# 15.11 Aromatic Substitution

The replacement of an atom, generally hydrogen, or a group attached to the carbon of the benzene ring by another group is known as aromatic substitution. Like the substitution at aliphatic system, aromatic compounds may also be substituted by three mechanisms : (i) free-radical (homolytic cleavage), (ii) electrophilic (attack by electrophilic or electron-seeking reagents) and (iii) nucleophilic (attack by nucleophilic or electron donating reagents). But unlike aliphatic system, electrophilic substitution reactions are common in aromatic compounds and all the common well known substitution reactions, viz. nitration, halogenation, sulphonation, alkylation and acylation are examples of electrophilic substitution. So here we will deal electrophilic substitution first.

15.12 Electrophilic Aromatic Substitution

The experimental evidences indicate that all[1] the electophilic substitution reactions of the aromatic hydrocarbons proceed by a common mechanism. Therefore, we will first deal the mechanism, in general, and then apply it to specific substitution reaction, viz. nitration, halogenation, sulphonation, etc.

The electophilic aromatic substitution reactions take place in two steps. In the first step the electrophilic reagent attacks on the π electrons of the aromatic ring to form an intermediate which is known as aronium cation, the σ-complex[2] or the pentadienyl cation[3].

Electromeric effect in benzene ring   Intermediate   I
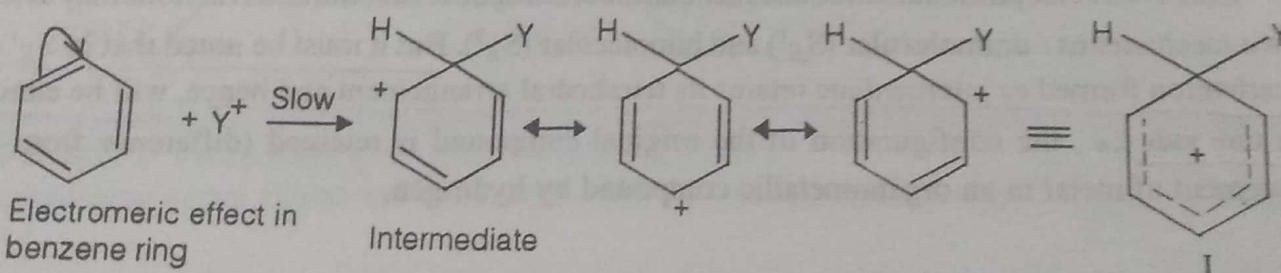
The intermediate is stabilised by resonance and the resonance hybrid[4] can be represented by the structure, I. The second step of the reaction involves the elimintion of a proton from the intermediate, by an anionic species, to form a substituted aromatic compound.

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[1] Note that at this time we are not concerned with the substituent present in the benzene nucleus and we will mainly be dealing the electrophilic substitution on benzene nucleus only.

[2] Since a discrete σ-bond has been formed.

[3] Since the intermediate has no longer a benzene structure but an unstable cation with four π electrons delocalized over five carbon nuclei (the sixth carbon atom is a saturated carbon and forms sp^3 hybrid bond), it is known as pentadienyl cation.

[4] For the sake of simplicity we will write only one of the resonating structures of the resonance hybrid in our further
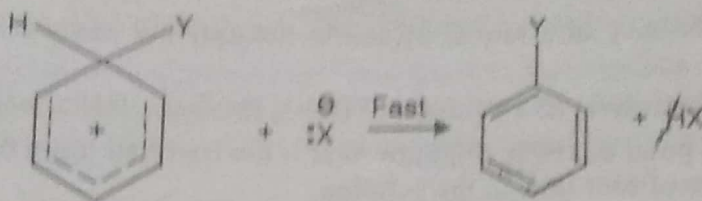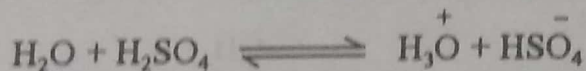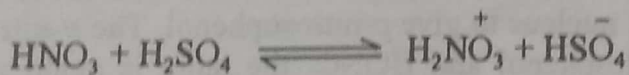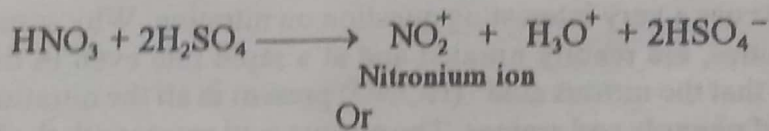
The retention of benzene nucleus in the product confers stability to the substituted product.

