

Treatment of the Steric Effect in Linear Free Energy Relationship

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自由에너지 直線關係式에서의 立体効果의 適用性

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Summary

The problems of systems that exhibit proximity or steric effects was examined and the applicability to the Hammett treatment was reviewed.

Significant correlations with the extended Hammett equation were to be obtained by dividing them into four cases:

- (1) The steric effect obeys a linear free energy relationship whence the equation $Q_x = \alpha\sigma_{1x} + \beta\sigma_{rx} + \rho\nu_x + h$ is applicable.
- (2) The steric effect does not obey a linear free energy relationship whence the equation $Q_x = \alpha\sigma_{1x} + \beta\sigma_{rx} + S_x + h$ is available.
- (3) The steric effect is constant whence the equation $Q_x = \alpha\sigma_{1x} + \beta\sigma_{rx} + h'$ is suitable.
- (4) The steric effect is nonexistent whence the extended Hammett equation is obeyed.

Introduction

Taft(I) isolated steric effects and also defined the steric parameters E_s from the assumption that for substituents that are not unsaturated (and therefore conjugated with the carbonyl group) are not hydrogen bonded. For the acid-catalyzed hydrolysis of esters in aqueous acetone, $\log(\frac{K}{K_0})$ was shown to be insensitive to polar effects. In cases where resonance interaction was absent, this value was proportional only to steric effects (and any others which are not field or resonance).

The equation is

$$\log\left(\frac{K}{K_0}\right) = E_s \dots\dots\dots(1)$$

The methyl group was taken as standard, with the value 0.

This treatment is restricted, since it requires more assumptions, but the E_s values are approximately in order of the size of the groups. Charton(2) has shown that E_s values for substituents of types CH_2X , CHX_2 , and CX_3 are linear function of the van der Waals radii for this groups.

Another set of E_s values, called E_s^* has been developed based on rates of hydrocarbon. The E_s^* scale is similar to the E_s scale except that the values are larger for tertiary systems.

An equation taking in to account both field effect and steric factors is the Pavelich-Taft equation(3).

$$\log\frac{K}{K_0} = \rho_1\sigma_1 + \delta E_s \dots\dots\dots(2)$$

where δ is analogous to ρ . However, not much work has been done on this.

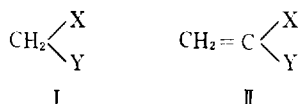
Since the Hammett equation has been so successful in the treatment of the effects of groups in the meta and para positions, much work has been done in attempting to apply it to ortho positions also(4). It has generally been believed that ortho substituents are not amenable to simple Hammett treatment because steric effects are important. Therefore much of the work on the ortho effect has involved equations which attempt to separate steric from electric effects. In an analysis of a vast amount of data, by means of such equations, Charton(5) reached the unexpected conclusion that the effect of ortho substituents is independent of steric effects(6) except for bulky substituents, such as I, Ph, or tertiary-Bu.

According to his analysis, ortho effects(except for bulky substituents, and for groups which are capable of intramolecular hydrogen bonding) are linear combinations of σ_I and σ_R , and the usual Hammett treatment fails for ortho substituents because σ_I and σ_R can make vastly different contributions to the hypothetical σ_0 , depending on which reaction is being studied.

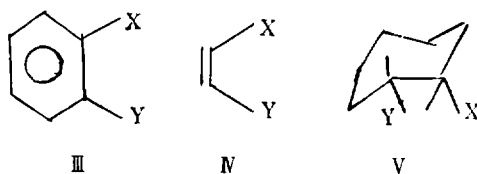
It is in this report to set forth the conditions that the Hammett treatments are to be successful for the steric problem, and to discuss applicability of them.

Set up cases

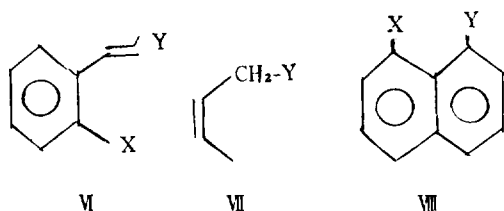
Three classes of systems that exhibit proximity or steric effects are to be considered: (1) Geminal systems, in which reaction site and substituent are attached to the same carbon atom:



(2) Vicinal systems in which reaction site and substituent are attached to adjacent carbon atoms:



(3) Systems in which the reaction site is separated from the group bearing the substituent by a side chain:



Proximity effects on reactivity and properties can be conceived of in terms of three factors: Proximity electrical effects are exerted in addition to the normal electrical effects of substituent that can be resolved into localized effects related to σ_I and delocalized effects which are a function of the σ_R . Thus,

$$\sigma_{p\rho\sigma} = \lambda_{p\rho\sigma}\sigma_I + \delta_{p\rho\sigma}\sigma_R \dots\dots\dots(3)$$

Steric effects are dependent on the size of the substituent.

They may consist of steric hindrance to solvation of the substituent and or the reaction site, steric hindrance to attack by the reagent, steric inhibition of resonance in the substituent and the reaction site, and steric control of reaction conformation.

