markownikoff** addition product in the presence of peroxides. For example,

Propyne -Bromopropene - Dibromopropane

**Important Note**: Addition of of to acetylene gives ***vinyl chloride***, , was of great industrial importance. Vinyl chloride is the monomer required for the familiar **polymer *PVC***.

1. **Hydroboration-Oxidation (Electrophilic) reaction in Alkynes**:

Monomer of diborane () adds to alkynes at in a **- manner** to form vinyl boranes which react with acetic acid to give **- alkenes**. The net effect of this hydroboration reaction is the reduction of an alkyne to - alkene (similar to the reduction of an alkyne with Lindlar’s catalyst). The reaction is **stereoselective** as only - product is formed in this reaction. For example,



The  **bond** can also be cleaved **oxidatively** by alkaline to form **alkenols** that *tautomerize* to **aldehydes** or **ketones**. Terminal alkynes give aldehydes whereas internal alkynes will give ketones. For example,



This method is valuable for the **synthesis** of **aldehydes** and **ketones**.

**Important**: In hydroboration-oxidation reaction of alkyne, ***enols*** have been shown to ***tautomerize*** to the more stable **ketonic** compounds. This transformation can be achieved by both acids and bases as outlined below:

**Acid Catalyzed Tautomerization**: It involves (*a*) **removal of a hydroxyl proton** by a base and (*b*) formation of a **carbanion** followed by the **addition of a proton** by the solvent as shown below:



**Base Catalyzed Tautomerization**: It involves (*a*) **addition of a proton** and (*b*) **elimination of hydroxyl proton**, as shown below:



1. **ElectrophilicAddition of Hypohalous Acids ()**:

Addition of hypohalous to alkynes proceeds in two steps to form dichlorocarbonyl compounds, as shown below:



1. **Nucleophilic Addition of Water to Alkynes (Hydration)**:**Use of - salts**

Alkynes add to water in presence of - salts as catalyst and the reaction follows **Markownikoff rule**. In this reaction, initially vinyl alcohol so formed undergoes rapid tautomerization to produce carbonyl compounds. Thus,



For example,



Similarly,



It is **important** to note that in this reaction acetylene (or any terminal alkyne) gives acetaldehyde, substituted acetylene yields acetone or other ketones.

**Mechanism Hydration of an Alkyne by Hg2+ - salts**:

Acceptable mechanism for the hydration of triple bond by of - salts involves a cyclic transition state involving of Hg2+ - ion, and can be written as:



1. **Nucleophilic Addition of Acetic Acid to Alkynes (Vinylation)**: **[- Addition]:**

Reaction of acetic acid with alkynes are **catalyzed by - salts** leads to the **introduction** of **vinyl group** in acetic acid (**vinylation**) to form vinyl acetate and finally alkylidene acetate. This reaction is known as **vinylation** reaction (replaces **H** of acetic acid by a vinyl group). Thus,



**Important**: Ethylidene acetate when heated to gives acetaldehyde and acetic anhydride. Further, vinyl acetate is the monomer for the polymer, polyvinyl acetate used as adhesive.

1. **Nucleophilic Addition of Alcohols to Alkynes (Vinylation)**:

Alcohols add to alkyne in the presence of potassium alkoxide to form **vinyl** ethers. This reaction may be viewed as **replacement of alcoholic hydrogen** by **vinyl** group. Thus,



For example,



**Important**: This reaction is also known as **vinylation** of alcohol. (**H** of alcoholic group replaced by vinyl group)

**Mechanism**: Vinylation of alcohol is a nucleophilic addition reaction and involves the addition of nucleophile followed by protonation.



**Important**: The vinyl ethers are readily hydrolysed by dilute to give carbonyl compounds, presumably through the tautomerization of vinyl alcohols.



1. **Nucleophilic Addition of with Alkynes**:

Alkynes undergo nucleophilic addition with in the presence of to form vinyl cyanides. For example,



**Important**: Vinyl cyanide is used in the synthesis of **synthetic rubber** ().

**Question**: Discuss the comparative **reactivity** of **alkenes** and **alkynes** towards **nucleophilic addition** reactions.