Thus, the electrophilic aromatic substitution reactions are bimolecular since the rate determining (first) step involves two molecules.

Role of σ- and π-complexes in electrophilic aromatic substitution. Experimental evidence suggests that the formation of the above type of σ-complex follows the initial formtion of a π-complex in which electrophile is loosely held near the π-electron cloud of the aromatic ring. However, in most of aromatic substitutions, formation of a π-complex is found to be a reversible and rapid step which is followed by the slow (rate-determining) and irreversible step of σ-complex formation. Thus, a complete picture of the first step (formation of σ-complex) can be represented as below.


Benzene   Electophile   π-Complex   σ-Complex
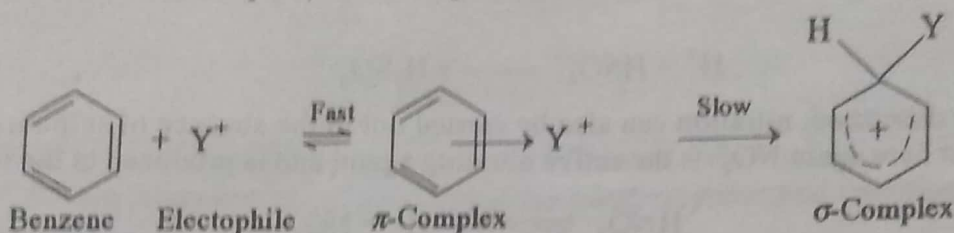
Now let us discuss some common electrophilic substitution reactions of benzene.

1. Nitration : Among all the aromatic substitution reactions, nitration has been studied in the most detail. Nitration is generally carried out with a mixture of concentrated nitric and sulphuric[1] acids (*nitrating mixture*). The reaction proceeds very slowly when nitric acid alone is used which indicates that sulphuric acid converts the HNO_3 into a form that is capable of reacting with benzene with a great ease. Now there is a considerable evidence to show that H_2SO_4 helps in converting the HNO_3 into *nitronium ion* which is the real nitrating agent.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$
$$\text{Nitronium ion}$$

Or

$$HNO_3 + H_2SO_4 \rightleftharpoons H_2\overset{+}{N}O_3 + H\overset{-}{S}O_4$$

$$H_2\overset{+}{N}O_3 \rightleftharpoons \overset{+}{N}O_2 + H_2O$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3\overset{+}{O} + H\overset{-}{S}O_4$$

Now the question arises that if the function of H_2SO_4 is to provide a strongly acidic medium for release of nitronium ion from HNO_3,[2] then other strong acids should also serve the purpose. It is indeed found to be so, *e.g.*, HF and BF_3 also catalyse nitration by assisting the release of nitronium ion.

$$BF_3 + HNO_3 \longrightarrow NO_2^+ + HO-BF_3^-$$

$$2HF + HNO_3 \longrightarrow NO_2^+ + H_3O^+ + 2F^-$$
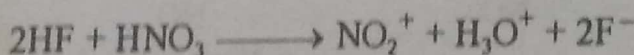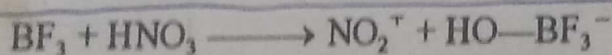
[1] It must be noted that H_2SO_4 has no action on benzene itself under the conditions of nitration.

[2] Nitric acid itself is a weak nitrating agent : in O_2N-OH the OH group exerts a very weak pull on the bonding electrons.
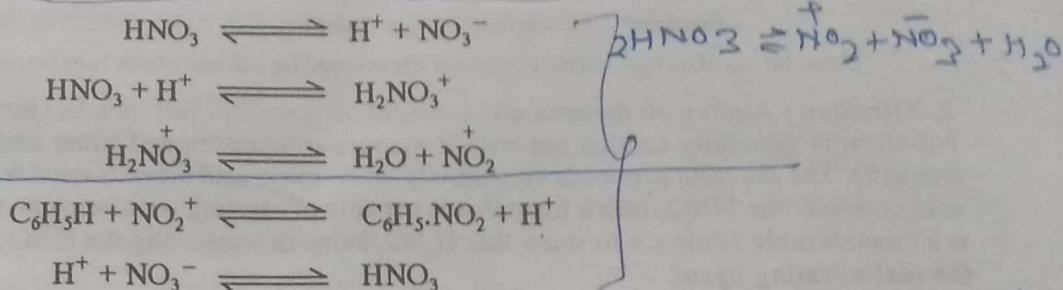
However, the presence of a nitronium ion in the nitrating mixture has been confirmed by the following points.

