Substituent Effects. II.[1] Calculation of Mesomeric Para Interaction Energies and Comments on the Relation between Equations Obtained by Hine and by Yukawa and Tsuno

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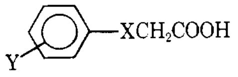
Abstract: It is shown that the Yukawa–Tsuno equations are implicit in Hine's more general extended Hammett equations. A new expression for the calculation of mesomeric para interaction energies is proposed, and some applications are indicated. The behavior of the systems $ArXCH_2COOH$ is described by a special form of this expression.

In forthcoming papers[2] the dissociation constants of the carboxylic acid group in series of compounds of type I with, *inter alia*, X = NH, O, and CH_2, will be



I

discussed. In these reaction series para substituents with a −M effect (*e.g.*, NO_2, CN) do not follow the Hammett equation[3]

$$\log K - \log K^0 = \rho\sigma^{\mathrm{n}} \qquad (1)$$

and the exaltations of σ_{p} are dependent on the nature of both Y and X. Specifically, it has been found that the deviations from eq 1 expressed as[4]

$$-\Delta\Delta G_{\mathrm{p}} = 2.3RT\rho(\sigma - \sigma^{\mathrm{n}}) \qquad (2)$$

are proportional to (a) the $\Delta\sigma_{\mathrm{R}}^-$ values of Y (when X is constant), and (b) the $\Delta\sigma_{\mathrm{R}}^+$ values of X–CH_3 (when Y is constant). Combination of these proportionalities yields the more general equation

$$-\Delta\Delta G_{\mathrm{p}} = (\text{constant})\Delta\sigma_{\mathrm{R}}^-(\mathrm{Y})\Delta\sigma_{\mathrm{R}}^+(\mathrm{XCH_3}) \qquad (3)$$

This equation can be regarded as a special case of equations derived by Hine[5-7] and prompts us to the following comments on these equations and their relation to those of Yukawa and Tsuno.[8,9]

For the equilibrium

II

Hine derived[5,7]

$$\log K/K^0 = \tau(\sigma_{\mathrm{X_1}} - \sigma_{\mathrm{X_2}})\sigma_{\mathrm{Y}} \qquad (4)$$

as an equivalent of the Hammett equation, identifying ρ as $\tau(\sigma_{\mathrm{X_1}} - \sigma_{\mathrm{X_2}})$ where τ is the dimensionless, solvent- and temperature-dependent transmission factor for the "polar interaction" between Y and X. For equilibria and reactions of para-substituted compounds in which mesomeric para interaction (through-resonance) occurs, the extra interactions were accommodated by addition of a term of the same form, leading to[6]

$$\log K/K^0 = \tau_{\mathrm{p}}[(\sigma_{\mathrm{X_1}} - \sigma_{\mathrm{X_2}})\sigma_{\mathrm{Y}} + (\sigma_{\mathrm{X_1}}{}^{\mathrm{R}} - \sigma_{\mathrm{X_2}}{}^{\mathrm{R}})\sigma_{\mathrm{Y}}{}^{\mathrm{R}}] \qquad (5)$$

where the σ^{R} factors represent "resonance substituent constants"[10] of the respective groups. In a trial and error procedure to obtain optimum fit it was found that eq 5 could account satisfactorily for the acid–base equilibria of the series ArCOOH, ArOH, and $ArNH_3^+$ in water at 25°, and the S_N1 reactivities in the series $ArCMe_2Cl$ in 90% acetone at 25°. The fitting procedure obviously also generated numerical values for τ, σ_{m}, σ_{p}, and σ^{R}.

Yukawa and Tsuno observed proportionality of the exaltations of σ_{p} in different reaction series and expressed this in equations of the form

$$\log K/K^0 = \rho\sigma^{\mathrm{n}} + \rho r^+\Delta\sigma_{\mathrm{R}}^+(\mathrm{Y}) \qquad (6)$$

and

$$\log K/K^0 = \rho\sigma^{\mathrm{n}} + \rho r^-\Delta\sigma_{\mathrm{R}}^-(\mathrm{Y}) \qquad (7)$$

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[1] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **78**, 815 (1959), is to be regarded as part I of this series.

