Hammett Equation - Brief Summary

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- σ is the substituent constant: for X = H, $\sigma = 0.0$
where $\sigma > 0$, X is electron withdrawing
where $\sigma < 0$, X is electron donating

- σ is position dependent: *meta* groups act only by induction
para groups also act by resonance

- ρ is the reaction constant; for benzoic acid ionization in water at 25 °C the reaction constant is defined as 1.00

- ρ is sensitive to reaction conditions such as temperature & solvent

- where ρ is > 0, the process is aided by electron withdrawing groups

- where ρ is < 0, the process is aided by electron donating groups

- the absolute value of ρ indicates if the process is more ($|\rho| > 1$) or less ($|\rho| < 1$) sensitive to the electronic effect of the group than the references reaction

- when the charge on the reacting centre can be delocalized onto the substituent, the σ values are modified:
σ^+ for reactions with positive charges
σ^- for reactions with negative charges