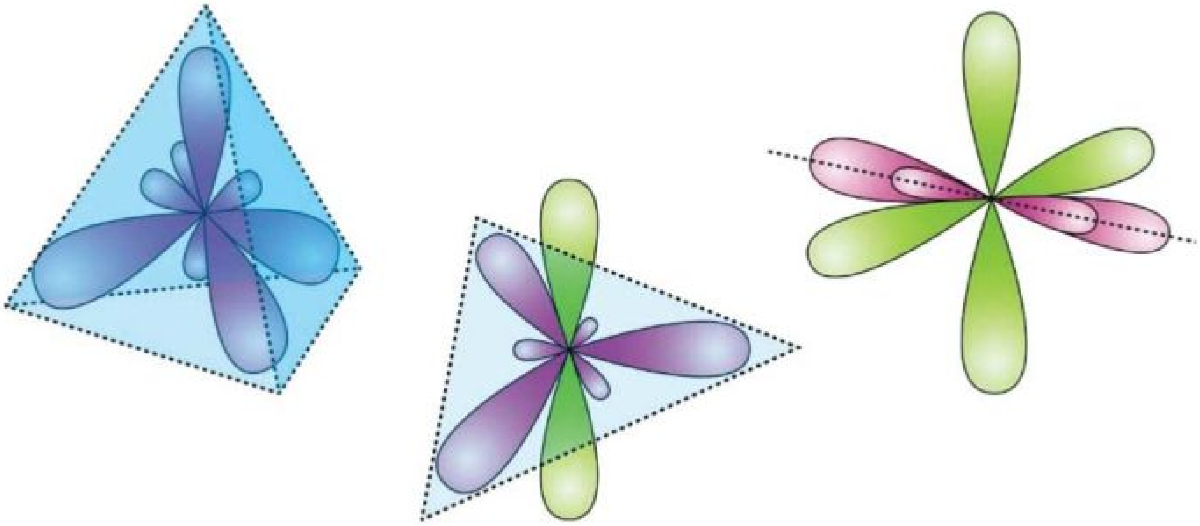


2. Hydrocarbons & Halohydrocarbons

Content

Introduction

Hydrocarbons are compounds containing only carbon and hydrogen. We have already discussed that aliphatic hydrocarbons are classified as alkanes, alkenes and alkynes. Halohydrocarbons are compounds containing one or more halogen atoms in addition to carbon and hydrogen.

2.1 Structure, physical properties and nature of bonds of aliphatic hydrocarbons

Alkane hydrocarbons are saturated hydrocarbons. Only carbon-hydrogen and carbon-carbon single bonds are found in these compounds. Methane (CH_4) is the simplest alkane hydrocarbon and it contains only one carbon atom. There are four hydrogen atoms attached to this carbon atom by four single bonds. The alkane which contains two carbon atoms is ethane (C_2H_6). In ethane the two carbons are bonded to each other with a single bond and each of these carbon atoms is bonded to three hydrogen atoms. The alkane with three carbon atoms is propane (C_3H_8). It will be noticed that the formula of ethane differs from that of methane by CH_2, and that the formula of propane differs from that of ethane also by CH_2. If two consecutive members of a series of compounds differ only by a CH_2 unit, such a series of compounds is called a homologous series.

A homologous series is a series of compounds with similar chemical properties which share the same general formula in which consecutive members of a series of compounds differ only by a CH_2 *unit. The general formula of an alkane is* C_nH_{2n+2} *(where n = 1, 2, 3, ...) and all alkanes except cyclic alkanes follow this general formula.*

2.1.1 Properties of alkanes

An alkane molecule is non-polar or very weakly polar. The attractive forces between two non-polar molecules are the dispersion forces. While the first few members of the series are gases at room temperature, the higher members are liquids and solids. As a result of increase in surface area down the series, dispersion forces also increase. While this leads to the aforesaid variation in the physical states of hydrocarbons, it also results in increase of the boiling points and melting points of unbranched hydrocarbons with the increase in molecular weight **(Table 2.1).**

Table 2.1 Melting points, boiling points and densities of some straight chain alkanes, showing regular increase of the property with the carbon number

Name	Formula	Melting point/ °C	Boiling point/ °C	Density (at 20 °C)/ g cm^{-3}
methane	CH_4	-183	-162	
ethane	CH_3CH_3	-172	-88.5	
propane	$CH_3CH_2CH_3$	-187	-42	
butane	$CH_3(CH_2)_2CH_3$	-138	-0.5	
pentane	$CH_3(CH_2)_3CH_3$	-130	36	0.626

Name	Formula	Melting point/ °C	Boiling point/ °C	Density (at 20 °C)/ $g\ cm^{-3}$
hexane	$CH_3(CH_2)_4CH_3$	-95	69	0.659
heptane	$CH_3(CH_2)_5CH_3$	-90.5	98	0.659
octane	$CH_3(CH_2)_6CH_3$	- 57	126	0.659
nonane	$CH_3(CH_2)_7CH_3$	- 54	151	0.718
decane	$CH_3(CH_2)_8CH_3$	- 30	174	0.730

With branching of the carbon chain the surface area of a molecules decreases and consequently dispersion forces become weaker and the boiling point decreases. As can be seen from the data given in **Table 2.2** the boiling points of alkanes with five carbon atoms decrease with the increase in branching of the carbon chain.

Table 2.2 Reduction of boiling points of isomeric pentanes as the branching occurs

Compound	Boiling point/ °C
pentane	36
2-methylbutane	28
2,2-dimethylpropane	9

2.1.2 Structure of alkanes

Let us consider the bonding of the simplest alkane, methane (CH_4). The carbon atom forms four covalent bonds with four hydrogen atoms. A covalent bond is formed by the overlap of two orbitals of two different atoms, each of which contains one electron. As the carbon atom in its ground state has only two *p* orbitals (p_x and p_y) containing one electron each, it could form only two covalent bonds at right angles to each other (recall that electronic configuration of C in its ground state is $1s^2 2s^2 2p^2$). If the two electrons in the $2s$ orbital are unpaired and one electron is promoted to the p_z orbital, then the carbon atom would have four orbitals, each containing one electron to form four bonds to four hydrogen atoms. The energy required to unpair and promote an electron could be compensated by the energy released by the formation of two extra bonds.

However, this overlap would result in a CH_4 molecule where three of the C–H bonds will be at right angles to each other and one C-H bond will not have any directionality. This would lead to a methane molecule which would have two types of C–H bonds. In order to explain the fact that in methane all four C–H bonds are equivalent, the $2s$ orbital and the three $2p$ orbitals are considered to be mixed with each other, to generate four equivalent orbitals pointing to the apices of a tetrahedron **(Figure 2.1)**.

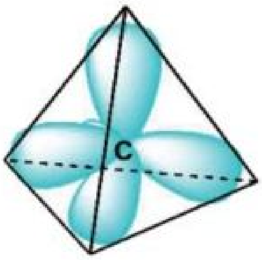


Figure 2.1 Shape and arrangement of sp^3 hybrid orbitals of carbon

The mixing of orbitals to generate new orbitals is termed 'hybridization'. The new orbitals are termed hybrid orbitals to differentiate them from pure atomic orbitals. In methane, the four hybrid orbitals of carbon are called sp^3 hybrid orbitals as one s orbital and three p orbitals are mixed to generate them. Such carbon atoms are referred to as **'sp^3 hybridized carbon'**. The energy of the sp^3 hybrid orbitals lies between the energy of the s orbital and the p orbitals **(Figure 2.2)**.

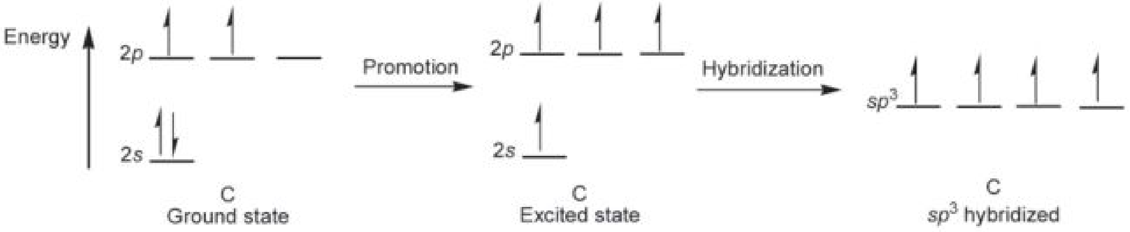


Figure 2.2 Graphical representation of hybridization of carbon in methane

In methane each of these four sp^3 hybridized orbitals overlap with s orbital of H atoms and forms four C–H bonds. The angle between any of these two C–H bonds is 109.5° and the four H atoms of methane are located at the apices of a tetrahedron **(Figure 2.3)**.

