

## SUBSTITUENTS AND THEIR DIRECTING AND ACTIVATING (DEACTIVATING) EFFECTS

There are two general types of electronic interaction of a substituent with the benzene ring:

1. Inductive Effect:
  - A. Negative Inductive Effect - the substituent withdraws electron density from the benzene ring via the frame of  $\sigma$ -bonds. Such substituents are termed *S-acceptors*.
  - B. Positive Inductive Effect – the substituent donates electron density to the benzene ring via the frame of  $\sigma$ -bonds. Such substituents are termed *S-donors*.
2. Resonance Effect:
  - A. Negative Resonance Effect - the substituent withdraws electron density from the benzene ring via conjugation with the benzene's  $\pi$ -system. Such substituents are termed *p-acceptors*.
  - B. Positive Resonance Effect - the substituent donates electron density to the benzene ring via conjugation with the benzene's  $\pi$ -system. Such substituents are termed *p-donors*.

**NOTE:** A particular substituent may have opposite inductive and resonance effect!!! Thus, a hydroxyl group, **OH**, has a negative Inductive Effect (because oxygen is more electronegative than carbon) but positive Resonance Effect (because oxygen's lone pair conjugates with the benzene's  $\pi$ -system, donating electron density to the ring, via an oxonium ion resonance structure). In this particular case (but not necessarily in every case) the Resonance Effect is greater, and the hydroxyl group is an overall electron donor group to the benzene ring.

Groups, which have an overall electron-donating ability tend to accelerate electrophilic aromatic substitution and are called **ACTIVATING** groups. They can be further split into:

1.  $\sigma$ -donors – alkyl groups (**R**) and aryl groups (**Ar**).
2.  $\sigma$ -acceptors,  $\pi$ -donors (with a predominant  $\pi$ -donor effect) – **NH<sub>2</sub>, NHR, NR<sub>2</sub>, OH, OR, NHCOR**.

Groups, which have an overall electron-accepting ability tend to decelerate electrophilic aromatic substitution and are called **DEACTIVATING** groups. They can be further split into:

1.  $\sigma$ -acceptors – **<sup>+</sup>NR<sub>3</sub>, CF<sub>3</sub>, CCl<sub>3</sub>**.
2.  $\sigma$ -acceptors,  $\pi$ -acceptors – **CO (ketone), CHO (aldehyde), COOH, COOR, NO<sub>2</sub>, CN, SO<sub>3</sub>H**

Some groups, which are  $\sigma$ -acceptors and  $\pi$ -donors, have a predominant  $\sigma$ -acceptor effect. Such groups are also **DEACTIVATING**. In this category are the halogen substituents: **F, Cl, Br, I**

### DIRECTING RULES:

- ALL  $\sigma$ -donors are *ortho, para* directing groups.
- ALL  $\sigma$ -acceptors,  $\pi$ -donors are *ortho, para* directing groups.
- ALL  $\sigma$ -acceptors are *meta* directing groups.
- ALL  $\sigma$ -acceptors,  $\pi$ -acceptors are *meta* directing groups.