"Makeup of Substituent Constants and Reaction Parameters in Linear Free energy Relationship"

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"自由에너지 直線關係式에서의 置換常体數와 反應파라미터의 組合"

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Summary

In this paper the simple and the extended Hammett eguations of linear free energy relationships were traced, their uses were examined for correlating rates and eguilibria and then theoretical advances were revivewed by making up of substituent constants and reaction parameters.

To consider the factors upon which the reaction parameters (ρ, α, β) depend, structural features of the reaction ; that are, the effects of G, Y constant substituents are remarked.

α as a function of G was also calculated by means of a relationship derived from the Kirkwood-Westheimer eguation.

The linear fits of α in the from of the equation derived by the make up of Hammett equation and Kirkwood-Westheimer equation were also examined.

The agreement between calculated and observed value of α is generally very good. Calculation of α for the alkaline hydrolysis of esters gives some what poorer results.

Introduction

Hammett(1) formulated his general relatioship for correlating rates and   equilibrium constans of meta-and para substituted benzene derivates with the ionization constants of the corresponding substituted benzoic acids. This equation was written as

$$\log\frac{K_x}{K_H} = \rho\sigma_x \qquad (1)$$

where K_x and K_H are the rate or equilibrium constants for the substituted and unsubstituted benzene derivates, respectively, ρ is the reaction parameter and σ is the substituent parameter.

The reaction parameter, ρ , is specific for each reaction and reflects the effect of reaction condition such as medium, temperature, pressure , reaction site, reagent, and side chain if any. The substituent constant is supposed to be independent of reaction. In any set of molecules, I , in which X is varied while Y and Z are held constant, the reaction site Y is the group of atoms that is responsible for the phenomenon being studied, while Z represents a side chain that may or may not be present.

(I)

(Ⅲ)

(Ⅳ)
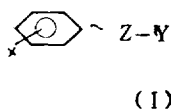
The data sets studied by Hammett consisted only of equilibrium and rate constants. Jaffe(2) surveyed the application of the Hammett equation. The equation he used conveniently written in the form

$$Q_x = \rho \sigma_x + h \qquad (2)$$

where Q_x is the quantity to be correlated, and h is an intercept equal to Q calculated for the unsubstituted compound(thecompound for which X is H)

At this point, consider the problem of multiple substitution and a molecule with nonequivalent substituents such as Ⅱ.

Then, according to Jaffe

$$Q_{x^n} = \rho_1 \sigma_{x1} + \rho_2 \sigma_{x2} + \cdots\cdots + \rho_n \sigma_{x^n} + h \qquad (3)$$
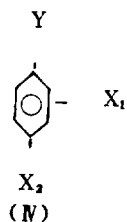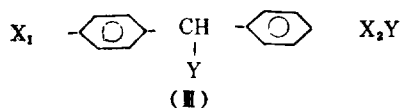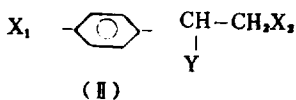
For the extended Hammett equation, the equivalent relationship is

$$Q_{x^n} = \alpha_1 \sigma_{1x1} + \beta_1 \sigma_{Rx1} + \alpha_2 \sigma_{1x2} + \beta_2 \sigma_{x2} + \cdots$$
$$\cdots \alpha_n \sigma_{1x}{}^n + \beta_n \sigma_{x^n} + h \qquad (4)$$

when a molecules has two equivalent substituents, such as Ⅲ

$$\rho_1 = \rho_2 \text{ and } Q_{x1x2} = \rho \sum \sigma_x \qquad (5)$$

or $Q_{x1x2} = \alpha \sum \sigma_{1x} + \beta \sum \sigma_{Rx} \qquad (6)$

(Ⅱ)

Where X_1 and X_2 are in the m and p positions of the benzene ring, as in Ⅲ, if the m and p substituent constant are used, is of course the same and equation 5 applies.

Miller(3) proposed for two nonequivalent substituents the equation

$$Q_{x1x2} = \rho_1 \sigma_{x1} + \rho_2 \sigma_{x2} + \rho_{12} \sigma_{x1} \sigma_{x2} + h \qquad (7)$$

$$Q_{x1x2} = \alpha_1 \sigma_{1x1} + \beta_1 \sigma_{Rx1} + \alpha_2 \sigma_{1x2} + \beta_2 \sigma_{Rx2} +$$
$$\beta_{12} \sigma_{Rx1} \sigma_{Rx2} + \chi_{12} \sigma_{1x1} \sigma_{Rx2} + \chi_{21} \sigma_{1x2} \sigma_{Rx1} + h \qquad (8)$$