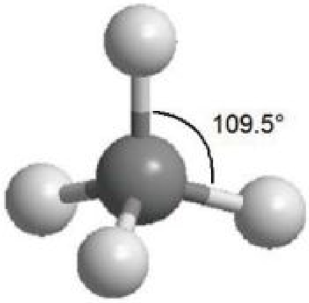


Figure 2.3 Tetrahedral shape of methane (CH_4) molecule

All carbon atoms joined to four other atoms in any organic compound are considered sp^3 hybridized. In alkanes, the carbon-hydrogen bonds are formed by the overlap of a sp^3 hybrid orbital of carbon with a 1s orbital of hydrogen while the carbon-carbon bonds are formed by the overlap of two sp^3 hybrid orbitals of two carbon atoms **(Figure 2.4)**.

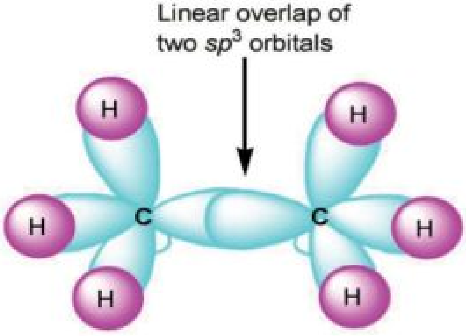


Figure 2.4 Structure of ethane showing overlap of orbitals to form C–C and C–H bonds

The overlap of the two sp^3 orbitals to form the carbon-carbon bond takes place along the direction of the orbitals. Such an overlap is called a **linear overlap** and results in the formation of a **σ bond.**

2.1.3 Properties of alkenes and alkynes

Both alkene and alkyne hydrocarbons are unsaturated compounds. Alkenes contain at least one carbon-carbon double bond while alkynes contain at least one carbon-carbon triple bond. Acyclic alkenes with one double bond but without any other functional group form the homologous series of alkenes with the general formula C_nH_{2n}. Alkynes with one triple bond and without any other functional group form the homologous series of alkynes with the general formula C_nH_{2n-2}.

Carbon-carbon double bond of an alkene and carbon-carbon triple bond in alkyne are stronger and shorter than a carbon-carbon single bond **(Table 2.3)**.

Table 2.3 Bond energies and bond lengths of carbon-carbon single, double and triple bonds

Bond	**Bond energy/ kJ mol^{-1}**	**Bond length/ pm**
C–C	347	154
C=C	611	133
C≡C	839	120

Alkenes show boiling points very similar to those of alkanes with the same number of C atoms. Ethene, propene and the isomeric butenes are gases at room temperature. All the rest are liquids. As with alkanes, boiling points of alkenes increase with the increase of molecular mass (chain length). Intermolecular forces of alkenes become stronger with increase in the size of the molecules. As the polarity of alkynes is also low, their physical properties are very similar to those of the corresponding alkanes and alkenes.

2.1.4 Structure of alkenes

Ethene (C_2H_4) is the simplest alkene. It contains a carbon-carbon double bond. Each carbon atom in ethene is sp^2 hybridized and forms three equivalent sp^2 hybrid orbitals which lie in the same plane and point to the three corners of an equilateral triangle **(Figure 2.5)**. The unhybridized *p* orbital lies perpendicular (90°) to this plane.

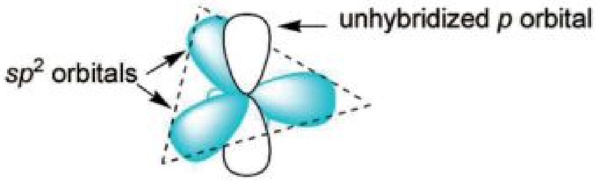


Figure 2.5 Shape and arrangement of sp^2 hybrid orbitals an unhybridized *p* orbital of carbon

These sp^2 orbitals are formed by mixing of the 2*s* orbital with two 2*p* orbitals leaving one unhybridized *p* orbital **(Figure 2.6)**.

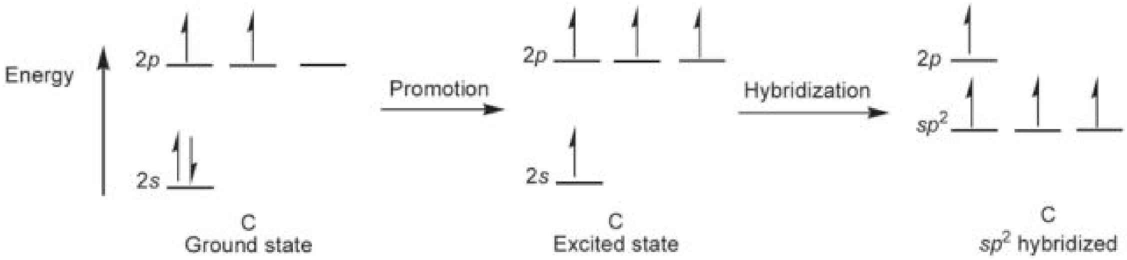


Figure 2.6 Graphical representation of sp^2 hybridization of carbon in ethane

In ethene each carbon uses two sp^2 orbitals to form two C–H bonds each. The remaining sp^2 orbital in each carbon is used to form a carbon-carbon σ bond by linear overlap. The unhybridized *p* orbitals of each carbon atom which are parallel to each other overlap laterally to form another carbon-carbon bond. This bond formed by the lateral overlap of *p* orbitals is called a π bond. All alkenes contain a carbon-carbon double bond which consists of a σ bond and a π bond. The π bond is weaker than the σ bond **(Figure 2.7)**.

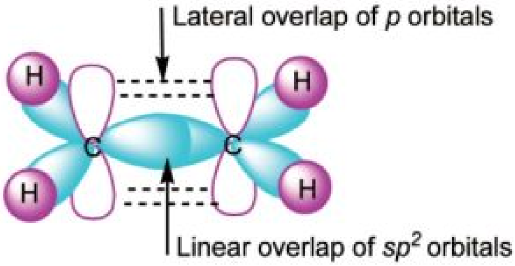


Figure 2.7 Structure of ethene showing overlap of orbitals to form C–C and C–H bonds

The 2 carbon atoms used to form the double bond and the four atoms attached directly to them lie in the same plane. The angle between any two atoms attached to the sp^2 hybridized carbon will be 120° **(Figure 2.8).**

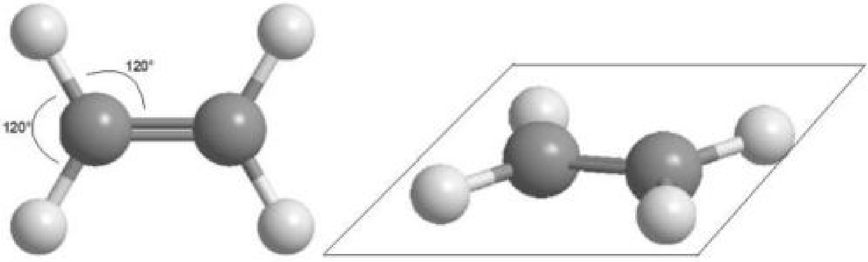


Figure 2.8 Planar shape of ethene (C_2H_4) molecule

2.1.5 Structure of alkynes

Ethyne (C_2H_2) is the simplest alkyne. It contains a carbon-carbon triple bond. Each carbon atom in ethyne is *sp* hybridized and forms two equivalent *sp* hybrid orbitals which lie in the same straight line and point in opposite directions **(Figure 2.9)**. The two unhybridized *p* orbitals lie perpendicular (90°) to each other and to these two *sp* orbitals.

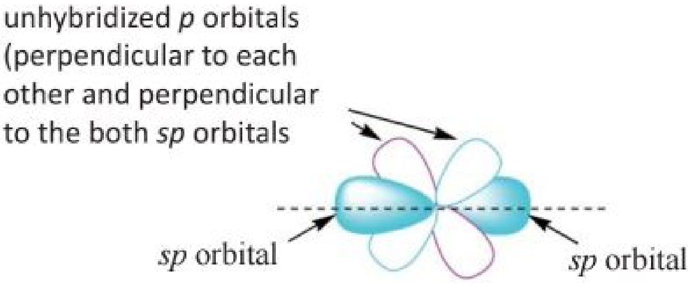


Figure 2.9 Shape and arrangement of *sp* hybrid orbital and unhybridized *p* orbitals of carbon

These *sp* orbitals are formed by mixing of the *2s* orbital with one *2p* orbital leaving two unhybridized *p* orbitals **(Figure 2.10)**.

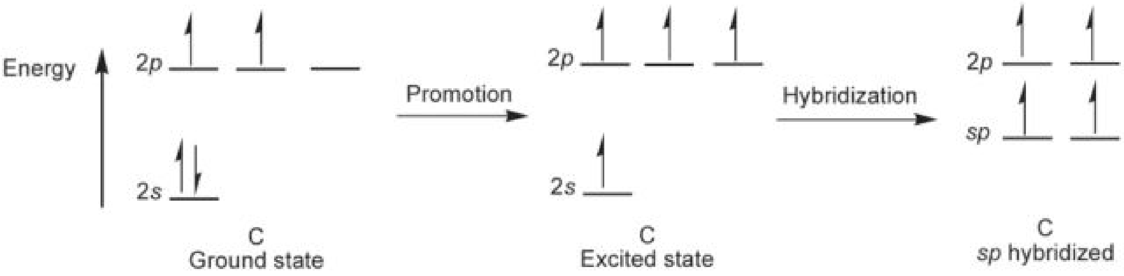


Figure 2.10 Graphical representation of *sp* hybridization of carbon in ethyne

In ethyne each carbon uses one *sp* orbital to form a C–H bond each. The remaining *sp* orbital in each carbon is used to form a carbon-carbon σ bond by linear overlap. The two unhybridized *p* orbitals of each carbon atom overlap laterally to form another two carbon-carbon bonds (two π bonds). Thus all alkynes contain a carbon-carbon triple bond which consists of a σ bond and two π bonds **(Figure 2.11)**.

