

Seperation of the Electrical Effects in Linear Free Energy Relationship

Sung-bin Han

自由에너지 直線關係式에서의 場效果, 誘發效果 및 共鳴效果의 分離

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Summary

Theoretical advances in the separations of electrical effects on the linear relationship were reviewed and discussed.

The theoretical analysis show that Taft equation is best of all the separations of the electrical effects and that the most general and useful approach to the correlation of data for any kind of groups is the use of the extended Hammett equation, $Q_x = \alpha \sigma_{1x} + \beta \sigma_{RX} + h$ with the σ_R and σ_I constants.

Introduction

It is sometimes instructive to divide substituent effects in to two categories, localized and delocalized. Localized effects include inductive and field affects, with the latter probably predominating. Delocalized effects are resonance effects

A good discussion of substituent effects is given is given by Katritzky and topsom(1). It should be possible then to dissect the overall effects of a substituent into localized and delocalized contributions.

$$\sigma_x = \lambda \sigma_{1x} + \delta \sigma_{RX} \quad (1)$$

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 $Q_x = \rho \sigma_x + h$ gives

$$Q_x = \rho \lambda \sigma_{1x} + \rho \delta \sigma_{RX} + h \quad (2)$$

or

$$Q_x = \alpha \sigma_{1x} + \beta \sigma_{RX} + h \quad (3)$$

Equation 3, the extended Hammett equation, was first proposed by Taft (2), and first attempt to resolve substituent effects into localized and delocalized contributions was carried out by Taft and Lewis(3). The essence of their treatment may be written as follows. From Equation 1,

$$\sigma_m = \lambda_m \sigma_{1x} + \delta_m \sigma_{RX} \quad (4)$$

$$= \lambda_p \sigma_{1x} + \delta_p \sigma_{RX} \quad (5)$$

Assume $\lambda_m = \lambda_p$.

$$\delta_m / \delta_p = c \quad (6)$$

Now from Equation 2,

$$Q_{mX} = \rho \lambda_m \sigma_{1x} + \rho \delta_m \sigma_{RX} + h \quad (7)$$

$$Q_{pX} = \rho \lambda_p \sigma_{1x} + \rho \delta_p \sigma_{RX} + h \quad (8)$$

Then

$$\frac{Q_{PX} - h - \rho \delta_P \sigma_{RX}}{Q_{MX} - h - \rho \delta_M \sigma_{PX}} = \frac{\rho \lambda_P \sigma_{1X}}{\rho \lambda_M \sigma_{1X}} = \rho \frac{\lambda_P}{\lambda_M} \sigma_{1X} \quad (9)$$

or

$$Q_{PX} - Q_{MX} = \rho(\delta_P - \delta_M) \sigma_{RX} \quad (10)$$

Thus,

$$\sigma_{RX} = \frac{Q_{PX} - Q_{MX}}{\rho(\delta_P - \delta_M)} \quad (11)$$

From 5,

$$\sigma_{PX} = \lambda_P \sigma_{1X} + \delta_P \left(\frac{Q_{PX} - Q_{MX}}{\rho(\delta_P - \delta_M)} \right) \quad (12)$$

From 6,

$$\sigma_{PX} = \lambda_P \sigma_{1X} + \left(\frac{Q_{PX} - Q_{MX}}{\rho(c-1)} \right) \quad (13)$$

and

$$\sigma_{1X} = \frac{1}{\lambda_P} \left[\sigma_{PX} - \left(\frac{Q_{PX} - Q_{MX}}{\rho(c-1)} \right) \right] \quad (14)$$

Theoretical review

An equation analogous to Equation 3 was proposed by Yukawa and Tsuno(4) It may be written as

$$\log k_x = \rho[\sigma_x + \gamma(\sigma_x^+ - \sigma_x)] + \log k_H \quad (15)$$

From Equation 1,

$$\log k_x = \rho \lambda_{1X} + \rho \delta_{RX} + \rho_r (\lambda \sigma_{1X} + \delta^+ \sigma_{RX} - \lambda \sigma_{1X} - \delta \sigma_{RX}) + \log k_H \quad (16)$$

$$= \rho \lambda_{1X} + \rho \delta_{RX} + \rho_r (\delta^+ - \delta) \sigma_{RX} + \log k_H \quad (17)$$

$$= \alpha \sigma_{1X} + \beta \sigma_{RX} + \log k_H \quad (18)$$

equivalent to 3 with

$$\beta = \rho \delta + \rho \gamma (\delta^+ - \delta) \quad (19)$$

Equation 15, which unlike Equation 3 can be included both meta- and para- substituted compou-

nds in the same data set, is intended for use with the same type of reaction that Brown and his coworkers devised the σ^+ constants for. It is intended for the fact that sets will vary in their resonance component, and therefore correlations with simple substituent constants such as σ_p and σ_p^+ will show deviations. An equation analogous to that of Yukawa and Tsuno but intended for use with reactions of the type to which the σ_p^- constants are applied has also been devised(5). It is

$$\log k_x = \rho[\sigma_x + \gamma(\sigma_x^- - \sigma_x)] + \log k_H \quad (20)$$

