ALKYNES

(C_nH_{2n-2})

The chemistry of the alkynes is very similar to that of the alkenes due to the presence of two Π-bonds in the C ≡ C triple bond. Since there is a triple bond between the two C - C atoms, this means that there must be a minimum of two C-atoms, .: the first member is C_2H_2, ethyne or acetylene (probably familiar to you because of the oxyacetylene torches used in welding). The IUPAC ending for alkynes is -yne, the corresponding alkane is named by using the suffix – yne. The position of the first carbon atom of the triple bond is given the lowest number and the C ≡ C unit must be in the longest continuous chain.

Examples of alkynes ...

Penta-1,3-diyne	pent-3-ene-1-yne	5-chloro-4-phenyl-hept-2-yne
octa-3,6-diyne	5,5-dibromo-hex-1-yne	3-cyclohexyl-but-1-yne

Structure of Alkynes

Alkynes are organic hydrocarbons that contain a C≡C bond, which is composed of two π−bonds (formed by overlap of two perpendicular pairs of p-p orbitals), that are perpendicular to one another and overlap forming a cylinder of electron cloud around the molecule, and one σ- bond (formed by sp-sp orbital overlap). One pair of overlapping p orbitals results in a cloud of electrons above and below the σ-bond, and the other pair results in a cloud of electrons in front of and behind the
σ-bond. The end result can be thought of as a cylinder of electrons wrapped around the σ-bond. The type of bonding present is sp hybrid orbital - for the σ-bond, and two electrons in the p-orbitals for the two π−bonds . . .

sp - hybrid orbitals are less elongated, consequently the σ-bond is shorter . . .

Bond Type	Hybridisation	Bond Length (nm)	Bond Enthalpy (kJ mol^{-1})
C - C	sp^3	0.154	348
C = C	sp^2	0.134	612
C ≡ C	sp	0.120	837

Because of the electron pair repulsion, the two π−bonds of an alkyne are weaker than the π−bond in the alkenes, .: more easily displaced from their position. However, a triple bond is stronger but shorter than a double bond which in turn is stronger and shorter than a single bond.

However, the cylindrical cloud of electrons surrounding the σ-bond of an alkyne presents a high concentration of negative charge, it is a nucleophile to an attacking reagent, therefore, approach by an electrophile will be attractive.

It is energetically favourable to make a single bond from double or triple bonds, .: addition reactions are favoured.

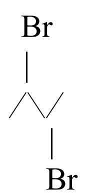
The presence of the electrons in the weaker π−bonds indicate that alkynes are likely to undergo **electrophilic addition reactions** and the electrophilic reactions will be faster than in alkenes.
In accordance with the general rule that molecular geometry is determined by an attempt to minimise electron-pair repulsion in the bonds, the alkyne molecule is thus linear with bond angles of 180^0.

Alkynes of the type: a - C ≡ C - b are flat, linear molecules, where ‘a’ and ‘b’ have free rotation, thus **no geometrical isomerism** is possible, only structural isomerism is exhibited, e.g. but-1-yne and but-2-yne.

Preparation

1. Ethyne, (acetylene) can be prepared by the hydrolysis of calcium carbide, CaC_2 ...

2. By the action of boiling alcoholic potash, KOH on a dihalogeno alkane, (FYI: halogen atoms on an adjacent C-atoms), eliminating two molecules of HX. Alcoholic KOH is preferred, because aqueous KOH would produce substitution reaction to produce the diol, whereas the alcoholic KOH encourages an elimination reaction ...



$\longrightarrow$ $CH_3C \equiv CCH_3$ + 2HBr

Physical Properties

These are similar to those of the analogous alkanes and alkenes:
gas ---------> liquid ----------> solid, due to . . .
All are insoluble in water and all are soluble in solvents with low polarity such as benzene and ether. Alkynes are more linear than alkenes, this gives them stronger van-der-Waals interactions and therefore higher boiling points. Melting point and boiling point increases as molar mass increases . . . (why?)

C_2H_2 has a sweet garlic odour.

Chemical Properties

1. **Combustion**

Ethyne (formerly called acetylene) burns in air in an extremely exothermic reaction, with a very sooty flame, due to the high carbon content, complete and incomplete combustion result in the production of different products ...

$$CH{\equiv}CH_{(g)} + 5/2\ O_{2(g)} \longrightarrow 2\ CO_{2(g)} + H_2O_{(l)} \qquad \Delta H^{\theta} = -1300\ kJmol^{-1}$$

Oxy-acetylene flames are used for cutting and welding metals.

Write an equation for the incomplete oxidation of acetylene yielding soot, C.