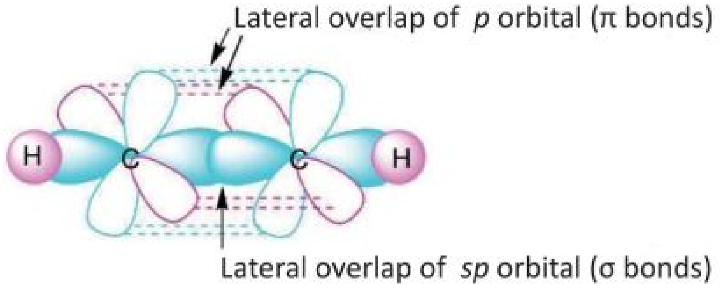


Figure 2.11 Structure of ethyne showing overlap of orbitals to form C–C and C–H bonds

The 2 carbon atoms used to form the triple bond and the two atoms attached directly to them lie in the same straight line. The angle between the two atoms attached to the *sp* hybridized carbon will be 180° **(Figure 2.12)**.

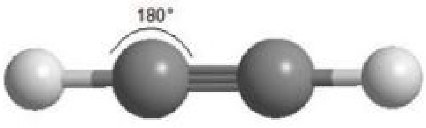


Figure 2.12 Linear shape of ethyne (C_2H_2) molecule

2.2 Chemical reactions of alkanes, alkenes and alkynes in terms of their structures

Covalent bond cleavage during organic reactions

Any organic reaction involves the cleavage (breaking) and formation of covalent bonds. Bond cleavage can take place in two different ways.

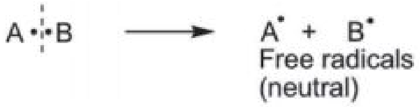
(i) Heterolytic cleavage

In heterolytic cleavage the two electrons involved in the bond will remain with one of the atoms (the more electronegative atom). This will result in a positively charged species (cation) and a negatively charged species (anion).

When writing mechanisms, heterolytic cleavage is shown by a curved arrow which indicates the movement of a pair of electrons.

(ii) Homolytic cleavage

In homolytic cleavage the two electrons involved in the bond will be equally divided such that one electron will remain with each atom. This will result in two neutral species each having one unpaired electron. Such species are called free radicals.



When writing mechanisms, homolytic cleavage is shown by a pair of fishhooks. Each fishhook indicates the movement of a single electron.

2.2.1 Reactions of alkanes

In alkanes all the bonds are either C–C or C–H bonds. Because the polarity of those C–C and C–H bonds is low, alkanes do not have atoms which bear high positive (electron deficient) or negative charges (electron rich). Therefore, they do not react with common polar reagents such as OH^-, CN^-, H^+ under normal conditions.

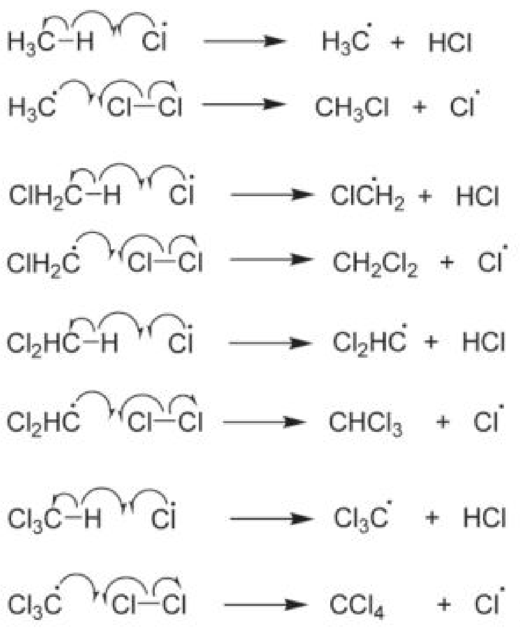
2.2.1.1 Chlorination of alkanes

Although alkanes do not react with common polar reagents, they tend to react with free radicals by homolytic cleavage of C–H bonds. For example, alkanes react with reagents such as chlorine and bromine free radicals (Cl atoms and Br atoms) which can be generated by the homolytic cleavage Cl_2 and Br_2. This can be achieved by irradiation of Cl_2 or Br_2 with ultra-violet light. Thus, methane in the presence of ultra-violet light reacts with Cl_2 to give a mixture of chloromethanes, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4. These products are formed by a sequence of reactions where the product of one reaction, becomes the starting material for the subsequent reaction of the sequence. Such reactions are called **chain reactions**.

The mechanism of the reaction is given below. The first step of the reaction is the formation of chlorine free radicals by the homolysis of the covalent bond between two chlorine atoms. This is called the **chain initiation step**.

Chain initiation step

The chlorine free radical reacts with CH_4 to produce methyl free radical ($\bullet CH_3$). The methyl free radical reacts with another molecule of chlorine (Cl_2) producing CH_3Cl and $Cl^\bullet$. The chlorine radical produced in this step can react either with a molecule of CH_4 or a molecule of CH_3Cl to produce the corresponding carbon free radicals as shown in the reaction sequence given below.

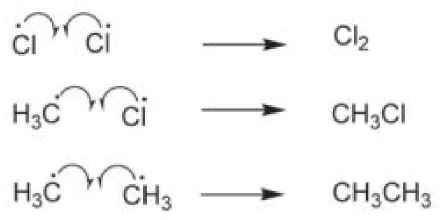


Chain propagation steps

Chain propagation steps

These steps are called **chain propagation steps.** In these chain propagation steps, free radicals are used and are also generated. Therefore the reaction sequence can proceed without stopping until all the H atoms in CH_4 are replaced by Cl. The carbon free radicals produced in this reaction sequence are called **reactive intermediates** in the free radical chlorination of methane.

A chain reaction can be stopped by **chain terminating reactions**. There are many chain terminating reactions (steps) that can occur during a chain reaction. In these chain terminating reactions the radicals are used but not generated. A few such chain terminating reactions are shown below.



Chain terminating steps

It should be noted that, as free radical chlorination (and bromination) of alkanes produces a mixture of products, it is of limited use in the synthesis of chloro or bromo hydrocarbons in the laboratory.

2.2.2 Reactions of alkenes

The reactions of alkenes take place at the carbon-carbon double bond. Carbon-carbon double bond is formed from a σ bond and a π bond. The double bond of an alkene is an electron rich area due to the presence of the pi-electron cloud above and below the plane of the alkene. Therefore it can attract a species which can accept a pair of electrons. Such species are electron deficient and are known as **electrophiles**.

As each of the doubly bonded C atoms is bonded only to three atoms, they are unsaturated and another atom can be attached (added) to each of these two carbon atoms during a reaction.

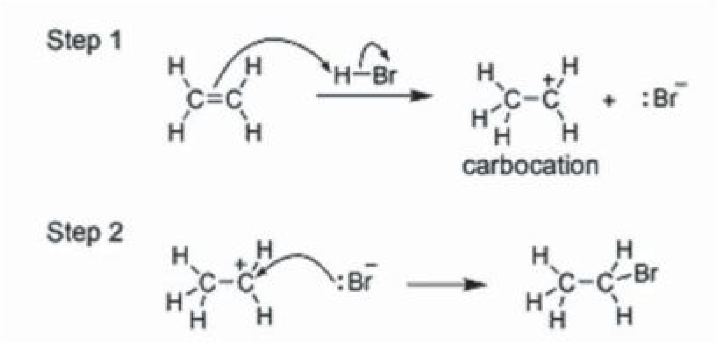
Therefore the typical reactions of alkenes are **electrophilic addition reactions**. Let us study the electrophilic addition reaction with its mechanism, using a few examples.

2.2.2.1 Addition of hydrogen halides (HCl, HBr or HI)

The electron deficient pole of a hydrogen halide molecule is H (eg. $H^{\delta+}-Br^{\delta-}$). This acts as an electrophile and reacts initially with the double bond. During the reaction the H-Br bond breaks releasing a Br- ion. Thus, the H reacts as if it was a H^+ ion and forms a bond with carbon using the two electrons from the π-bond.