There has been considerable interest in obtaining a separation of localized and delocalized electrical effects that will not depend on Taft's assumption that λ_m and λ_p are equal. An attempt to evaluate the ratio λ_m/λ_p was made by Exner (1), who plotted $\log K_{PX} - \log K_H$ vs. $\log K_{MX} - \log K_H$ for the substituted benzoic acids. Only substituted groups that are presumed to have little or no resonance effects were included. Exner found that in two solvent systems

$$\log K_{PX} - \log K_H = 1.14 (\log K_{MX} - \log K_H) \quad (21)$$

From the Hammett equation $\log \frac{K_x}{K_H} = \rho \sigma_x$

$$\rho \sigma_{PX} = 1.14 \quad (22)$$

$$\sigma_{PX} = 1.14 \sigma_{MX} \quad (23)$$

From Equation 4 and 5, and the assumption that $\sigma_R = 0.00$,

$$\lambda_P \sigma_{1X} = 1.14 \lambda_M \sigma_{1X} \quad (24)$$

or

$$\lambda_m/\lambda_p = 0.878 \quad (25)$$

There is a flaw in Exner's approach however.

If $\sigma_R \neq 0.00$,

to substituent effects than are the 4-substituted bicyclo (2.2.2) octane-1-carboxylic acids and therefore give more accurate values of σ_1 for weak substituted. Second, Substituted acetic acids are generally water soluble, permitting accurate determination of the ionization constant by potentiometric titration or conductivity. And third, substituted acetic acids are easy to synthesize and purify.

Values of σ_1 have also been defined from the F^{19} chemical shifts of m-substituted fluorobenzenes(16).

The various σ_R constants may now be defined as

$$\begin{aligned} \sigma_R &= \sigma_p - \sigma_1, \sigma_R^{\circ} = \sigma_p^{\circ} - \sigma_1, \sigma_R = \\ &\sigma_p^+ - \sigma_1, \sigma_R = \sigma_p - \sigma_1 \end{aligned} \quad (32)$$

There is some argument over whether one σ_R scale is sufficient for all types of reactions or whether a number of σ_R scales are necessary for good correlation. Swain and Lupton argue that only one resonance parameter can accommodate all observed variations, and this approach has been adopted by others. Taft's group(17) and Exner(18) recently suggested that, in fact, the best correlations require use of more than one resonance parameter.

A method based on the calculation of substituent constants for any system under consideration from localized and delocalized effects is due to Dewar and Grisdale(19). According to this treatment, F and M are factors representing localized and delocalized effects, respectively. Substituent constants are then defined by.

$$\sigma_{x, DG} = \frac{F_x}{\gamma_{ij}} + Mq_{ij} \quad (33)$$

The quantity γ_{ij} represents the distance between the atom i of the skeletal group G to which the reaction site X is attached and the atom j of G to which the reaction site Y is attached, expressed in

units of the benzene bond length. The quantity b_{ij} is the charge on the atom bearing Y in the carbanion : CH_2GY . The charge q is calculated by the method of Longuet-Higgins(20). The F and M values can be calculated from the σ_m and σ_p constants, as

$$\sigma_{m, X} = \frac{F_x}{1.73}, \quad \sigma_{p, X} = \frac{F_x}{2} + \frac{M_x}{7} \quad (34)$$

With E_x and M_x known, values of $\sigma_{x, DG}$ may be calculated for any system. It must be noted that when the Dewar treatment is applied to XGY the substituent constants for the effects of both X and G, and therefore for a given Y, ρ should be constant. Correlations with the simple Hammett equation and the $\sigma_{x, DG}$ constants do not give a constant value of ρ , however(21). It should also be noted, that the Taft and Dewar treatments are mutually exclusive. If the Taft treatment is correct, then, the Dewar F values include a resonance effects. In a more recent paper, Dewar et al.(22) modified the above method. These authors propose that substituent constants be given by the equation.

$$\sigma_{i, m, X} = \frac{F_x}{K_{i, m}} + M_x q_{i, m} + M_{F, X} \sum_{k \neq m} \frac{q_{i, k}}{k_{r, n}} \quad (35)$$

The quantity F and M represent the field and mesomeric effects as before, while the quantity M_F represents the mesomeric field effect, which is an additional resonance effect. $R_{i, m}$ is given by.

$$R_{i, m} = \frac{1}{\gamma_{i, m}} - \frac{0.9}{\gamma_{j, n}} \quad (36)$$

where γ values are expressed, as before, in units of the benzene bond length. The F_x parameters are now evaluated from the ionization constants of 4-substituted bicyclo (2.2.2) octane-1-carboxylic acids. The M_x and $M_{F, X}$ parameters are there evaluated from the σ_m and σ_p constants.

