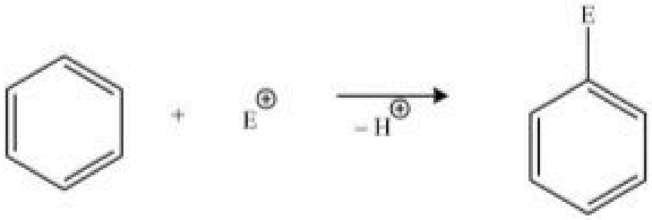
Aromatic Electrophilic Substitution

❖ The Arenium Ion Mechanism

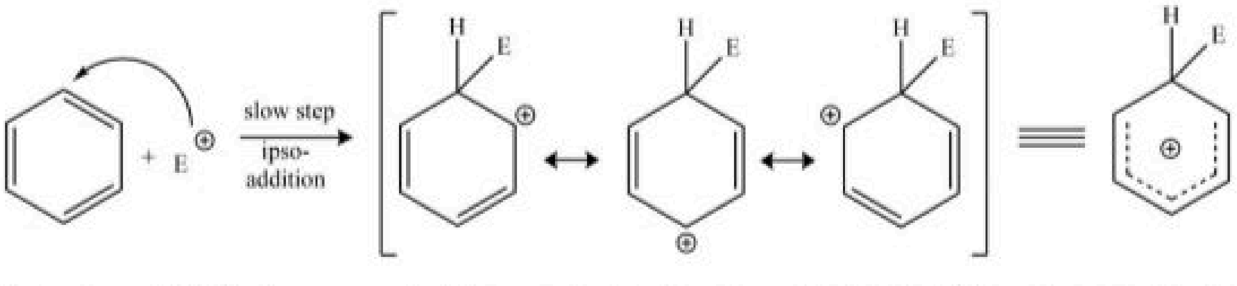
Electrophilic aromatic substitution (EAS) is the organic reaction in which an atom that is attached to an aromatic system (typically hydrogen) is replaced by an electrophile. This is quite possible in aromatic systems because there is π-electron density above and below the plane which is easily available for attacking electrophile; and nucleophilic attack is opposed because of π-cloud shields the carbon from such invasions.

Illustrative reaction: The general reaction showing the electrophilic substitution in aromatic compounds is shown below (E is electrophile).

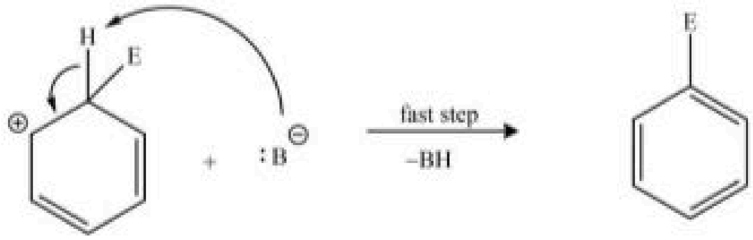


Mechanism involved: The proposed mechanism for the reaction given above involves three steps which must be discussed before we give salient features of the same.

i) Attack of the electrophile on aromatic ring forming carbocation intermediate: In this step, the electrophile attacks the aromatic ring to form a resonance stabilized carbocations.