**Solution**: The possible addition reaction pathway of alkynes and alkenes initiated by a nucleophile can be represented as —



The charge on the vinylic is **- hybridized** whereas in allyl it is **- hybridized**. The **electron pair** on an - orbital having more - character () would be **held more tightly than - orbital** (). The charge stability would thus, be in the order - - . In other words, the **vinylic** carbanion would be **more stable** (and hence more easily formed) than the alkyl carbanion. Assuming that the carbanion formation step, in the nucleophilic addition, to a multiple linkage is the ***rate-determining*** step. It is therefore, reasonable to expect that **alkynes** would be relatively **more reactive** towards **nucleophilic reagents**.

1. **Reduction Reactions of Alkynes**:

Alkynes can be reduce either **catalytically**or **chemically**

1. **Catalytic Reduction of Alkynes**: [**- Addition**]

Alkynes can be **hydrogenated** catalytically first to alkenes and then to alkanes. Direct reduction can be achieved by in the presence of **finely divided** . However, reduction to the alkene stage can be achieved by **Lindlar’s catalyst**or **nickel boride**() catalyst (also known as **- catalyst**). For example,



1. **Metal Reduction (Metal-Ammonia reduction)of Alkynes**: [**- Addition**]

Chemical or metal- ammonia reduction, involves the **reduction of alkynes** by in **liquid** . The reduction if fully **stereoselective** and gives exclusively **- alkene**. This reagent ( in liquid ) is used by **Birch** for **reduction** and hence, known as **Birch reduction**. Thus,



For example,



**Mechanism**: The **sodium-ammonia reduction** of an alkyne involves three steps —



From the above mechanism, it is evident that the first electron from goes into an anti-bonding - orbital to form **radical anion** (strong base), in step (1). Ammonia acting as an acid, protonates the radical anion, gives vinyl radical in step (2). The vinyl radical so obtained takes another electron from to form **vinyl anion** (strong base). Followed by protonation by to give - alkene, - **addition** is favoured due to **greater stability** of - **vinyl radical** (formed in step 2) than - vinyl radical (alkyl groups in - configuration are farther apart).

1. **Oxidation Reactions of Alkynes**:

This includes the following oxidation reactions —

1. Ozonolysis, and
2. Permanganate oxidation.
3. **Oxidation of Alkynes by Ozonolysis**:

Ozone adds to alkynes to form **ozonides**, which can be hydrolysed to **- dicarbonyl** compounds. Thus,



**Mechanism**: Formation of ozonide involves the following three steps:



***Important Note***: Hydrogen peroxide formed during the course hydrolysis of ozonide, undergoes oxidative cleavage of bond of - dicarbonyl compounds to form a mixture of carboxylic acids. Thus,



1. **Permanganate Oxidation of Alkynes**:

When an alkyne is treated with under almost neutral conditions, - diketones results, as shown below:



For example,



In the oxidation of alkyne by neutral , each of the two - bonds of the alkyne gets hydroxylated (as in alkene) and the **tetrahydroxylated intermediate** then loses **two** molecules of **water** to give diketone. If the reaction mixture is warmed under basic conditions, the diketone intermediate undergoes **oxidative cleavage** to produce, free carboxylic acids on acidification. Thus,



For example,



Terminal alkyne (e.g. propyne) would give carboxylic acid and .



**Analytical Importance**: Both the oxidation reactions () are of analytic importance. By identifying the carboxylic acids formed from an alkyne, we can **locate** the position of the **triple bond** in the parent alkyne.

1. **Polymerization Reactions of Alkynes**:

Under suitable conditions, alkynes add two or more molecules to form **dimers**, **trimers** or **tetramers**, as illustrated below:

**Dimerization of Alkynes**: Acetylene when passed through a solution of **cuprous chloride** in **ammonium chloride**, acetylene **dimerizes** to form **vinyl acetylene** and **divinyl acetylene**.



