Class : B.Sc. part II (Hons.)
Subject : Chemistry, paper - organic chemistry
Topic : Electrophilic substitution of Benzene

Electrophilic substitution reaction of benzene is the one where an electrophile substitutes the hydrogen atom of benzene. Basic examples of electrophilic substitution reaction of benzene are nitration, halogenation, sulphonation, Friedel craft's alkylation and acylation etc.

* Electrophilic substitution reactions — Electrophile

(i) Nitration — NO_2^+

(ii) Halogenation — X^+ (X = Cl, Br, I)

(iii) Sulphonation — SO_3

(iv) Friedel crafts alkylation — R^+ (R = CH_3, C_2H_5, C_3H_7 etc.)

Friedel craft's acylation — RCO^+ (R = CH_3)

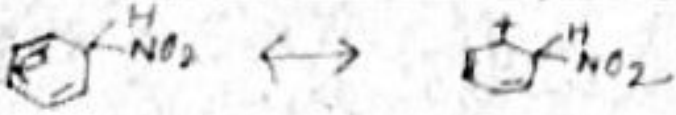
* Mechanism of Nitration reaction:

When benzene is allowed to react with concentrated nitric acid and sulphuric acid, nitrobenzene is formed. This reaction is known as nitration of benzene. The mixture of nitric acid and sulphuric acid is called nitrating agent. In nitration of benzene nitric acid acts as a base. The mechanism of nitration of benzene involves various steps:

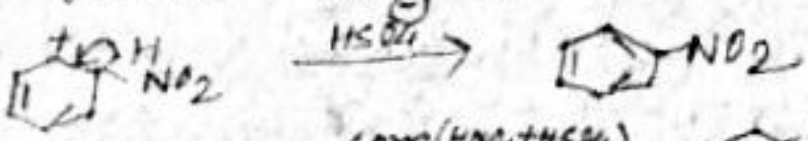
(a) Generation of electrophile nitronium ion:
Nitrating agent produces electrophile NO_2^+ as:

$$2H_2SO_4 \text{ (conc.)} + HNO_3 \text{ (conc.)} \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$$

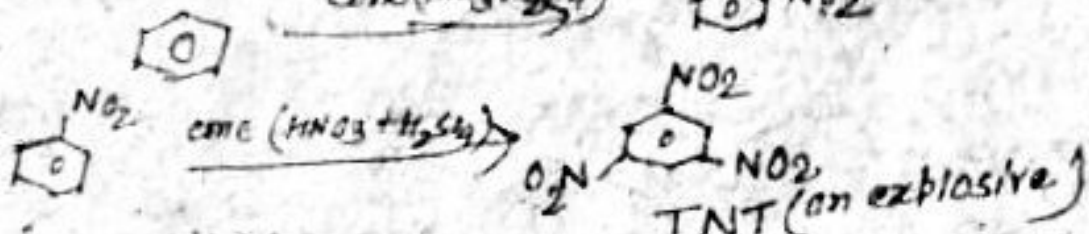
(b) Attack of NO_2^+ at benzene ring:
Benzene is a electron rich system and acts as nucleophile. It has delocalized π-electrons where electrophiles easily attack. NO_2^+ attacks on benzene to produce σ (sigma) complex, Non aromatic system.



(c) HSO_4^- present in reaction mixture abstract H^+ ion from σ-complex and produce H_2SO_4. Finally, nitrobenzene is obtained. Here H_2SO_4 is regenerated after the course of reaction. So, H_2SO_4 acts as catalyst.

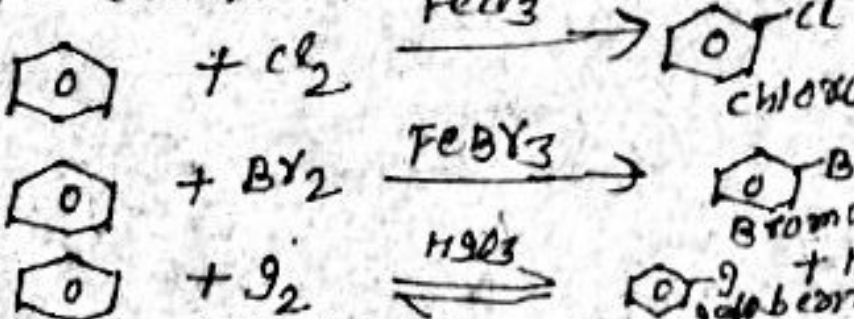


Thus,



Note: Nitrobenzene is less reactive than benzene towards electrophilic substitution because NO_2 is an electron withdrawing group which reduces the electron density of benzene ring and thus attack of electrophile in benzene ring becomes difficult due to poorer of delocalized electron system.

** Mechanism of halogenation in benzene:
Benzene undergoes electrophilic substitution reaction with halogen in presence of catalyst FeX_3 (Lewis acids). In this reaction halobenzene is produced. The reaction is called halogenation of benzene.
For example,

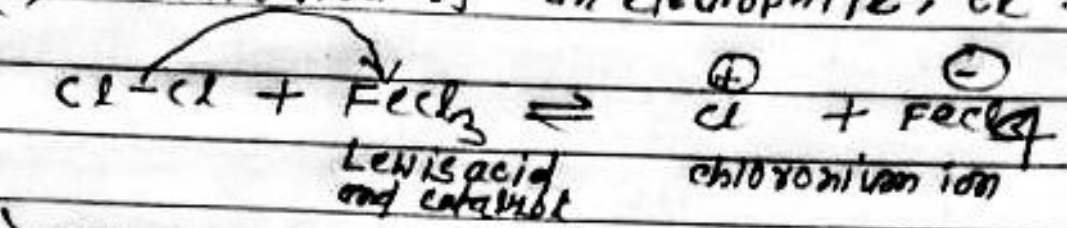


$5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$

Since, iodination of benzene is a reversible process, so it is allowed in presence of an O.A. (HIO_3) in order to remove byproduct (HI, R.A.) from reaction mixture

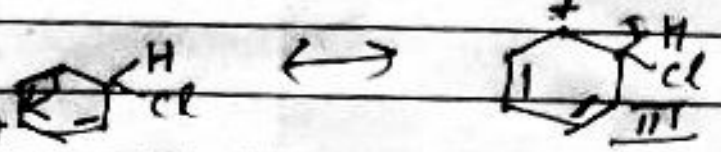
The mechanism of chlorination of benzene involves various steps given below:

(i) Generation of an electrophile, $Cl^{\oplus}$:

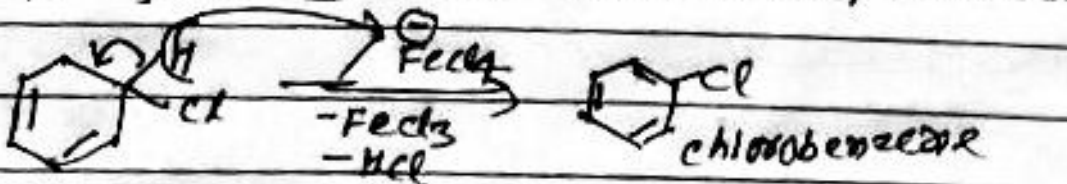


(ii) Attack of electrophile on benzene ring to produce σ-complex

Here, Cl is attached with sp^3 hybridized carbon of benzene ring and system becomes non-aromatic.



(iii) $FeCl_4^-$ present in reaction mixture abstracts H^+ from III and thus forms chlorobenzene.



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