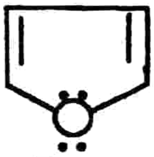
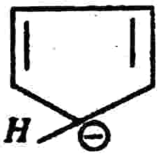
Huckel's rule or (4n + 2) rule of aromaticity

Eventhough most of the aromatic compounds are derivatives of benzene, presence of a benzene ring is not an essential condition for a compound to show aromatic character. The modern theory for aromaticity was advanced by Huckel. Huckel's rule states that *a conjugated, planar, cyclic system will be aromatic if it contains (4n + 2) delocalised pi electrons, where n represents an integer*. Thus, benzene is aromatic because it is a conjugated, planar, cyclic compound containing 6 pi electrons ($n = 1$). Similarly, naphthalene and anthracene are aromatic because they contain 10 ($n = 2$) and 14 ($n = 3$) delocalised π electrons respectively.

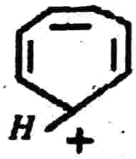
We have already seen that the presence of benzene ring is not necessary for a compound to be aromatic. Some examples of non-benzenoid aromatic species are given below:



Furan



Cyclopentadienyl anion



Cyclohepta-trienyl cation

Preparation of benzene and its derivatives

Benzene is mainly obtained from coal tar. The following are some other methods of formation.

(i) From alkynes

Alkynes polymerise at high temperatures to form arenes. Thus ethyne, when passed through a red hot iron tube, polymerises to form benzene. Similarly, propyne polymerises to form 1, 3, 5 - trimethyl benzene (mesitylene).

(ii) Decarboxylation of aromatic acids

In the laboratory, benzene is prepared by the decarboxylation of sodium benzoate with soda lime.

$$C_6H_5COONa + NaOH \xrightarrow{CaO, heat} C_6H_6 + Na_2CO_3$$

(iii) Reduction of phenol

Phenol when heated with zinc dust gives benzene.

$$C_6H_5OH + Zn \xrightarrow{\text{heat}} C_6H_6 + ZnO$$

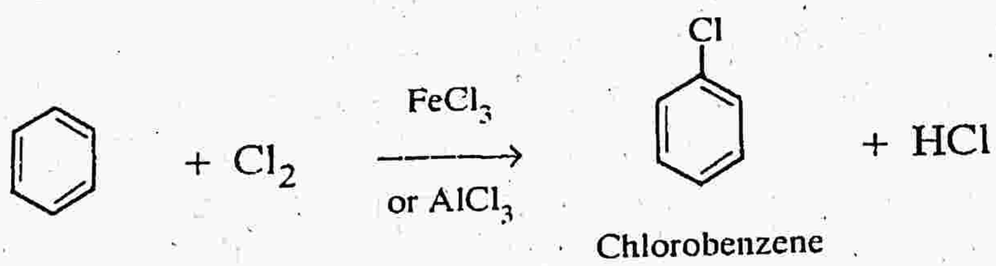
Reactions of aromatic hydrocarbons

I Electrophilic Substitution reactions

The most characteristic and useful reactions of arenes are those in which a hydrogen of the aromatic ring is substituted by another atom or group. Such aromatic substitution reactions are, in fact, initiated by electrophiles and hence they are referred to as **electrophilic aromatic substitution reactions.** Some important electrophilic substitution reactions of arenes are discussed below.

(a) Halogenation

Benzene reacts with chlorine or bromine in the presence of Lewis acids like ferric halide or aluminium halide to give chloro or bromo benzene.

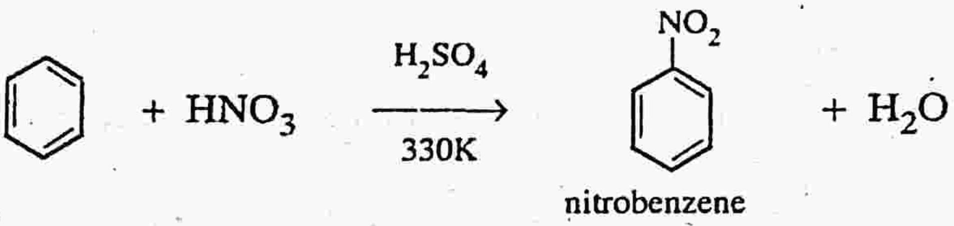


With excess chlorine, benzene gives hexachlorobenzene

$$\underset{\text{Benzene}}{C_6H_6} + 6Cl_2 \xrightarrow[\text{dark, cold}]{\text{Anhyd. }AlCl_3} \underset{\text{Hexachlorobenzene}}{C_6Cl_6} + 6HCl$$

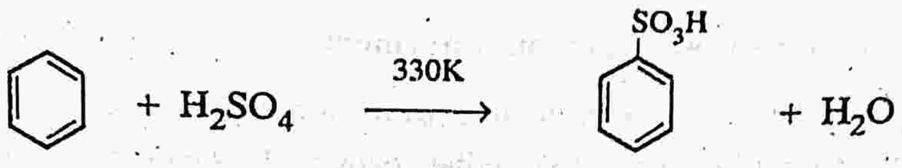
(b) Nitration

The replacement of a hydrogen atom of an aromatic ring by nitro group is called nitration. It is carried out by heating benzene (or other arenes) with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture). For example,