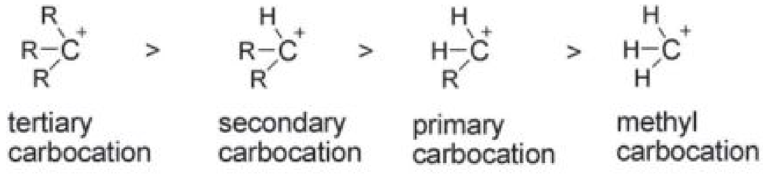
During these electrophilic addition reactions, intermediate carbocations are formed *(Carbocations are electron deficient positively charged trivalent carbon species).*

Let us look at the mechanism of addition of HBr to ethene. The reaction proceeds in two steps.

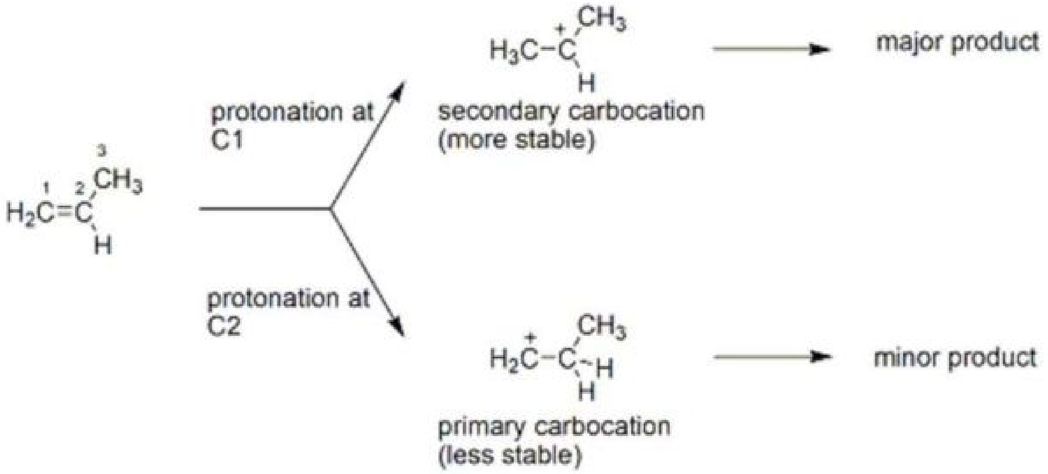


Carbocations are classified as primary, secondary and tertiary carbocations depending on the number of hydrogen atoms attached to the positively charged carbon atom.

Stability of these carbocations follows the order shown below.

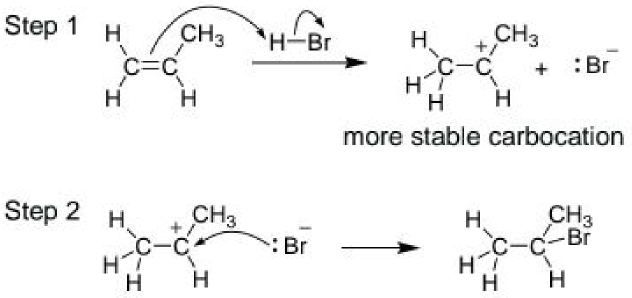


When alkyl groups are attached to the positively charged C atom of the carbocation, stability of the carbocation increases. The reason for this is the release of electrons by the alkyl groups through C–C bonds towards the positively charged carbon atom to which they are attached. This results in spreading the positive charge thereby stabilizing the ion. When asymmetrically substituted alkenes undergo electrophilic addition reactions with hydrogen halides, two different carbocations can be formed after the bonding of the electrophile (H^+). The more stable of these two carbocations forms more easily. Let us take addition of HBr to propene as an example.



The more stable carbocation is obtained when the electrophile gets attached to the carbon atom to which the higher number of hydrogen atoms is attached. This is the explanation for 'Markovnikov's rule' which states that when a protic acid HX adds to an asymmetric alkene, the H adds to the carbon atom bonded to the higher number of H atoms.

The mechanism of addition of HBr to propene can be shown as follows.



Hydrogen bromide adds in the opposite way to this rule (anti-Markovnikov addition) when there are peroxides in the reaction medium (i.e. the H adds to the carbon bonded to the lower number of H atoms). The reason for this is that in the presence of peroxides the reaction between hydrogen bromide (HBr) and the alkenes takes place via a free radical mechanism and not the ionic mechanism described above. *A description of the mechanism of this reaction is not expected.* It is to be noted that the direction of addition of HCl and HI is not changed in the presence of peroxides.

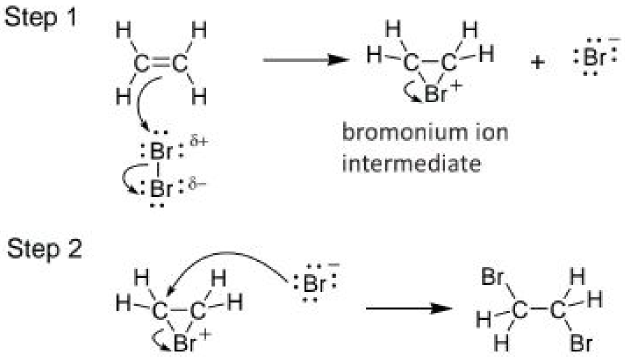
$$CH_3CH{=}CH_2 + HBr \xrightarrow[\text{(peroxide)}]{\text{RO}-\text{OR}} CH_3CH_2CH_2Br$$

2.2.2.2 Addition of bromine to alkenes

Bromine is a not a polar molecule, but polarity is induced in it during the reaction with alkenes. When a bromine molecule approaches the electron rich double bond, a dipole is induced with the Br atom closer to the pi-bond having a partial positive charge. In the first step of the reaction, this Br atom reacts with the double bond and forms a bromonium ion, which is a three membered cyclic intermediate with a positive charge on the Br atom.

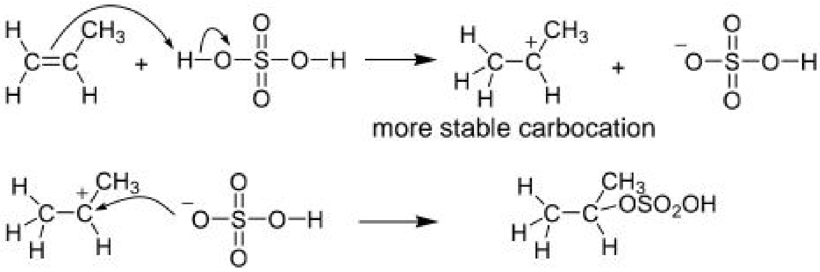
In the second step of the reaction, a bromide ion (Br^-) acting as a nucleophile, forms a bond to one of the carbon atoms bonded to Br^+. The bond formed by that carbon atom to Br^+ is broken during this step, giving an open chain structure again.

The mechanism is as follows.

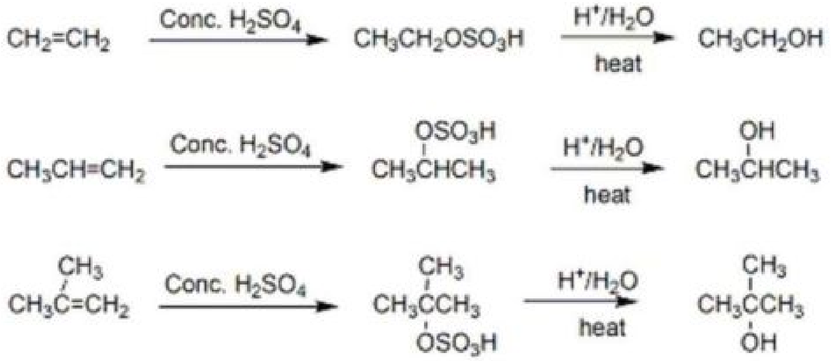


2.2.2.3 Addition of sulphuric acid and the hydrolysis of the addition product

Alkenes react with cold concentrated sulphuric acid to form alkyl hydrogen sulphates. The reaction is an electrophilic addition reaction and proceeds *via* a carbocation intermediate as in the case of the addition of HBr.



The reaction is carried out by passing the gaseous alkene through cold concentrated H_2SO_4 or stirring the liquid alkene with the cold concentrated H_2SO_4. When the solutions of alkyl hydrogen sulphates are diluted with water and heated, they undergo hydrolysis to give an alcohol bearing the same alkyl group as the original alkyl hydrogen sulphate. Let us look at few examples of this reaction.



It is seen that the final product of this sequence of reactions is the alcohol that would be obtained by the Markovnikov addition of water (H-OH) to the alkene. The same products can be obtained directly by the direct addition of water to alkenes in the presence of dilute sulphuric acid. However the preparation of ethanol by direct addition of water to ethylene is difficult under laboratory conditions.