Reaciont parameter as a function of reagent and solvent

To desribe the variation of the reaction parameter with change in reagent, consider a linear free energy relationship that describes reagent reactivity,

$$Q_{Rg} = m \xi_{Rg} + h \qquad (9)$$

in which ξRg is a parameter characteristic of the reactivity of the reagent Rg. For some data set for which the substituent is varied and the reagent is constant,

$$Q_{x1Rg} = \sigma_{Rg} \sigma_x + h_{Rg} \qquad (10)$$

From Equation 9

$$h_{Rr} = m\xi_{Rr} + h \qquad (11)$$

Then,

$$Q_{X_1Rr} = \rho_{Rr}\sigma_x + m\xi_{Rr} + h \qquad (12)$$

Applying the Miller equation to a data set varing in both substituent and reagent gives

$$Q_{X_1Rr} = \rho\sigma_x + m\xi_{Rr} + \chi\sigma_x\xi_{Rr} + h \qquad (13)$$

Setting the right side of Equation 12 equal to the right side of Equation 13,

$$\rho_{Rr} = \chi\xi_{Rr} + \rho \qquad (14)$$

Thus, the reaction parameter is a linear function of the reagent parameter.

By means of an analalogous derivation, it can be shown that the reaction parameter as a function of solvent variation may be presented as

$$\rho_{sv} = \chi\pi_{sv} + \rho \qquad (15)$$

where π_{sv} is the solvent parameter.

Reaction parameter as a function of constant substituent.

To treat the problem of the effect of a constant substituent's effect on the reaction parameter, consider a set in which both a variable substituent X_1 and a constant substituent X_2 are present. It can be correlated by the equation.

$$Q_{X_1X_2} = \rho_{X_2}\sigma_{X_1} + h_{X_2} \qquad (16)$$

The term h_{X_2} must represent the calculated value of $Q_{X_1X_2}$ for which $X_1 = H$. Then

$$h_{X_2} = \rho_2\sigma_{X_2} + h \qquad (17)$$

Combining Equation 16 and 17 gives

$$Q_{X_1X_2} = \rho_{X_2}\sigma_x + \rho_2\sigma_{X_2} + h \qquad (18)$$

However, $Q_{X_1X_2}$ is also given by the Miller equation(Equation 17).

Setting the right side of Equation 7 equal to the right side of Equation 18 gives

$$\rho_{X_2}\sigma_{X_1} + \rho_2\sigma_{X_2} + h = \rho_1\sigma_{X_1} + \rho_2\sigma_{X_2} + \rho_{12}\sigma_{X_1}\sigma_{X_2} + h \qquad (19)$$

which simplifies to

$$\rho_{X_2} = \rho_{12}\sigma_{X_2} + \rho_1 \qquad (20)$$

Thus, the reaction parameter is a linear function of the substituent constant for the constant substituent. Equations analogous to Equation 20 can be derived for the effect of constant substituents on α and β of the extended Hammett equation. These relationships are

$$\alpha_{X_2} = \alpha_{12}\sigma_{1X_2} + \chi_{12}\sigma_{RX_2} + \alpha_1 \qquad (21)$$

$$\beta_{X_2} = \chi_{21}\sigma_{1X_2} + \beta_{12}\sigma_{RX_2} + \beta_1 \qquad (22)$$

Estimation of substituent constants

Consider some skeletal group G that may be divided into subgroups G_1 and G_2 (4). The data set XG_2G_1Y may be correlated with the Hammett equation in either of two ways. In the first case, the substituent constant represents the effect of X, and the reaction constant accounts for G_2G_1Y.

Then,

$$Q_x = \rho_{G2G1}\sigma_x + h_{G2G1} \tag{23}$$

In this case the unsubstituent compound is HG_2G_1Y. In the second case the substituent constant represents XG_2. the reaction constant accounts for G_1Y, and.

$$Q_{XG2} = \rho_{G1}\sigma^x{}_{G2} + h_{G1} \tag{24}$$

Then. the unsubstituted compound is HG_1Y.
As the same data set is involved in both equations. oviously

$$Q_x \equiv Q_{XG2} \tag{25}$$

Setting Equation 23 equal to Equation 24. and rearranging gives

$$\sigma_{G2X} = \frac{\rho_{G2G1}}{\rho_{G1}}\sigma_x + \frac{h_{G2G1} - h_{G1}}{\rho_{G1}} \tag{26}$$

Which is equivalent to

$$\sigma_{G2X} = m\sigma_x + C \tag{27}$$

Reaction Parameter ; A function of G

For rigid systems, α as a function of G can be calculated by means of a relationship derived kirkwood-westheimer equation (5) ;

$$\log\left(\frac{K_x}{K_H}\right)_G = \frac{e \cdot \mu_x \cdot \cos\theta_G}{2.303RT \cdot D_{EG} \cdot r_G{}^2} \tag{28}$$