(c) Sulphonation

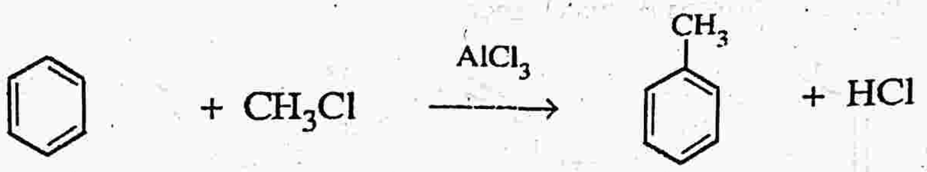
The replacement of a hydrogen atom of an aromatic ring by a sulphonic acid group ($-SO_3H$) is known as sulphonation. It is carried out by heating benzene (or other arenes) with fuming sulphuric acid (concentrated sulphuric acid containing dissolved SO_3).



Benzene sulphonic acid

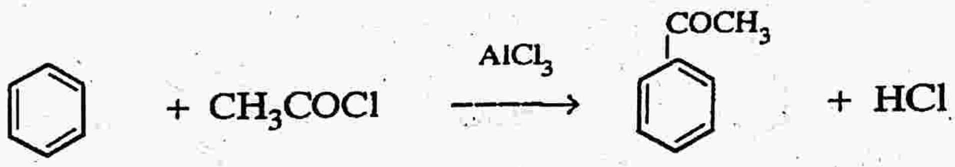
(d) Friedel - Crafts reaction

When benzene is treated with an alkyl halide or acyl halide in the presence of anhydrous aluminium chloride, alkyl benzene or acyl benzene is formed. This is known as Friedel - Crafts reaction. For example, benzene reacts with CH_3Cl in presence of anhydrous aluminium chloride to form toluene.



Since this reaction involves the introduction of an alkyl group, it is called **Friedel - Crafts alkylation.** It is a convenient method for the preparation of homologues of benzene.

Benzene reacts with acetyl chloride or acetic anhydride in presence of anhydrous aluminium chloride to form acetophenone.



This is known as **Friedel - Crafts acylation.**

Mechanism of aromatic electrophilic substitution

The mechanism of all electrophilic aromatic substitution reactions are basically the same. The various steps involved are,

(i) Generation of electrophile (E^+)

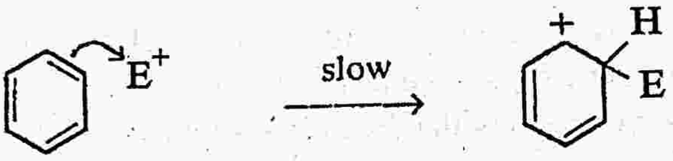
The attacking electrophile is first produced from the reagent. For example, in nitration the electrophile is $\overset{+}{N}O_2$ (nitronium ion) and it is formed as follows:

$$HNO_3 + H_2SO_4 \rightleftharpoons \overset{+}{N}O_2 + HSO_4^- + H_2O$$

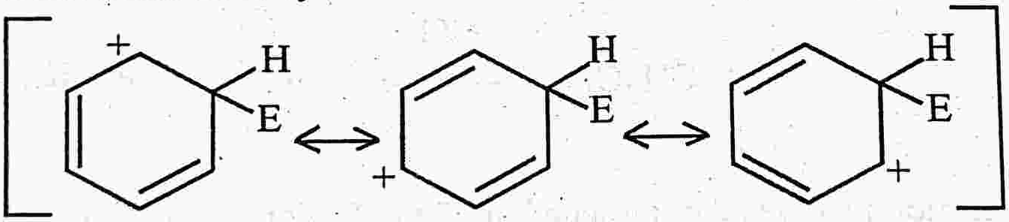
In chlorination, Cl^+ is the electrophile and in Friedel–Crafts alkylation the electrophile is the carbocation R^+

(ii) Formation of carbocation (or arenium ion) intermediate

The electrophile approaches the π electron cloud of the aromatic ring and forms a bond with carbon. This results in the formation of an intermediate cation. This cation is called arenium ion or σ–complex. If the electrophile is represented as E^+, then the arenium may be represented as



The arenium ion is stabilised by resonance.



(iii) Elimination of proton from the arenium ion

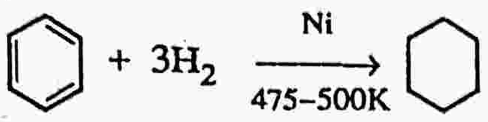
The σ–complex then loses a proton to a base produced in the medium. In nitration, HSO_4^- acts as the base.

II Addition reactions

Benzene and its homologues undergo addition reactions under special conditions.

(i) Addition of hydrogen

Benzene reacts with H_2 in presence of nickel or platinum at 475– 500K to form cyclohexane.



Cyclohexane

or $C_6H_6 + 3H_2 \xrightarrow{Ni} C_6H_{12}$

(ii) Addition of chlorine

Benzene reacts with chlorine in presence of uv light to form benzene hexachloride (BHC).