2.2.2.4 Catalytic addition of hydrogen (Hydrogenation)

In the presence of catalysts such as finely powdered Pt, Pd or Ni, alkenes react with hydrogen to produce alkanes.

$$CH_3CH{=}CH_2 \xrightarrow[\text{Pt or Pd or Ni}]{H_2} CH_3CH_2CH_3$$

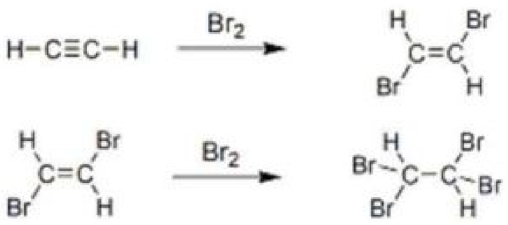
2.2.2.5 Reaction of alkenes with cold, alkaline, dilute potassium permanganate

Alkenes react with cold, alkaline, dilute $KMnO_4$ solution to produce diols (glycols). When this reaction takes place the purple colour of permanganate is disappeared and a brown precipitate of MnO_2 is formed. This reaction is used as a test for unsaturation (carbon-carbon double bonds and triple bonds). This is named as Baeyer test for unsaturation. However easily oxidisable substances such as aldehydes will also answer this test.

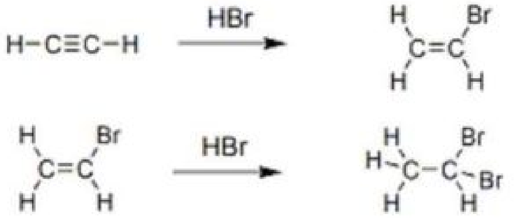
2.2.3 Reactions of alkynes

Alkynes have a triple bond which consists of one sigma bond and two π bonds. Alkynes also undergo electrophilic addition reactions with reagents that add to alkenes. The two pi-bonds react independently of each other.

2.2.3.1 Addition of bromine

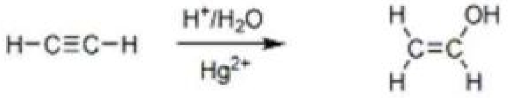


2.2.3.2 Addition of hydrogen halides



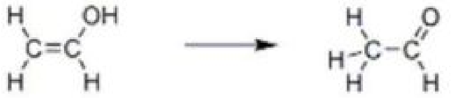
2.2.3.3 Addition of water

In the presence of Hg^{2+} and dilute H_2SO_4, one molecule of water adds to an alkyne producing an enol. A molecule containing a hydroxyl group attached to a carbon atom in a carbon-carbon double bond is known as an **enol.**



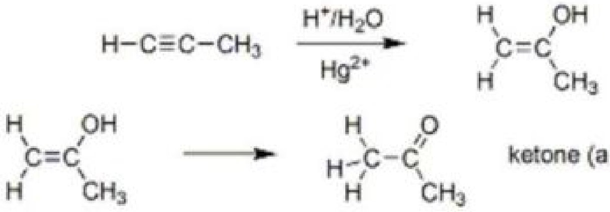
(enol)

Enols are unstable and rapidly rearrange to a more stable keto form (aldehydes or ketones)



aldehyde (a keto compound)

The addition of water to alkynes takes place according to the Markovnikov's rule as shown below by the reaction of propyne.



(enol)

ketone (a keto compound)

2.2.3.4 Catalytic addition of hydrogen (Hydrogenation)

Alkynes react with hydrogen in the presence of catalysts such as Pt, Pd or Ni to give alkanes.

$$HC{\equiv}CH \xrightarrow{H_2/Pd} H_3C{-}CH_3$$

During this reaction the alkyne is first reduced to the alkene which is further reduced to the alkane under the reaction conditions. The reaction can be stopped at the alkene stage by using a less active catalyst. Very often, Pd catalyst deposited on $BaSO_4$ deactivated (poisoned) by quinoline is used.

$$HC{\equiv}CH \xrightarrow[\text{quinoline}]{H_2/Pd\text{-}BaSO_4} H_2C{=}CH_2$$

2.2.4 Acidic nature of alkynes with terminal hydrogen

The triple bond C atoms are *sp* hybridized. A C-H bond involving a triple bond carbon is formed by the linear overlap of a *sp* orbital of C and a *s* orbital of H.

Since a *sp* orbital has more *s* character (50% *s* character) than sp^2 or sp^3 orbitals, the bonding electrons in the C–H bond of alkynes are closer to the carbon nucleus than in the case of C–H bonds in alkenes and alkanes. Therefore the H attached to a triple bond carbon has a higher acidity than the H in alkene or alkane C–H bonds. However, the acidity of H attached to terminal alkynes is less than that of water and alcohol.

The H of a terminal alkyne can react as H^+ with strong bases such as $NaNH_2$ and active metals such as Na. The resulting acetylide anion is stable because the two non-bonded electrons (negatively charged) are close to the carbon nucleus (positively charged).

$$H_3C-C\equiv C-H \xrightarrow{Na} H_3C-C\equiv \overset{-}{C}\ Na^+ \quad + \quad H_2$$

$$H_3C-C\equiv C-H \xrightarrow{NaNH_2} H_3C-C\equiv \overset{-}{C}\ Na^+ \quad + \quad NH_3$$

Terminal alkynes react with certain heavy metal ions such as Ag^+ and Cu^+ to form insoluble metal acetylides. These two reactions can be used to identify terminal alkynes.

$$H_3C-C\equiv C-H \xrightarrow{NH_3/Cu_2Cl_2} H_3C-C\equiv C-Cu\downarrow$$

$$H_3C-C\equiv C-H \xrightarrow{NH_3/AgNO_3} H_3C-C\equiv C-Ag\downarrow$$

2.3 The nature of bonding in benzene

The molecular formula of benzene is C_6H_6 which indicates that it is an unsaturated compound. Under normal conditions benzene does not answer the tests for unsaturation. Therefore, benzene cannot have a structure similar to that of a simple alkene or an alkyne.

2.3.1 Structure of benzene

The structure proposed for benzene by Kekulé contained a six-membered ring of carbon atoms with alternating three double and three single bonds **(Figure 2.13)**.

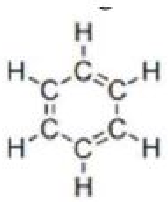
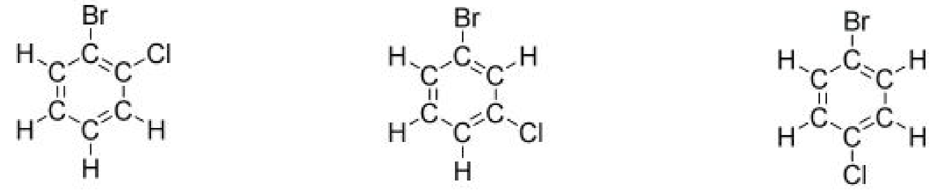


Figure 2.13 Structure of benzene proposed by Kekulé in 1865

This structure was based on the evidence available regarding the relationships of aromatic isomeric compounds. No isomer has been found for any mono-substituted benzene (C_6H_5X; X= $-CH_3$, $-C_2H_5$, -OH, -Cl, -Br, -CHO etc.), implying that all six atoms in benzene are equivalent. Therefore substitution at any one carbon atom will always give a single compound.

It was found that there are three isomeric disubstituted benzenes. Kekulé proposed structures with 1,2-disubstitution, 1,3-disubstitution and 1,4-disubstitution **(Figure 2.14)**, later named as *-ortho, -meta* and *-para* isomers.



1,2-bromochlorobenzene (*ortho*-bromochlorobenzene) 1,3-bromochlorobenzene (*meta*-bromochlorobenzene) 1,4-bromochlorobenzene (*para*-bromochlorobenzene)

Figure 2.14 Three isomeric disubstituted benzenes

However these structures implied that two distinct *ortho*- disubstituted benzenes are possible, depending on whether the substituted carbons are separated by a double bond or a single bond. Since two different *ortho*- isomers have never been found, Kekulé proposed that benzene molecule could be represented by two equivalent structures which are in equilibrium **(Figure 2.15)** so that single and double bonds continually interchange positions.

Figure 2.15 Proposed rapid equilibrium of two equivalent structures of *ortho*-bromochlorobenzene

This proposal explains that benzene has two possible structures and that both of them exist at room temperature. However, no experimental evidence has been found for the existence of two such structures for benzene.

Further the bond length between any two adjacent carbon atoms in benzene is the same. The carbon-carbon bond length of benzene is 1.39×10^{-10} m which is in-between the length of a carbon-carbon double bond (1.34×10^{-10} m) and the length of a carbon-carbon single bond (1.54×10^{-10} m).

The structure of benzene is now considered to be a resonance hybrid of two structures as given in **Figure 2.16**.

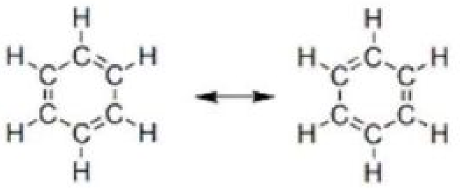
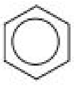


Figure 2.16 Resonance structures of benzene

For convenience, the resonance hybrid of benzene is written as shown below.



Take note of the difference between the resonance sign (the double headed arrow) and the equilibrium sign. In an equilibrium, the compounds shown by structures really exist while in the concept of a resonance hybrid, none of the compounds represented by the structures really exist. They are drawn because there is no other way of representing the real molecule. Each structure contributes to the real structure of the compound. The extent of contribution depends on the relative stability of each resonance structure with the more stable structure making a larger contribution to the real structure. In the case of benzene, both structures have the same stability and contribute equally.