Where e is the charge on an electron, μ_x is the bond moment of the X-G bond, R is the gas constant, T is the absolute temperature, D_E the effective dielectric constant, r is the distance from the midpoint of the XG bond to the reacting atom, and θ is the angle made by r with the XG bond (Figure 1) .
According to the simple Hammett equation

$$\log\left(\frac{K_x}{K_H}\right)_G = \rho_G\sigma_x \tag{1}$$

Then equating Equations 5 and 28

$$\rho_G\sigma_x = \frac{e \cdot \mu_x \cdot \cos\theta_G}{2.303\ RT \cdot D_{EG} \cdot r_G{}^2} \tag{29}$$

For some reference group $G°$ the analogous equation may be written

$$\rho_G{}^0\sigma_x = \frac{e \cdot \mu_x \cdot \cos\theta_G{}^0}{2.303\ RT \cdot D_{EG} \cdot r_G{}^{02}} \tag{30}$$

Dividing Equation 29 by 30 gives

$$\frac{\rho_G}{\rho_G{}^0} = \frac{\cos\theta_G r^2{}_G{}^0 D_{EG}{}^0}{\cos\theta_G{}^0 r^2{}_G\ D_{EG}} \tag{31}$$

Assuming

$$D_{EG} = D_{EG}{}^0 \tag{32}$$

gives

$$\frac{\rho_G}{\rho_G{}^0} = \frac{\cos\theta_G\ \gamma^2{}_G{}^0}{\gamma^2{}_G\ \cos\theta_G{}^0} \tag{33}$$

as $\quad \alpha = \rho\lambda$

$$\alpha_G = \frac{\cos\theta_G}{\gamma^2{}_G} \cdot \frac{\gamma^2{}_G{}^0}{\cos\theta_G{}^0} \cdot \alpha_G{}^0$$
$$= \frac{\cos\theta_G}{\gamma^2{}_G}\phi \tag{34}$$
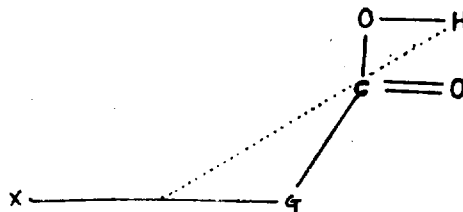
Figure 1. Definition of γ and θ.
The carboxylic acids are used as an example.

Table 1. Results of calculation of α for carboxylic acids.

C	Comment	α-calcd.	α obs.	Δ	%error
$-C\equiv C-$	H_2O	1.78	1.86	$-.08$	4.30
$T-CH=CH-$	S-Trans, H_2O	2.36	2.26	$+.10$	4.42
$T-CH=CH-$	S-cis, Substituent XC_6H_4, H_2O	1.70	1.64	$+.06$	3.66
⬡-⬡	50% Butylcellosolve-H_2O	0.482	0.529	-0.47	9.75
	H_2O, S-trans	1.19	1.40	$-.21$	14.8
	80% methylcellosolve- H_2O, S-trans	2.01	1.90	$+.11$	5.91
	H_2O, S-trans	1.09	1.08	$-.01$	0.92

Results and Disscusion

Value of α calculated and observed for some carboxylic acids are given in Table 1 (6). The group G° chosen was the p-phenylene group.

Value of θ and r were calculated from the molecular geometry of the carboxylic acids or of analogous compounds (7).

The agreement between calculated and observed values of α is generally very good.

Calculation of α for the alkaline hydrolysis of esters gives some what poorer results. It is likely that this is due to uncertainities in the values of α observed.

The use of Equation 34 with the p-phenylene group as the reference group fails when G is phCH₂, phCH₂−CH₂, or CH₂=C<

It seems likely that for these groups, the assumption of Equation 37 is unjusted. Another assumption must be thought.

The equation $\sigma_{G_2X} = {}_m\sigma_X + C$ has been succesfully applied to the calculation of σ_m and σ_p constants with G_2 equal to carbonyl, oxa, thia, and o, −m, −and p-phenylene groups (8). It will make possible the estimation of substituent constants for groups for which direct experimental determination is difficult.

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〈국 문 초 록〉

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韓　　性　　彬

變型 Hammett 方程式의 反應 파라미터를 나타내는 因子 α 및 置換体常數 G의 關係를 調査하고 Kirkwood-Weistheimer 方程式과 Hammett 方程式을 組合하여 誘導한 方程式에 의한 G函數로서의 α直를 算出하였다. α의 計算直와 觀測直를 比較檢討한 結果 에스테르의 알칼리 加水分解 反應에 對한 α의 計算直를 除外하고는 一般的으로 兩者는 잘 一致되었음이 確認되었다.