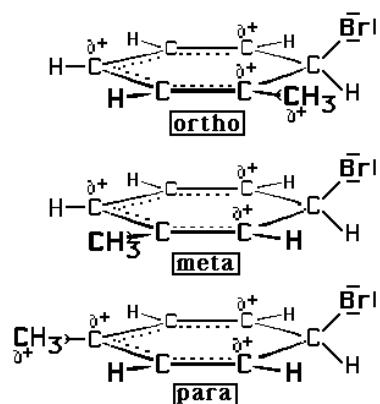


Chemistry 0320 - Organic Chemistry 2

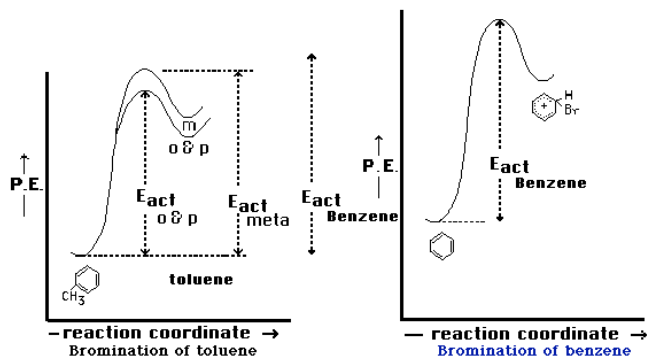
Substituent Effects on Electrophilic Aromatic Substitution

When substituted aromatic compounds undergo electrophilic substitution reactions, constitutional isomers can be formed. Electron-donating substituents on the ring facilitate further substitutions and direct the incoming electrophile to the *ortho*- and *para*-positions. Electron-withdrawing substituents deactivate further substitutions and are *meta*-directing. The halogens are an exception; they deactivate the ring but are *ortho,para*-directing. These effects can be rationalized by considering the resonance stabilization of the σ -complex. Substituents on aromatic rings can therefore be classified as **ortho,para**- and **meta**-directing groups:

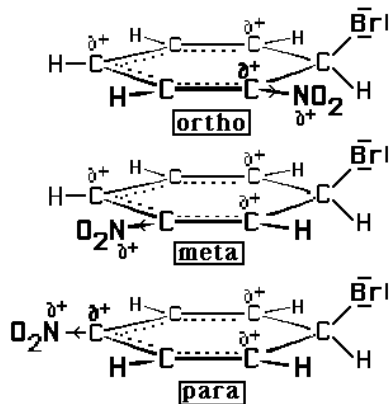
ortho,para: HO, H₂N, R₂N > RO > AcHN > R > Cl, Br, I (mildly deactivating).



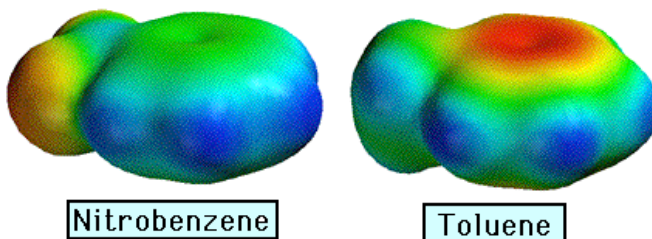
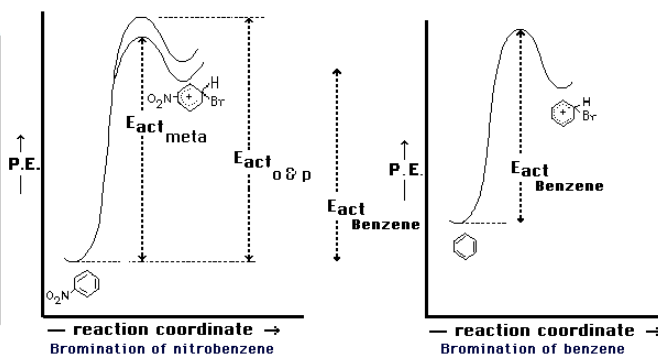
Both the pentadienyl carbocations shown and the π complexes leading to these intermediates are stabilized by the substituent methyl group which assists in the positive charge dispersal. The effect of the methyl is most pronounced when the methyl is *ortho* and *para* to the position of attack. The stabilization effect is less in the *meta* isomer.



meta: R₃N⁺, O₂N, N≡C (strongly deactivating) > HO₃S > OHC > ORC > HO₂C > RO₂C > H₂NOC.



Both the pentadienyl carbocations shown and the π complexes leading to these intermediates are destabilized by the substituent nitro group which exacerbates the positive charge (δ^+ vs δ^+). Charge dispersal leads to stabilization while charge concentration leads to destabilization. The effect of the nitro group is least pronounced when the group is *meta* to the position of attack.



Note: The electron density is much higher on the aromatic ring of toluene (activating) than on the aromatic ring of nitrobenzene.

With more than one substituent already present on the aromatic ring, the most electron-donating groups are generally more important in directing the electrophile.