2. Electrophilic Addition Reaction

Electrophilic addition to alkynes occurs in the same manner as it does for alkenes. The reaction occurs according to Markovnikov's Rule. The addition can generally be stopped at the intermediate alkene stage, or carried further.

a) **Halogenation**: Rate of Reaction: $Cl_2 > Br_2 > I_2$
On the approach of a halogen molecule to the alkyne, the electron pair binding the halogen molecule is repelled by the electrons in the π−bond. Since the electrons in the π−bond can not move anywhere, so the electrons in the halogen shift and thus inducing a small dipole on the halogen molecule . . .

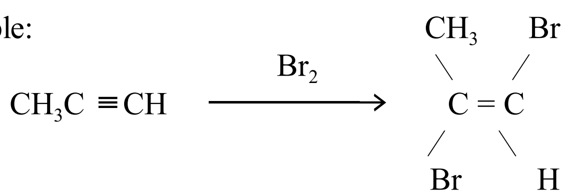
The halogen molecule undergoes heterolysis . . .

The second stage occurs when the halide ion attacks the carbocation . . .

Cis- and trans- isomers are obtained, (although the trans isomer predominates due to steric and electronic repulsive forces).

Finally, the whole process is repeated to break the double bond producing a single bond . . .

Example:



$$CH_3C \equiv CH \xrightarrow{2\,Br_2} CH_3CBr_2CBr_2H$$

What is the product of the reaction of chlorine with hex-3-yne?

(Answer: 3,3,4,4-tetrachlorohexane)

Test for Unsaturation: Reaction with $Br_{2(l)}$

In compounds that contain both a C = C bond and a C ≡ C bond, when they react with an electrophile such as halogens, then the halogen will preferentially attack the -ene group and not the -yne. No adequate explanation is required , but the most likely explanation is due to the stability of the intermediate formed.

3. **Reaction with HX, Rate of reaction: HI > HBr > HCl**

Markovnikov's Rule has been facetiously summarized as:

"To the carbon that hath shall be given."

The reason for this preference is the fact that the reaction proceeds through a carbocation intermediate that has greater stability : $3^0 > 2^0 > 1^0$

A tertiary carbocation can carry a positive charge more easily than a secondary carbon which can carry a positive charge more easily than a primary carbon. The product is a **germinal** dihalide, a molecule with two halogens on the same carbon. (FYI: Germinal comes from germinus, which is Latin for "twin.")

Example: pent-1-yne + HBr ⟶ 2,2-dibromopentane (A germinal dihalide)

Propyne + HI ⟶ 2,2-di-iodopropane

Reaction with HCl is important since it produces chloroethene (vinyl chloride) -------> PVC

4. **Reaction with Hydrogen: Reduction**

Catalytic Hydrogenation: Alkynes ---------> Alkenes --------> Alkanes

The conversion of an alkyne to an alkane requires two equivalents of hydrogen gas, along with an appropriate catalyst such as Pt, Pd or Ni ...

Hex-1-yne ⟶

5. **Hydration in the presence of dil. $H_2SO_4 + Hg^{+2}$ catalyst**

Water adds to alkynes in the presence of sulphuric acid and mercuric sulphate:

$$R\text{-}C\equiv C\text{-}H \xrightarrow{2\ H\text{–}OH} R\text{-}C(O)CH_3$$

(The product of addition of one molecule of water to the alkyne is unstable, and rearranges to a carbonyl compound: example: $CH\equiv CH$ ------> $CH_2 = CH(OH)$ -----> CH_3CHO)

6. **Oxidation using an oxidising agent such as $KMnO_{4(aq)}$ or $K_2Cr_2O_{7(aq)}$**

$H\text{-}C\equiv CH$ ⟶ ethandioic acid (oxalic acid)

7. **Polymerisation**

Ethyne when passed through a red hot silica tube at 400°C, can be polymerised to form benzene...

Assignment

1. Calculate the ΔH^θ value using Bond Energy, Table 10 from the Data Book, for the following reactions:

a) $HC\equiv CH + Br_2 \longrightarrow CHBr = CHBr$

b) $CHBr = CHBr + Br_2 \longrightarrow CHBr_2 - CHBr_2$

2. Using 1-butyne as a typical alkyne, write equations predicting its reaction with the following reagents:

a) Br_2 in carbon tetrachloride (b) HBr (c) H_2O, H_2SO_4, Hg^{+2}

3. Suppose you were given three unlabelled bottles, each of which is known to contain one of the following compounds: pentane, pent-1-ene, pent-2-yne. Explain how you could use simple chemical tests, (preferably test-tube reactions), to identify the contents of each bottle. (note that all three are low-boiling liquids.)