All C atoms of benzene are sp^2 hybridized. Each carbon bears an unhybridized p orbital which can overlap with the unhybridized p orbitals on either sides of it **(Figure 2.17)**. From this, a cyclic delocalized electron cloud common to all six carbon atoms is formed. Hence, the real structure of benzene is considered to be a hybrid of two Kekulé structures. The real structure of benzene with delocalized electrons is more stable than the hypothetical Kekulé structure with three double bonds. The concept of resonance is used when there are delocalized electrons to be depicted using conventional structures which are drawn using localized bonds.

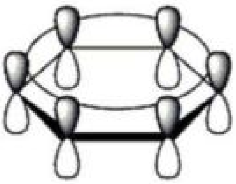
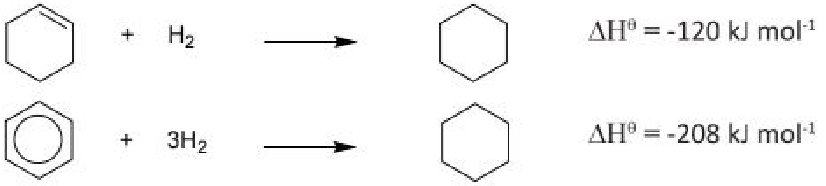


Figure 2.17 Benzene showing lateral overlap of p orbitals forming a cyclic delocalized electron cloud

2.3.2 Stability of benzene

The data for the standard enthalpy of hydrogenation helps to illustrate the stability of a benzene molecule.



Since the standard enthalpy of hydrogenation of cyclohexene (six-membered cyclic hydrocarbon with one double bond) is -120 kJ mol^{-1}, the standard enthalpy of hydrogenation of benzene should be 3 x -120 kJ mol^{-1} = -360 kJ mol^{-1} if it possesses three double bonds similar to alkenes. The standard enthalpy of hydrogenation of benzene is found to be -208 kJ mol^{-1}, which is -152 kJ mol^{-1}

less than the expected value for the hydrogenation of three double bonds **(Figure 2.18)**. Hence, benzene is more stable than its Kekulé structure by an amount equal to (360-208) = 152 kJ mol^{-1}. This stability is due to the cyclic delocalization of six pi-electrons, and is termed the resonance stabilization (or aromatic stabilization) energy of benzene.

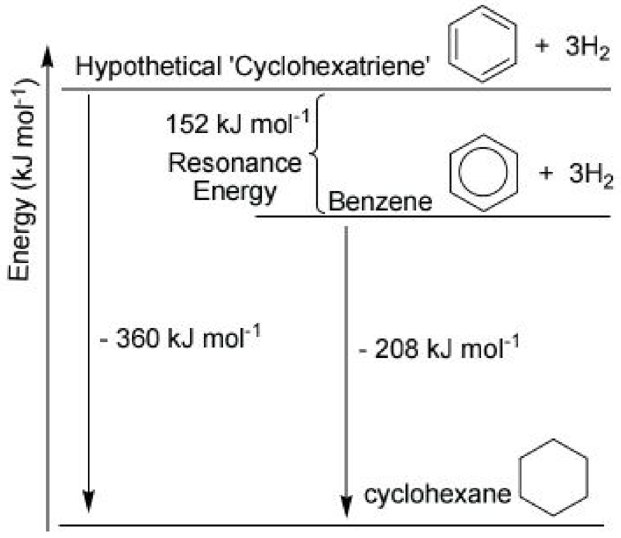


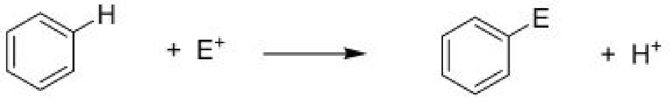
Figure 2.18 Standard enthalpies of hydrogenation of benzene and hypothetical cyclohexatriene.

2.4 Characteristic reactions of benzene exemplifying its stability

Benzene contains loosely bound delocalized electron cloud on both faces of the planar benzene molecule. This makes benzene ring electron rich and hence reactive toward electrophiles, similar to alkenes. As we have discussed, benzene shows extra stability due to this delocalization of electrons. Therefore benzene does not easily undergo reactions which destroy this cyclic delocalization. Hence the characteristic reactions of benzene are electrophilic substitution reactions and not electrophilic addition reactions as in the case of alkenes.

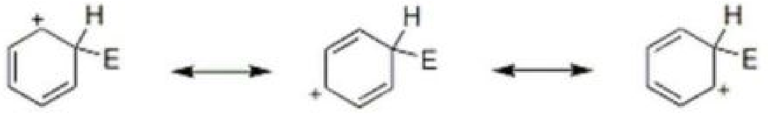
2.4.1 Electrophilic substitution reactions of benzene

In electrophilic substitution reactions, hydrogen atoms attached to the benzene ring are substituted by electrophiles (E$^+$).



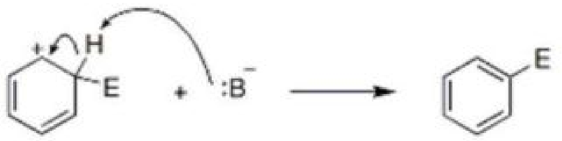
The first step in this reaction is the formation of a bond between the electrophile (E$^+$) and a carbon atom in the benzene ring giving rise to a carbocation (arenium ion). This step is very similar to the first step of the electrophilic addition of HBr to an alkene.

The intermediate carbocation thus formed is stabilized by the delocalization of the positive charge by conjugation with the two π bonds. This can be shown by resonance as follows.



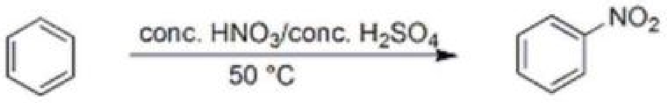
However, in going from benzene to the above carbocation the cyclic delocalization of π electrons is broken, and the aromatic stabilization energy is lost. It is energetically more favourable for the intermediate carbocation to lose a proton and re-establish the cyclically delocalized electron cloud, than to react with a nucleophile and give an addition product as in the case of alkenes.

The proton is usually taken up by one of the bases ($B:^-$) present in the reaction mixture. Thus, the result is the substitution of a H atom on the benzene ring with E.



2.4.1.1 Nitration

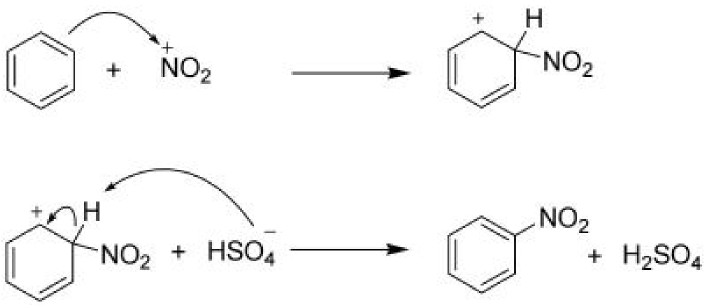
Benzene reacts with a mixture of conc. HNO_3 and conc. H_2SO_4 to give nitrobenzene which is formed by the substitution of H by a nitro group.



The electrophile in this reaction is $^+NO_2$ which is generated in the medium by the dehydration of nitric acid by sulphuric acid as follows.

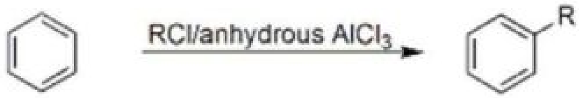
$$H_2SO_4 + HONO_2 \longrightarrow HSO_4^- + H-\overset{+}{\underset{H}{O}}-NO_2 \longrightarrow H_2O + \overset{+}{N}O_2$$

The $^+NO_2$ ion reacts with benzene and in the final step the proton is removed by the hydrogensulphate (bisulphate) ion which act as the base.



2.4.1.2 Friedel - Crafts alkylation

Benzene reacts with alkyl halides in the presence of a Lewis acid such as anhydrous $AlCl_3$ to give alkyl benzene, in which a H attached to the benzene is substituted by an alkyl group.



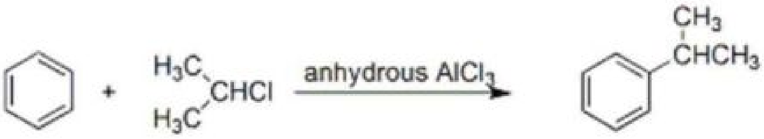
In the case of secondary and tertiary halides (see section 8.6) the electrophile of this reaction is R^+, and is generated in the first step by the reaction between alkyl halide and the Lewis acid.

$$RCl + AlCl_3 \longrightarrow \overset{+}{R} + Al\overset{-}{Cl_4}$$

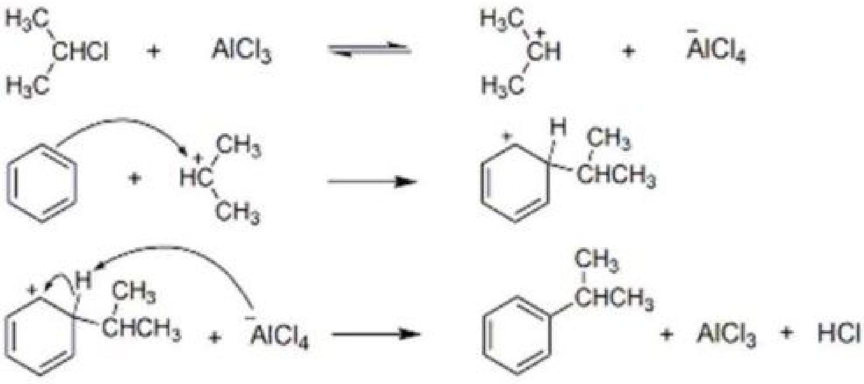
In the final step a proton is removed by $AlCl_4^-$.

$$Al\overset{-}{Cl_4} + H^+ \longrightarrow AlCl_3 + HCl$$

Let us see an example.