A correlation of the $\sigma_{i, m, X}$ constants calculated

$$\lambda_P \sigma_{1X} + \delta_P \sigma_{RX} = 1.14 \lambda_m \sigma_{1X} + 1.14 \delta_m \sigma_{RX} \quad (26)$$

$$(\lambda_P - 1.14 \lambda_m) \sigma_{1X} = (1.14 \delta_m - \delta_P) \sigma_{RX} \quad (27)$$

$$\sigma_{1X} = \frac{(1.14 \delta_m - \delta_P)}{(\lambda_P - 1.14 \lambda_m)} \sigma_{RX} \quad (28)$$

$$= c \sigma_{RX} \quad (29)$$

A plot of σ_1 against σ_R suggest that Equation 29 is obeyed for many substituents.

Another alternative separation of electrical effects is that suggested by Swain and Lupton (7). As a measure of the localized effect $\log (K_X/K_H)$ for the ionization of 4-substituted bicyclo(2.2.2) octane-1-carboxylic acid in 50% aqueous ethanol at 25° were chosen, from these quantities, F value were defined. Resonance parameters designated R were defined from the equation

$$\sigma_P = \alpha F + R \quad (30)$$

The value of α was determined to be 0.56 by setting $R=0$ for Me_3N^+ . The basis for this assumption is the fact that the ultraviolet spectrum of the trimethylanilium ion resemble that of benzene. It is argued that as uv spectra depend on resonance effects this similarity in the spectra suggests that the resonance effects of NMe_3^+ must be similar to that of H, for which the resonance effect is zero.

Results and Discussion

There are two major objections to the Swain-Lupton approach. They are ;

(1) The separation proposed by Swain and Lupton depends on the σ_m and σ_P values of the trimethylammonium group. McDaniel and brown (10) reported probable errors of ± 0.2 for these substituent constants. A separation based on such doubtful values is certainly suspected.

The Swain-Lupton treatment is based on the assumption that the trimethylammonium group has a resonance parameter value of zero and exhibits absolutely no resonance effect. Trimethylammonium

is isoelectronic with tertiary butyl, and there is general agreement that the latter is a resonance donor. It seems likely, then, that the trimethylammonium group should also be considered a donor by resonance, and Charton has summarized evidence for his position (11). More recently Cutress and coworkers(12) discuss the existence of a donor resonance effect of the trimethylammonium and ammonium groups based on infrared evidence. It thus seems reasonable to reject the Swain-Lupton separation of the electrical effect. At present, in the absence of a better approach, Taft's method described previously seems to be the most useful technique for factoring overall substituent effects.

Taft and Lewis (13) defined the σ_1 constants to agree with the constants of Roberts and Moreland. The defining equation is

$$\sigma_{1X} = 0.45 \sigma_{XC_2H_5} \quad (31)$$

The σ_1 constants proposed by Taft when correlated with the ionization constants of substituted acetic acids, which are known to four or five significant figures, give excellent correlations(14). Charton has therefore proposed that for most substituents σ_1 may be conveniently defined from the ionization of substituted acetic acids.

This has the advantage that the ionization constants for many substituted acetic acids have already been accurately reported.

There are two disadvantages to this method of defining σ_1 : (1) Ionization constants of strong acids are difficult to measure with accuracy thus, the value of σ_1 reported by Charton for the nitro group seems high by 0.07 σ unit. In such cases better values are obtainable from the 4-substituted bicyclo(2.2.2) octane-1-carboxylic acids. (2) Large substituents such as bulky aryl groups have been reported to give rise to steric effects(15).

There are fundamental advantages to using substituted acetic acid ionization constants for defining σ_1 . First, substituted acetic acids are more sensitive

<국문초록>

自由에너지 直線關係式에서의 場效果 誘發效果 및 共鳴效果의 分離

電子效果의 세가지 類型, 즉 場效果, 誘發效果 및 共鳴效果를 特定한 自由에너지 直線關係式에 의거 그 相互作用을 比較檢討하였다.

理論的 分析의 結果는, 置換体常數 σ_R 및 σ_1 를 變型 Hammett 方程式 $Q_x = \alpha\sigma_{1x} + \beta\sigma_{Rx} + h$ 에 適用하여 使用할 경우가 가장 좋은 直線關係式의 相關關係를 나타내었다.

with σ_x constants defined from the ionization of the appropriate carboxylic acids gives, excluding data for which steric factors may be important,

$$\sigma_x = 0.892\sigma_{i.m.x} + 0.0087 \quad (37)$$

Thus the Dewar method still, I think, does not

give complete agreement.

Conclusively, of all the separations of electrical effect described so far, I feel that Taft's is best. The most general and useful approach to the correlation of data for any kind of group G is the use of the extended Hammett equation with the σ_R and σ_I constants.

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