***Ortho*-Effect**

Linear free energy relationship to the Hammett type that has been used to correlate vast numbers of rate (k) and equilibrium constant (K) for reactions of *meta-* and *para*- substituted derivatives. Since the Hammett equation has been so successful in the treatment of the effects of groups in the *meta-* and *para-* position, it is not surprising that attempts have been made to apply it to *ortho-*positions also60,61. The effect on a reaction rate or equilibrium constant of a group in the *ortho-*position is called *ortho-* effect. The *ortho-*substituents are bound to the adjacent position of the side-chain, various kinds of proximity effects, such as steric and proximity electric effects, which are otherwise insignificant, generally operate on the side chain functions. Hydrogen bonding and other intramolecular interactions of *ortho-*substituents may sometimes play significant roles in reactivities of *ortho*-substituted derivatives. Unfortunately, these proximity effects contribute in varying degrees in different systems. Thus, the reactivities of *ortho-*substituted compounds are not explained by a single, generally applicable set of parameters. However, a correlation can be achieved in one of the following ways3.

log k = ρ\*σ\*o + h (14)

σ\* is the *ortho-*substituent constant and ρ\* is the susceptibility constant.

log k = δ Es + h (15)

Es is the steric substituent constant and δ is the susceptibility constant. The ratio of the rate constant for an *ortho-* to that of corresponding *para-*substituted benzene derivatives, ko/kp may frequently be taken as an approximate measure of the steric effect of the *ortho-*substituents62.

log (k/ko) = = ρ\*σ\*o + δ Es (16)

The above equations (14), (15) and (16) are due to the work of Taft.

Charton’s treatment, on the *ortho-*substituent effect, is considered to be a better treatment because of its wider applicability in understanding the nature of the *ortho-*effect. He derives two multiparameter equations. They are as follows,

log k = α σI + β σR + h (17)

where σI and σR  are the inductive and resonance substituent constants α and β are the localized and delocalized compounds and h is the intercept.

log k = α σI + β σR + φ ν + h (18)

where ν is the parameter for the steric effect and φ is the coefficient of the steric term. Thus, the separation of polar, resonance and steric effect has received much attention in recent years.