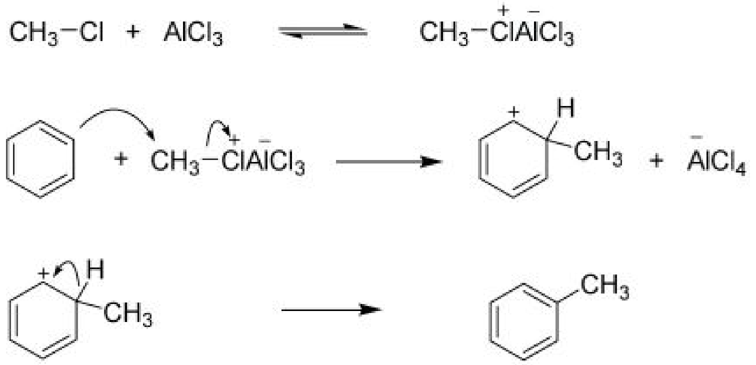
The mechanism of this reaction is as follows.



As you can see the first step of this reaction is formation of carbocation from the alkyl halide. In the second step benzene interacts with this carbocation to form an arenium ion. Removal of proton takes place in the final step restoring the aromatic stability in the product.

In cases where RX is a primary alkyl halide (eg. CH_3Cl) the species actually reacting with the benzene molecule may not be R^+, but be a R-Cl molecule polarized by coordination to $AlCl_3$, which will transfer R^+ to the benzene molecule during the reaction by cleavage of the R-Cl bond.

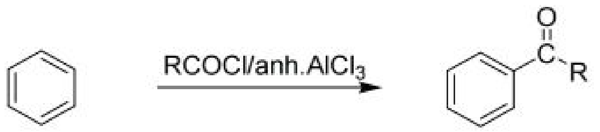
The possible mechanism is as follows.



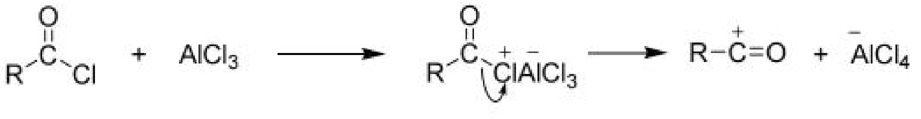
The Friedel - Crafts alkylation does not take place in mono substituted benzenes where the substituent group has a stronger electron attracting ability than halogen. (eg. nitrobenzene).

2.4.1.3 Friedel - Crafts acylation

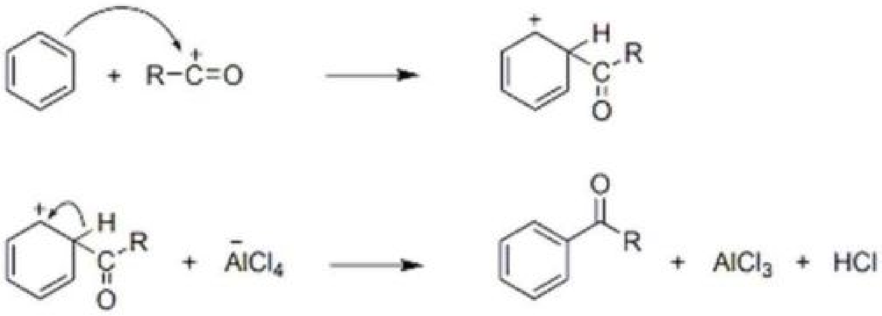
Benzene reacts with acid chlorides in the presence of a Lewis acid such as anhydrous $AlCl_3$, giving acyl benzene, in which a H is substituted by an acyl group.



The electrophile in this reaction is acylium ion (RCO^+). This is formed in the first step by reacting $AlCl_3$ with acyl chloride as follows.

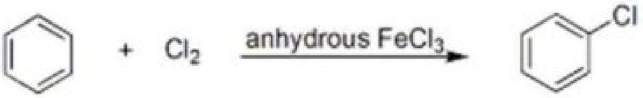


In the step 2, the acylium ion reacts with benzene to form an arenium ion and in the final step a proton is removed restoring the aromatic stability.

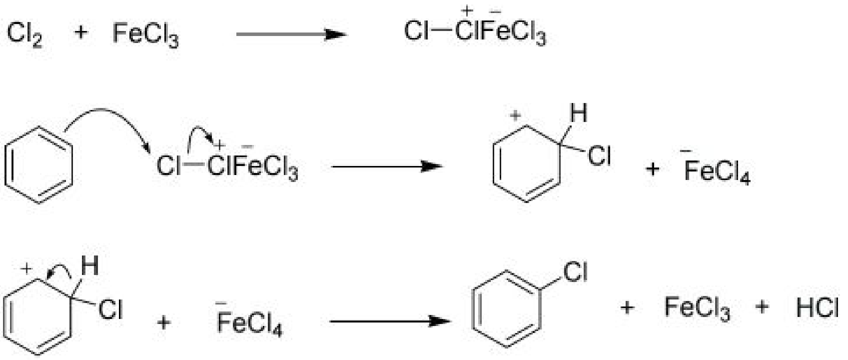


2.4.1.4 Halogenation

When benzene reacts with Cl_2 or Br_2 in the presence of a Lewis acid such as $FeCl_3$, $FeBr_3$, $AlCl_3$ or $AlBr_3$, under anhydrous conditions, substitution by a halogen atom takes place in the benzene ring.

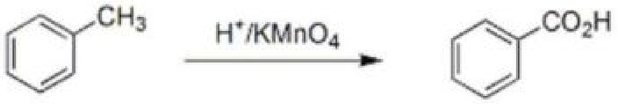


The effective electrophile in the above reaction is Cl^+. It is transferred to the benzene ring from the complex during the reaction. Proton is removed in the last step restoring the aromatic stability.



2.4.2 Resistance of benzene ring towards oxidation

Benzene does not get oxidized by normal oxidizing agents like $H^+/KMnO_4$ due to its stability. However, the alkyl group in alkyl substituted benzene can be oxidized by $H^+/KMnO_4$ to a carboxylic acid group. $H^+/K_2Cr_2O_7$ can also be used for this oxidation.



Tertiary alkyl groups do not get oxidized under the conditions in which primary and secondary alkyl groups get oxidized. More vigorous conditions under which tertiary alkyl groups can be oxidized also result in cleavage of the benzene ring.

2.4.3 Resistance of benzene ring towards hydrogenation

Although benzene does not undergo electrophilic addition reactions, like alkenes, it can undergo addition of hydrogen in the presence of suitable catalysts at higher temperatures in comparison to alkenes.

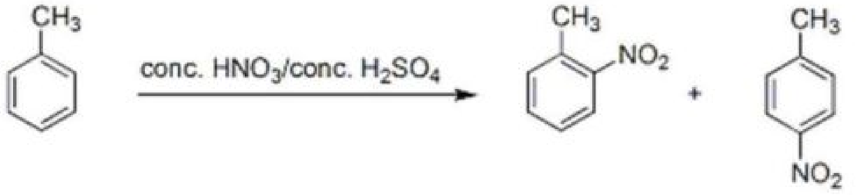
2.5 Directing ability of substituent groups of mono substituted benzene

When a monosubstituted benzene undergoes an electrophilic substitution reaction, the place where the second substituent group attaches will be determined by the nature of the first substituent group. Substituent groups can be categorized into two basic types.

2.5.1 Ortho para directing groups

eg. -OH, -R, $-NH_2$, -NHR, $-OCH_3$, halogens

Other than halogen, the *ortho para* directing groups activate the benzene ring towards electrophilic substitution by making it more electron rich than benzene.

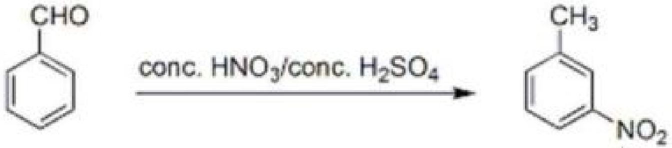


ortho para

2.5.2 Meta directing groups

eg. - NO_2, -CHO, -COR, -COOH, -COOR

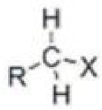
Meta directing groups deactivate the benzene ring towards electrophilic substitution by withdrawing electrons from it.