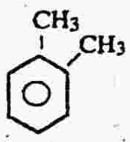
$$C_6H_6 + 3Cl_2 \xrightarrow{h\nu} C_6H_6Cl_6$$

BHC is used as an insecticide. It is also known as lindane, gammexane or 666.

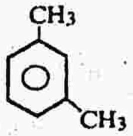
Isomerism in arenes

Since all the six hydrogen atoms in benzene are identical, only one mono substitution product is possible for benzene. Thus we have only one compound having the formula C_6H_5X where X is some monovalent group. But in the case of disubstitution products, three different isomers are possible which differ in the position of the substituents attached to the ring (position isomers). These three isomers are called **ortho** (o-), **meta** (m-) and **para** (p-) according as the relative positions of the two substituents are 1,2; 1,3; and 1,4 respectively.

For example, in the case of dimethyl benzene, commonly known as xylene, there can be three position isomers as given below:



o–xylene
(1,2–dimethyl benzene)



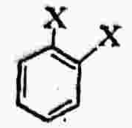
m–xylene
(1,3–dimethyl benzene)

p–xylene
(1,4–dimethyl benzene)

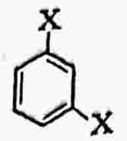
(In addition to the above three isomers, a fourth isomer ethyl benzene is also known for the molecular formula C_8H_{10}.).

Directive influence of substituents in aromatic compounds and their effect on reactivity

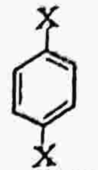
In benzene all the six hydrogen atoms are equivalent. Therefore, replacement of any one hydrogen atom by a substituent gives a single monosubstituted derivative of benzene. However, when a monosubstituted product is converted into a disubstituted benzene derivative, three different isomers can be obtained. They are,



Ortho isomer



meta isomer



para isomer

It has been found that the group already present in the benzene ring determines the position taken by the next entering group. This ability of a group present in the benzene ring to direct the incoming group to a particular position is called the directive influence of groups. Certain groups when present in the benzene nucleus will direct the incoming group to the ortho and para positions. Such groups are called *ortho, para - directing groups*. They are electron donating groups. Some examples of such groups are

$-CH_3$, $-OH$, $-NH_2$, $-Cl$, $-Br$, $-I$ etc.

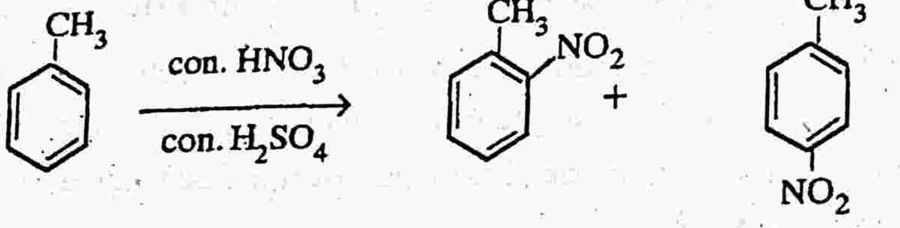
Such groups increase the electron density at the ortho and para positions due to resonance and inductive effect. So electrophilic attack occurs preferentially at the ortho and para positions. Since they increase the electron density in the benzene ring they are called *activating groups*. Activating groups increase the reactivity of the aromatic ring for electrophilic substitution. But Cl is a deactivating group (because of its strong –I effect) eventhough it is an ortho, para directing group.

The groups which direct the incoming group to meta position are called meta directing groups. They are electron withdrawing groups. Some examples are

$-NO_2$, $-CN$, $-CHO$, $COOH$, $-SO_3H$ etc.

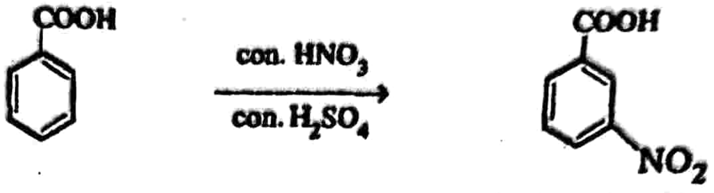
Such groups decrease the electron density at the ortho and para positions due to resonance effects. Thus meta positions become positions of comparatively higher electron density. Hence electrophilic attack occurs preferentially at meta position. Since these groups decrease the overall electron density in the benzene ring, they decrease the reactivity of the aromatic ring for electrophilic substitution. So they are called deactivating groups.

For example, nitration of toluene gives a mixture of ortho nitrotoluene and para nitrotoluene.



o-nitrotoluene p-nitrotoluene

Nitration of benzoic acid gives mainly meta nitrobenzoic acid.



m-nitrobenzoic acid

Polynuclear hydrocarbons and their toxicity

Polynuclear hydrocarbons contain two or more benzene rings fused together. Naphthalene and anthracene are simple examples of polynuclear hydrocarbons.

Certain polynuclear hydrocarbons have carcinogenic property. For example 1, 2 - benzanthracene (present in coal tar) produces skin cancer. 1,2-benzpyrene, 20–methyl cholanthrene etc. are some other examples of potent carcinogenic compounds.