(i) During the electrolysis of a solution of HNO_3 in oleum, HNO_3 migrates to the cathode.

(ii) The freezing point of 100% sulphuric acid is lowered four times the expected value by HNO_3; it indicates the presence of four ions in the solution.

(iii) The presence of NO_2^+ in the nitrating mixture has been confirmed by the Raman spectra.

(iv) By the actual isolation of the crystalline nitronium salts, viz. nitronium perchlorate ($NO_2^+ ClO_4^-$) and nitronium nitrate ($NO_2^+ NO_3^-$).

The nitronium ion formed above represents a powerful electrophile and attacks the benzene ring in the general pattern. So the nitration can be represented as below.

$$H^+ + HSO_4^- \longrightarrow H_2SO_4$$
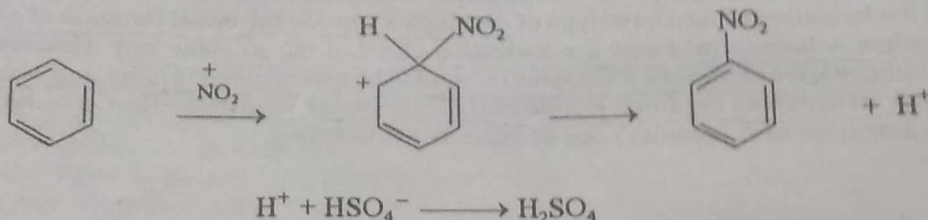
As already described, nitration can also be carried out in the absence of sulphuric acid or only by dil. nitric acid. But here again NO_2^+ is the active nitrating agent; and is produced in the following manner.

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

$$HNO_3 + H^+ \rightleftharpoons H_2NO_3^+$$

$$H_2NO_3^+ \rightleftharpoons H_2O + NO_2^+$$

$$C_6H_5H + NO_2^+ \rightleftharpoons C_6H_5.NO_2 + H^+$$

$$H^+ + NO_3^- \rightleftharpoons HNO_3$$

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

Now let us discuss a very interesting question on nitration. Why some highly reactive compounds, viz. phenols and amines, are readily nitrated and at a rapid rate even in dilute HNO_3 ? The question is answered by the fact that the nitrous acid* (HONO) present in all the nitrating mixtures plays an important role in the nitration of phenols and amines. The nitrous acid reacts with the HNO_3 to form the nitrosonium ion which nitrosates the reactive nucleus to give p-nitrosophenol. The p-nitrosophenol is oxidised very rapidly by HNO_3 to yield p-nitrophenol and HONO, the latter is again used and thus, the process progressively speeds up.

$$HNO_2 + 2HNO_3 \rightleftharpoons H_3O^+ + 2NO_3^- + NO^+$$

Phenol   p-Nitrosophenol   p-Nitrophenol
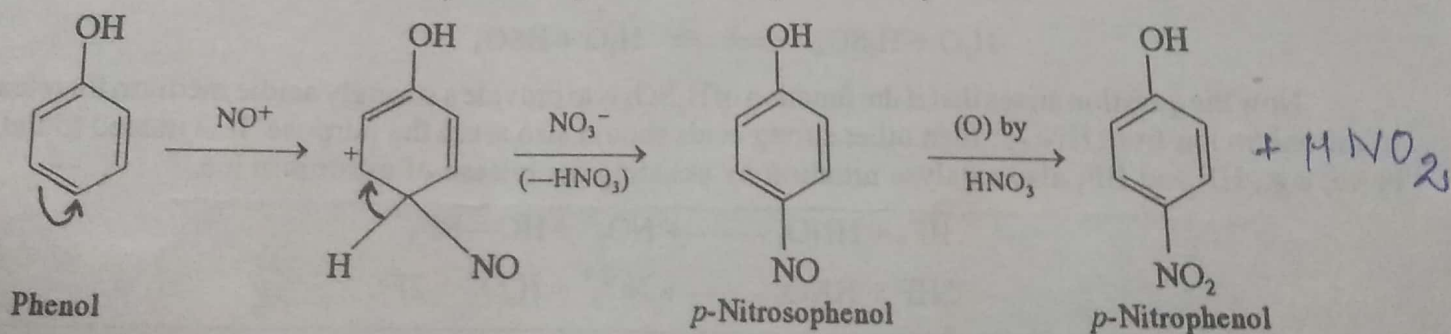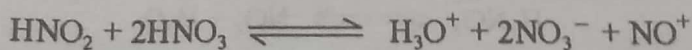
*Nitrous acid may also be produced by the oxidation of phenols with HNO_3.