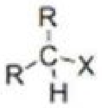
meta

2.6 Structure and reactions of alkyl halides

Alkyl halides are classified as primary, secondary or tertiary depending on the number of H atoms attached to the carbon atom which carries the halogen atom.



Primary alkyl halide



Secondary alkyl halide

Tertiary alkyl halide

Alkyl halides are polar compounds. Although they are polar, the solubility of alkyl halides in water is very low. One reason for this is that they do not form hydrogen bonds with water.

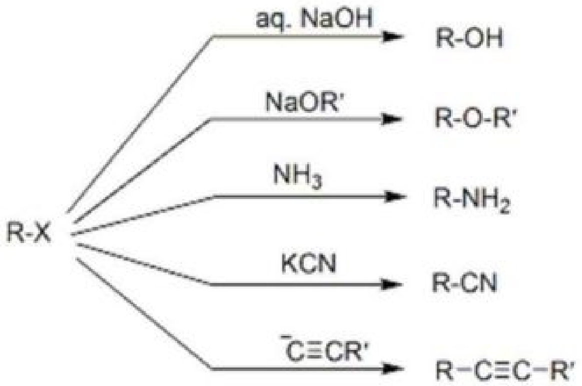
Due to the higher electronegativity of the halogen atom relative to the carbon atom, the carbon-halogen bond is polarized. As a result, there is a deficiency of electrons in that carbon atom. Therefore, it is possible that nucleophiles attack this position. Nucleophiles are basic, electron rich reagents which can utilize a pair of electrons to form a bond with an electron deficient carbon atom.

A few common examples are:

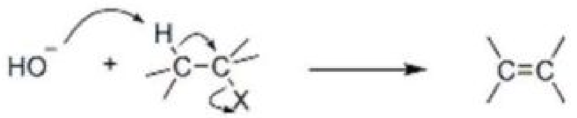
^{-}OH ^{-}OR $^{-}NH_2$ ^{-}CN $RC\equiv C^{-}$ H_2O NH_3

Characteristic reactions of alkyl halides are nucleophilic substitution reactions. During nucleophilic substitution reaction, the carbon atom forms a new bond with the nucleophile and the halogen atom leaves as a halide ion.

Let us look at some examples:



As a nucleophile possesses a pair of electrons, any nucleophile can also act as a base by forming a bond with H^+. Therefore, when an alkyl halide is reacted with a reagents such as: OH^-, OR^-, it can also undergo an elimination reaction by the mechanism shown below.



In this reaction, instead of reacting OH^- group as a nucleophile with carbon, it reacts as a base and removes a H^+ from the carbon atom adjacent to the carbon atom bearing halogen. The hydrogen atoms attached to the carbon atom adjacent to the carbon atom bearing the halogen atoms, have a low acidity due to the polarization of the C-X bond. Thus substitution and elimination are competing reactions in alkyl halides. The balance between substitution and elimination is influenced by the solvent used in the reaction. In the laboratory, aqueous KOH is used when substitution is desired, and ethanolic KOH is used when elimination is desired.

$$CH_3CH_2CH_2Br \xrightarrow{\text{alcoholic KOH}} CH_3CH{=}CH_2$$

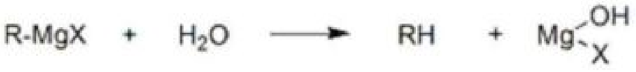
Alkyl halides react with Mg in the medium of **dry ether** to form **Grignard reagents.** Grignard reagents are organometallic reagents.

$$R\text{-}X + Mg \xrightarrow{\text{dry ether}} R\text{-}MgX$$

When an alkyl halide forms a Grignard reagent the polarity of the carbon atom originally joined to halogen, changes as shown below.

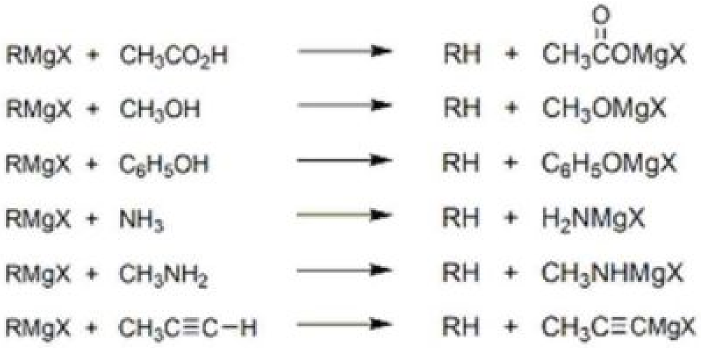
Thus, an electron deficient carbon atom is converted to an electron rich carbon atom. In fact, the alkyl group attached to Mg can utilize the pair of electrons in the C-Mg bond and behave as a strong base as well as a strong nucleophile.

Therefore Grignard reagents cannot be prepared or used in organic reactions in the presence of compounds which have even weakly acidic H atoms, including water.



$$R\text{-}MgX + H_2O \longrightarrow RH + Mg\begin{smallmatrix}OH\\X\end{smallmatrix}$$

The strong basic character of the Grignard reagent can be shown by the following reactions.



$$RMgX + CH_3CO_2H \longrightarrow RH + CH_3\overset{O}{\overset{\|}{C}}OMgX$$
$$RMgX + CH_3OH \longrightarrow RH + CH_3OMgX$$
$$RMgX + C_6H_5OH \longrightarrow RH + C_6H_5OMgX$$
$$RMgX + NH_3 \longrightarrow RH + H_2NMgX$$
$$RMgX + CH_3NH_2 \longrightarrow RH + CH_3NHMgX$$
$$RMgX + CH_3C{\equiv}C{-}H \longrightarrow RH + CH_3C{\equiv}CMgX$$

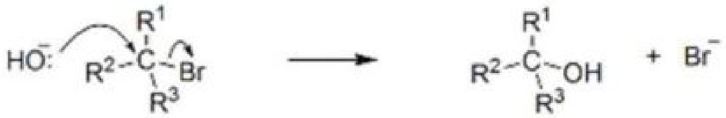
The last reaction of the above list is the reaction of a Grignard reagent with a terminal alkyne. Note that the product is also another Grignard reagent. This reaction can be used to prepare acetylenic Grignard reagents.

2.7 Nucleophilic substitution reactions of alkyl halides in terms of the timing of bond making and bond breaking steps

During reactions, bonds are broken and new bonds are formed. Nucleophilic substitution reactions of alkyl halides involve the breaking of a carbon-halogen bond and the formation of a carbon-nucleophile bond. To study the mechanism of nucleophilic substitution reactions of alkyl halides the time interval between bond breaking and bond making steps can be considered.

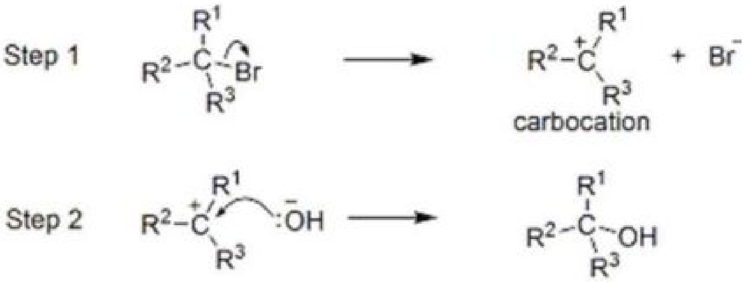
When the breaking of the C-X bond and the formation of the new bond to the nucleophile takes place simultaneously, the nucleophilic substitution reaction of the alkyl halide takes place as a one-step reaction.

Accordingly, for the reaction of an alkyl bromide with the hydroxyl ion, the one-step reaction can be presented as follows.



When the breaking of the C-X bond takes place at first and then the formation of the new bond to the nucleophile takes place, the nucleophilic substitution reaction of the alkyl halide takes place as a two-step reaction.

Accordingly, the reaction that takes place by two steps can be presented as follows

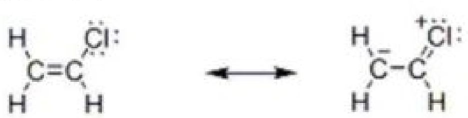


The reaction that takes place by two steps goes through a carbocation intermediate. On considering the stability of the carbocation formed, the tertiary alkyl halides (R^1, R^2, R^3 = alkyl) which are able to form a more stable tertiary carbocations tend to undergo nucleophilic substitution in two steps. The primary alkyl halides (R^1, R^2 = H, R^3 = H or alkyl) tend to undergo nucleophilic substitution reactions in one step as the primary carbocations they form are less stable.

Generally, both pathways are taken by the secondary alkyl halides (R^1 = H, R^2, R^3 = alkyl) to extents which depend on the reaction conditions.

Vinyl and phenyl carbocations are unstable and therefore, vinyl halides and aryl halides they do not react by the two step pathway. They also do not react by the one step pathway because the C-X bond is stronger than in alkyl halides due to its double bond character. This can be shown by resonance.

Resonance structures of vinyl halide:



Resonance structures of chlorobenzene: