

ACTIVATION AND DEACTIVATION

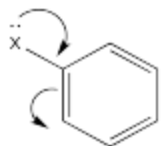
Because the benzene acts as a nucleophile in electrophilic aromatic substitution, substituents that make the benzene more electron-rich can accelerate the reaction. Substituents that make the benzene more electron-poor can retard the reaction.

In the mid-twentieth century, physical organic chemists including [Christopher Ingold](#) conducted a number of kinetic studies on electrophilic aromatic substitution reactions. In the table below, you can see that some substituents confer a rate of reaction that is much higher than that of benzene (R = H). Phenol, C₆H₅OH, undergoes nitration a thousand times faster than benzene does. Nitrobenzene, C₆H₅NO₂, undergoes the reaction millions of times more slowly.

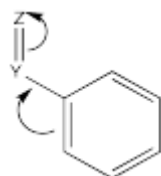
Rate of nitration in benzene derivatives	
R in C ₆ H ₅ R	Relative rate
OH	1,000
CH ₃	25
H	1
CH ₂ Cl	0.71
I	0.18
F	0.15
Cl	0.033
Br	0.030
CO ₂ Et	0.0037
NO ₂	6 x 10 ⁻⁸
NMe ₃ ⁺	1.2 x 10 ⁻⁸

These observations are consistent with the role of the aromatic as a nucleophile in this reaction. Substituents that draw electron density away from the aromatic ring slow the reaction down. These groups are called deactivating groups in this reaction. Substituents that readily donate electron density to the ring, or that effectively stabilize the cationic intermediate, promote the reaction. These groups are called activating groups in this reaction.

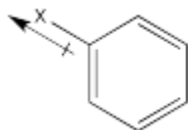
The roles of these groups are related to their electronic interactions with the electrons in the ring. Some groups might be π -donors, providing additional electron density to the benzene ring via conjugation.



Other groups may be π -acceptors, drawing electron density away from the ring via conjugation.



Still others may be σ -acceptors, drawing electron density away from the ring via a simple inductive effect which arises from the electronegativity of a substituent.



In some cases, there may be multiple effects, and the overall influence of the substituents is determined by the balance of the effects. One effect may be stronger in one case than the other, so it wins out in one case and loses in another.

Source: <http://employees.csbsju.edu/cschaller/Reactivity/aromadd/ARactive.htm>