[2] In preparation: A. J. Hoefnagel, J. C. Monshouwer, E. C. G. Snorn, and B. M. Wepster (part III); A. J. Hoefnagel and B. M. Wepster (part IV).

[3] In this paper we start out from the following definitions: ρ, reaction constant relative to $\rho \equiv 1$ for the dissociation constants of benzoic acids in water at 25° and calculated using only "primary" σ values[1] of meta substituents, giving ρ_{m}; σ^{n}, normal substituent constant,[1] representing the substituent parameter with the exclusion of possible through-resonance effects; σ, observed substituent parameter (σ_{p} for para substituents, σ_{m} for meta substituents); $\sigma - \sigma^{\mathrm{n}}$, exaltation of σ; $\Delta\sigma_{\mathrm{R}}^- = \sigma^- - \sigma^{\mathrm{n}}$, exaltation of σ for −M substituents as observed with a standard reaction (see text); $\Delta\sigma_{\mathrm{R}}^+ = \sigma^+ - \sigma^{\mathrm{n}}$, exaltation of σ for +M substituents as observed with a standard reaction (see text); $-\Delta\Delta G_{\mathrm{p}}$, deviation from the Hammett equation, taken to be due to the mesomeric para interaction (through-resonance) and expressed in terms of free energy differences between reactant and product (or transition state).

We retain[1] the notation σ^{n} (rather than changing to Taft's σ^0—see ref 4), since (a) σ^{n} has the older rights, being semantically suggested by H. H. Jaffé, *Chem. Rev.*, **53**, 230 (1953), when referring to "normal substituent constants" and their possible derivation from insulated systems; (b) the superscript n is less confusing, not being burdened by connotations indicating ortho, unsubstituted, or standard state; (c) it is used by others (*e.g.*, J. Hine, ref 7, and L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, pp 358, 362). Other symbols used will be introduced in the text.

[4] Reference 1, p 834, eq 3; p 841, eq 4; *cf.* also R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 577, eq 11; R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Amer. Chem. Soc.*, **81**, 5352, 5358 (1959).

[5] J. Hine, *ibid.*, **81**, 1126 (1959).

[6] J. Hine, *ibid.*, **82**, 4877 (1960).

[7] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, pp 81, 381, 382.

[8] Y. Tsuno, T. Ibata, and Y. Yukawa, *Bull. Chem. Soc. Jap.*, **32**, 960 (1959); Y. Yukawa and Y. Tsuno, *ibid.*, **32**, 965, 971 (1959); Y. Yukawa, Y. Tsuno, and M. Sawada, *ibid.*, **39**, 2274 (1966).

[9] Y. Yukawa, *Yuki Gosei Kagaku Kyokai Shi*, special ed, 69 (1962); M. Yoshioka, K. Hamamoto, and T. Kubota, *Bull. Chem. Soc. Jap.*, **35**, 1723 (1962).

[10] Hine's σ^{R} and Taft's σ_{R} differ not only in notation, but also in definition.

In eq 6,[8] applying if Y is a +M substituent (*e.g.*, OCH_3), $\Delta\sigma_R^+ \equiv \sigma^+ - \sigma^n$, where σ^+ is the observed σ_p value in the SN1 reaction of $ArCMe_2Cl$ in 90% acetone at 25°; this implies the definition of the proportionality factor $r^+ \equiv 1$ for this series. In eq 7,[9] applying if Y is a −M substituent, $\Delta\sigma_R^- \equiv \sigma^- - \sigma^n$, where σ^- is the observed σ_p value in the acid–base equilibrium of $ArNH_3^+$ in water at 25°, implying $r^- \equiv 1$ for this series.