Intramolecular secondary binding forces may consist of hydrogen bonding: dipole-dipole(Keesom), dipole-induced dipole(Debye), and induced dipole-

induced dipole(London), and charge transfer interaction(7)

It should be possible to dissect the effects of a substituent into localized and delocalized contributions(8).

$$\sigma_x = \lambda\sigma_{1x} + \delta\sigma_{Rx} \dots\dots\dots(4)$$

Thus where σ_x is any substituent constant, σ_{1x} is a measure of the localized effect, and σ_{Rx} is a measure of the delocalized effect. Substitution of Equation(4) in Equation(8).

gives

$$Q_x = \rho\lambda\sigma_{1x} + \rho\delta\sigma_{Rx} + h \dots\dots\dots(5)$$

or

$$Q_x = \alpha\sigma_{1x} + \beta\sigma_{Rx} + h \dots\dots\dots(6)$$

Thus we may represent quantitatively the effect Q_x of a substituent, X, on the characteristic of interest by means of the equation.

$$Q_x = \alpha_N\sigma_{1x} + \beta_N\sigma_{Rx} + \alpha_{prox}\sigma_{1x} + \beta_{prox}\sigma_{Rx} + \psi\nu_x + \nu\omega_x + h \dots\dots\dots(7)$$

The subscript N indicates the normal electrical effect, the subscript prox indicates the proximity electrical effect, $\psi\nu$ represents the steric effect, and $\nu\omega$ denotes the contribution due to secondary bonding. Combining coefficients of like terms cause Equation(7) to simplify to:

$$Q_x = \alpha\sigma_{1x} + \beta\sigma_{Rx} + \psi\nu_x + \nu\omega_x + h \dots\dots\dots(8)$$

Of the secondary bonding forces given above, intramolecular hydrogen bonding occurs only in special cases.

Keesom, Debye, and London forces may be proportional to σ_1 , if, in fact, they make any significant contribution. Charge transfer interactions

are a function of the σ_1 and σ_R .

Thus, excluding from the data sets studied any substituent for which intramolecular hydrogen bonding occurs, reduces Equation(8) to.

$$Q_x = \alpha\sigma_{1x} + \beta\sigma_{Rx} + \psi\nu_x + h \dots\dots\dots(9)$$

It has already pointed out that Taft's E_s steric parameter is a linear function of van der Waals radii as a steric parameter. The E_s has the disadvantage(9), however, that the quantity Q for the unsubstituted compound(for which X=H) is not equal to h, as is the case with the simple and the extended Hammett equations. To avoid this difficulty ν can be defined as.

$$\nu \equiv \gamma_{v,x} - \gamma_{v,H} = \gamma_{v,x} - 1.20. \dots\dots\dots(10)$$

Where $\gamma_{v,x}$ and $\gamma_{v,H}$ are van der Waals radii of the X group and the H atom, respectively.

There will be four possible cases which must now be considered:

1st: The steric effect obeys a linear free energy relationship whence Equation(9) is applicable.

2nd: The steric effect does not obey a linear free energy relationship whence, for any given members of the data set, the equation

$$Q_x = \alpha\sigma_{1x} + \beta\sigma_{Rx} + S_x + h \dots\dots\dots(11)$$

can be written where S_x is the steric effect of the substituent.

3rd: The steric effect is constant, that is.

$$\psi\nu_x = c \dots\dots\dots(12)$$

Then

$$Q_x = \alpha\sigma_{1x} + \beta\sigma_{Rx} + h' \dots\dots\dots(13)$$

where $h' = h + c$.

4th: The steric effect is negligible or nonexistent whence the extended Hammett equation is obeyed:

$$Q_x = \alpha\sigma_{1X} + \beta\sigma_{RX} - h \quad \dots\dots\dots(14)$$

Results and Discussion

A given set of data may be assigned to one of these cases by the following method: (a) If the correlation of a data set in the form of Equation (9) is significant, the set may belong to case 1st, case 3rd, or case 4th.

Case 1st may be distinguished from cases 3rd and 4th by a significance ("Student t") test of ϕ . If ϕ is significant, then the set is an example of case 1st. If ϕ is not significantly different from zero, then the set belongs to case 3rd or 4th.

(b) The set being examined is now correlated with Equation(14).

If the correlation is significant, then the set belongs to case 3rd or case 4th. This must be true because if the set were an example of case 1st or case 2nd, there is present a steric term not accounted for by Equation(6). Then, if the set belongs to case 1st or 2nd, it can not be correlated by Equation(6).

Case 3rd may be distinguished from case 4th by means of a "Student t" test for the significance of

the difference between the experimentally observed value of h (the data point for which $X=H$) and the calculated value of h obtained from the correlation.

In case 3rd $h_{obs} \neq h_{calc}$, whereas in case 4th, $h_{obs} = h_{calc}$.

If the correlations with both Equation(9) and (6) are not significant, then the set is probably an example of case 2nd.

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〈국문 초록〉

自由에너지 直線關係式에서의 立体効果의 適用性

電子効果와는 또 다른 相互메카니즘 즉 置換基와 反應中心이 近接되어 立體 효과가 誘發되는 系の 類型과 Hammett則에 對한 適用性を 檢討하였다.

立體 효과를 다음의 네가지 類型으로 分離하여 變型Hammett 方程式에 適用되는 경우가 가장 適切하다는 結論을 얻었다. ① 立體 효과가 自由에너지 直線式에 잘 符合될 때, $Q_x = \alpha\sigma_{1x} + \beta\sigma_{RX} + \psi_{1x} + h$. ② 立體 효과가 直線式과 一致되지 않을 때, $Q_x = \alpha\sigma_{1x} + \beta\sigma_{RX} + S_x + h$. ③ 立體 효과가 一定할 때, $Q_x = \alpha\sigma_{1x} + \beta\sigma_{RX} + h'$. ④ 立體 효과에 無關할 때, $Q_x = \alpha\sigma_{1x} + \beta\sigma_{RX} + h$.