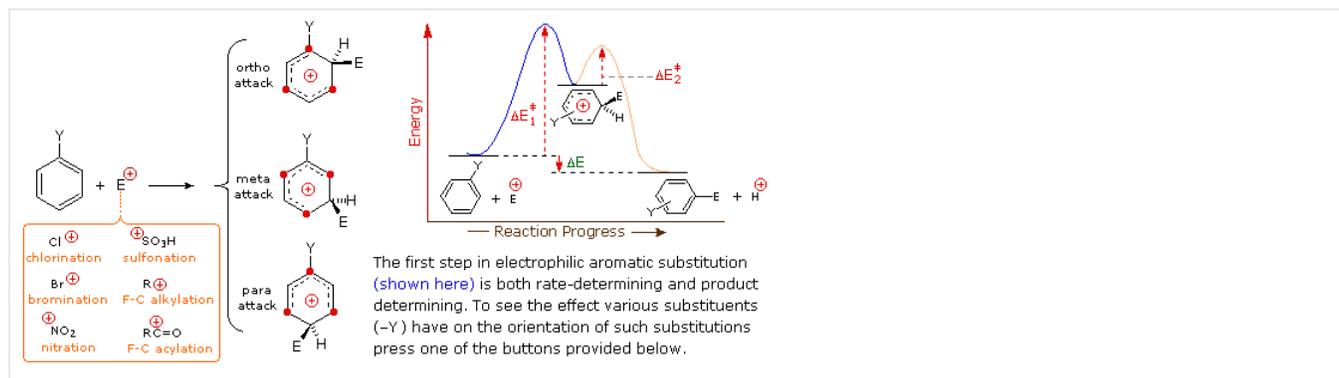


16.14: Why Substituents Activate or Deactivate a Benzene Ring

The manner in which specific substituents influence the orientation of electrophilic substitution of a benzene ring is shown in the following interactive diagram. As noted on the opening illustration, the product-determining step in the substitution mechanism is the first step, which is also the slow or rate determining step. It is not surprising, therefore, that there is a rough correlation between the rate-enhancing effect of a substituent and its site directing influence. The exact influence of a given substituent is best seen by looking at its interactions with the delocalized positive charge on the benzenonium intermediates generated by bonding to the electrophile at each of the three substitution sites. This can be done for seven representative substituents by using the selection buttons underneath the diagram.



In the case of alkyl substituents, charge stabilization is greatest when the alkyl group is bonded to one of the positively charged carbons of the benzenonium intermediate. This happens only for ortho and para electrophilic attack, so such substituents favor formation of those products. Interestingly, primary alkyl substituents, especially methyl, provide greater stabilization of an adjacent charge than do more substituted groups (note the greater reactivity of toluene compared with tert-butylbenzene).

Nitro (NO_2), sulfonic acid (SO_3H) and carbonyl ($\text{C}=\text{O}$) substituents have a full or partial positive charge on the atom bonded to the aromatic ring. Structures in which like-charges are close to each other are destabilized by charge repulsion, so these substituents inhibit ortho and para substitution more than meta substitution. Consequently, meta-products predominate when electrophilic substitution is forced to occur.

Halogen (X), OR and NR_2 substituents all exert a destabilizing inductive effect on an adjacent positive charge, due to the high electronegativity of the substituent atoms. By itself, this would favor meta-substitution; however, these substituent atoms all have non-bonding valence electron pairs which serve to stabilize an adjacent positive charge by pi-bonding, with resulting delocalization of charge. Consequently, all these substituents direct substitution to ortho and para sites. The balance between inductive electron withdrawal and p- π conjugation is such that the nitrogen and oxygen substituents have an overall stabilizing influence on the benzenonium intermediate and increase the rate of substitution markedly; whereas halogen substituents have an overall destabilizing influence.

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