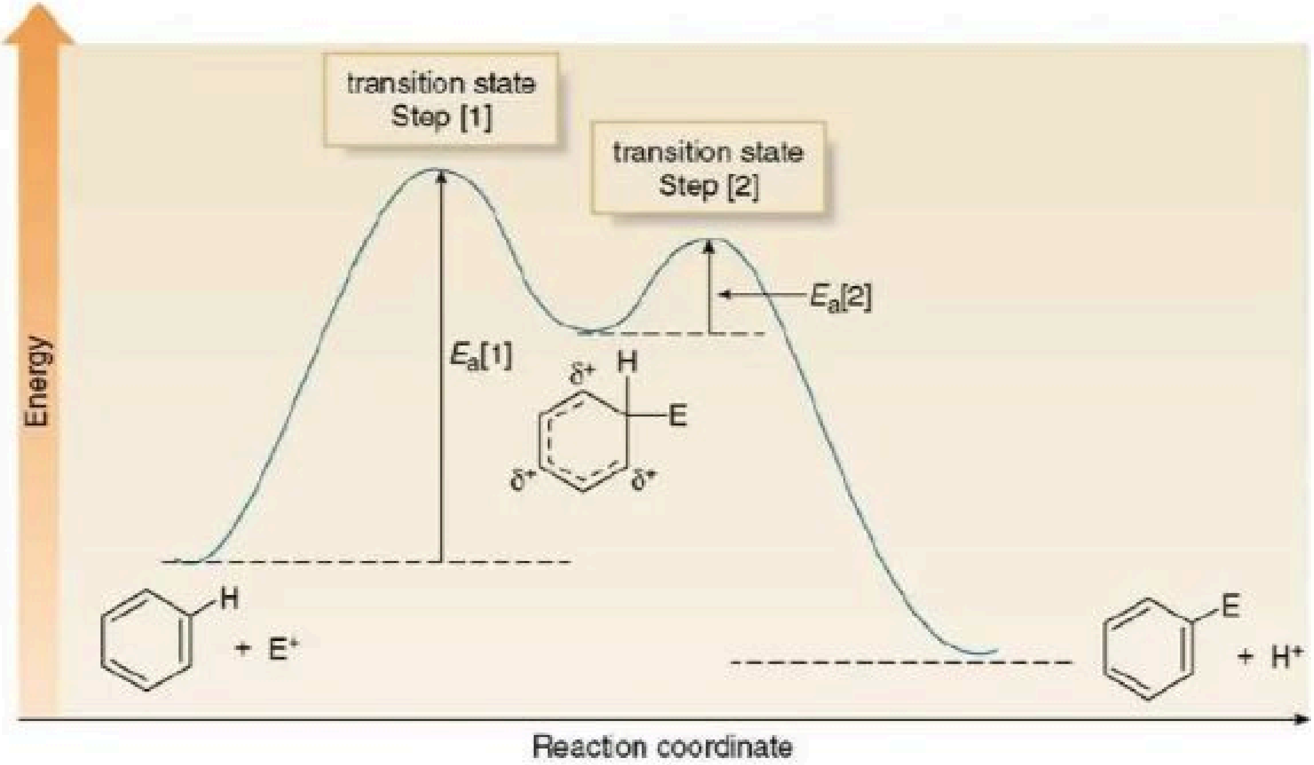


iii) Departure of the leaving group: In this step, the leaving group detaches itself from the aromatic ring to give rise to the final product.



The General Mechanism

- The energy changes in electrophilic aromatic substitution are shown below:

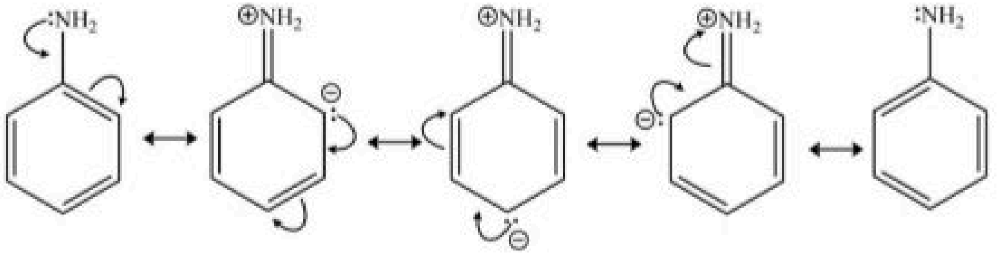


The orientation and reactivity in monosubstituted benzene for electrophilic substation reaction can be divided into four major types as discussed below.

- ***Ring Activator with o-, p-Directing Influence***

The substituents like −XY, where X has loan pairs of electrons and no conjugated double bond in extended part (Y), increase the electron density at the ring; and therefore, are strongly activating. Furthermore, these types of groups donate those loan pair of electrons to the π-system, creating a negative charge density at para and ortho sites; and therefore, become ortho/para-directing via resonance. Nevertheless, one might ask that what if these groups are electron-withdrawing via inductive effect. The answer would be the same (i.e., ring activated) because the electron donation via mesmeric effect is much dominant than the inductive effect in these types of groups. Some typical examples of this type of group are given below with NH_2 as reference.

$-NH_2, -NR_2, -NHR, -OH, -OR, -OCOR, -SR, -NHCOR$

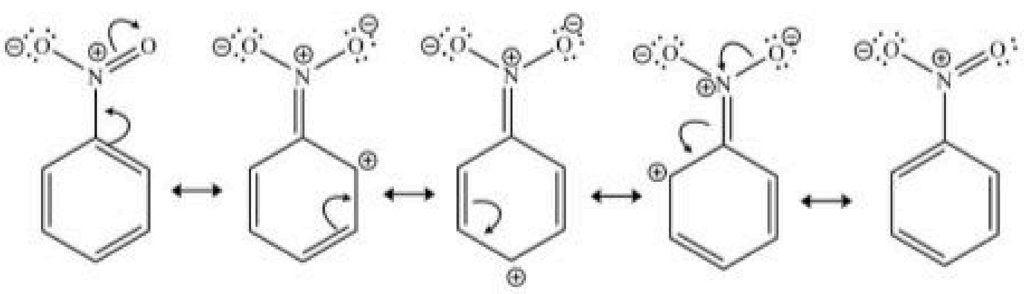


In other words, we can conclude that these groups make these positions more susceptible to an electron-deficient electrophile.

- ***Ring Deactivator with m-Directing Influence***

The substituents like −X=Y, where three is conjugated double bond (w.r.t ring), decrease the electron density at the ring; and therefore, are strongly deactivating. Furthermore, these types of groups accept those electrons from the π-system, creating a positive charge density at para and ortho sites; and therefore, become meta-directing via resonance. Some typical examples of this type of group are given below.

$-NO_2, -CN, -CHO, -COOH, -COOR, -CONH_2, -SO_3H$



In other words, we can conclude that these groups make *m*-positions more susceptible towards an electron-deficient electrophile.

Electrophilic Aromatic Substitution of Benzene