**Divinyl acetylene**is the starting material for **chloroprene**, a raw material used in the synthesis of **synthetic rubber** (**Neoprene**).



**Trimerization of Alkynes**:Acetylene **trimerizes** in the presence of -- (), to **benzene**.



This **trimerization** also occurs when acetylene is passed through **red hot iron** tube. Similarly, propyne **trimerizes** to **mesitylene**.



**Tetramerization of Alkynes**:Under high pressure and in the presence of **nickel cyanide** (catalyst), acetylene**tetramerizes** to form **cyclo-octatetraene**.



1. **Rearrangement Reactions of Alkynes**:

Alkynes tend to rearrange on heating with alcoholic potash with the migration of the triple bond. For example,



**Mechanism of Rearrangement**: Rearrangement of triple bonds in alkynes involves the following sequence of reactions, generating resonance stabilized intermediate carbanions.



1. **Miscellaneous Reactions of Alkynes**:

Following are the reactions of alkynes, not belonged to any one of the standard classified reactions of organic chemistry, and hence are termed as the miscellaneous reactions. These are —

1. Combustion reactions,
2. Addition of arsenic trichloride (), and
3. Addition of terminal alkynes to carbonyl compounds ()

**All these are discussed with representative examples and appropriate mechanisms**—

**() Combustion of Alkynes**: Alkynes get burnt in air or oxygen to form with the evolution of large amount of heat. For example,

Evolution of large amount of heat makes acetylene, useful in **welding**, **cutting**, etc. (**oxy-acetylene flame**).

**() Addition of Arsenic Trichloride with Alkynes**:Arsenic trichloride adds to alkynes, in the presence of anhydrous , to form adducts, often used as poisonous gases in warfare. For example,

Acetylene - Chlorovinyl dichloroarsine (**Lewisite**)

The adduct from acetylene is the well-known poisonous gas, **.**

**() Addition of Terminal Alkynes to Carbonyl Compounds (Ethinylation)**:Ethyne or terminal alkynes containing () group adds to carbonyl compounds under suitable conditions to form synthetic alcohols or other compounds. For example,





In the last additions, ethyne adds its active hydrogen () to carboxylic oxygen, and ethyne carbanion to **carbonylic carbon** of an aldehyde or a ketone. Therefore, this reaction is also known as **ethinylation** reaction, involving ethyne carbanion as nucleophile. It is evident from its mechanism.

**Mechanism of ethinylation**: **Ethinylation** is a nucleophilic addition of carbonyl compounds involving ethyne carbanion as nucleophile generated by methoxide ion ().

**Generation of Carbanion**:



**Attack of Carbanion (Nucleophile) on the Carbonyl Carbon**:



**Commercial Importance of Acetylenes**:

Alkynes like acetylene is extensively used

1. As a **fuel gas**, say in oxyacetylene flame, for welding and cutting of metals, and
2. As a key **synthetic chemical**.

Some important chemicals derived from acetylene are as follows —

1. Acetaldehyde, acetic acid, acetone, butyl alcohol, ethyl alcohol.
2. Tri and per- chloroethylenes, as the dry cleaning solvents, insecticides, etc.
3. Vinyl acetate, used in paints, adhesives, plastics, etc.
4. Vinyl chloride (), widely used in plastics (PVC), etc.
5. Acrylonitrile, used in the production of synthetic fibres (e.g. orlon, acrylon, etc.), synthetic rubbers and soil conditioners.
6. Tetrahydrofuran (THF), a solvent and a versatile intermediate.
7. Vinyl ethers, used in plastics, adhesives, rocket-fuels, etc.
8. Acetylene black, used in dry batteries, compounding rubber and plastics, etc.
9. Lewisite, the war gas.

It is, thus, evident from the above that acetylene can be extensively used to synthesise compounds of great applied interest. Acetylene is no longer a chemical curiosity as an illuminant. It is also a raw material of great synthetic importance in organic chemistry. //