Concentrating on the through-resonance terms, Hine's approach (eq 5) yields[11]

$$-\Delta\Delta G_p = 2.3RT\tau_p(\sigma_{X_1}{}^R - \sigma_{X_2}{}^R)\sigma_Y{}^R \tag{8}$$

and that of Yukawa and Tsuno (eq 6 and 7 combined)

$$-\Delta\Delta G_p = 2.3RT\rho r^\pm\Delta\sigma_R{}^\pm(Y) \tag{9}$$

These expressions are equivalent. Equation 8 reduces to the form of eq 9 for a specific reaction series since, then, $(\sigma_{X_1}{}^R - \sigma_{X_2}{}^R)$ is constant. Conversely it can be shown, *e.g.*, by algebraic manipulation[12] of the type used by Hine in deriving eq 4 and 5, that if both Yukawa–Tsuno proportionalities hold (eq 6 and 7) an equation of the form of eq 8 also holds. Accordingly, Hine's σ_m and σ_p are close to primary σ values[1] and σ^n values,[1] and $\Delta\sigma_R^+$ is about proportional to σ^R of +M substituents, $\Delta\sigma_R^-$ to σ^R of −M substituents. The numerical inequality of the resonance parameters σ^R and $\Delta\sigma_R$, as well as the difference in the two proportionality factors involved, can be traced back to differences in the scaling procedures. It should be realized that the above agreement adds little or nothing to the credibility of eq 5, 6, and 7 since the reactions chosen by Hine to test his relation are the standard reactions in the Yukawa–Tsuno approach and a very closely related one.

It is proposed here to express Hine's eq 8 as

$$-\Delta\Delta G_p = 2.3RT\omega_p\Delta\sigma_R{}^\pm(Y)\Delta\Delta\sigma_R{}^\mp(X_1,X_2) \tag{10}$$

where $\Delta\Delta\sigma_R{}^\mp(X_1,X_2)$ is $[\Delta\sigma_R^-(X_1) - \Delta\sigma_R^-(X_2)]$ or $[\Delta\sigma_R^+(X_1) - \Delta\sigma_R^+(X_2)]$ as applicable in combination with $\Delta\sigma_R^+(Y)$ or $\Delta\sigma_R^-(Y)$, respectively. The replacement of σ^R by $\Delta\sigma_R^\pm$, although providing a more cumbersome notation, would seem sensible since the latter are well defined and frequently used. The replacement of τ_p by ω_p is intended to avoid numerical confusion; the subscript p is retained in anticipation of a treatment of mesomeric ortho interactions for which a similar relation might hold, though with a (somewhat) different numerical value for ω (ω_0).

The numerical value of ω_p can be assessed from equilibria or reactions for which $\Delta\Delta G_p$ and the $\Delta\sigma_R$ values are known. Refraining from any statistics for the present, an obvious single choice is the acid–base equilibrium of 4-nitroanilinium ion at 25°, for which $-\Delta\Delta G_p = 1.8$ kcal/mol from eq 2;[13] this value is corroborated by independent data on derivatives in which the through-resonance is sterically inhibited.[14] Taking[2] $\Delta\sigma_R^-(NO_2) = 0.45$, $\Delta\sigma_R^+(NH_2) = -1.23$, and $\Delta\sigma_R^+(NH_3^+) = 0$, $\omega_p = 2.4$ follows.[15]

The eq 8 and 10 are more satisfactory than eq 9 since they present the free energy term as a function of parameters measuring both mesomeric electron attraction and mesomeric electron donation instead of only one of them. In this connection it may be noted that the r value of Yukawa and Tsuno is identified from

$$\rho r^\pm = \omega_p\Delta\Delta\sigma_R{}^\mp = 2.4\Delta\Delta\sigma_R{}^\mp \tag{11}$$

Some applications of eq 10 allow more complete restatements of previous results. Thus, using eq 2 it was calculated[1] that for the acid–base equilibrium of 4-nitrophenol $-\Delta\Delta G_p = 1.5$ kcal/mol, somewhat lower than that for 4-nitroanilinium ion, 1.8 kcal/mol, mentioned above. In terms of eq 10 this means that $\Delta\sigma_R^+(OH) - \Delta\sigma_R^+(O^-)$ is somewhat smaller than $\Delta\sigma_R^+(NH_3^+) - \Delta\sigma_R^+(NH_2)$, in the proportion 1.5:1.8. Taking[2] $\Delta\sigma_R^+(OH) = -0.79$, this implies $\Delta\sigma_R^+(O^-) = -1.8$. In addition, the individual through-resonance terms can now be calculated from

$$-\Delta G_p = 2.4\Delta\sigma_R{}^\pm\Delta\sigma_R{}^\mp 2.3RT \tag{12}$$

giving 1.2 kcal/mol in 4-nitrophenol and 2.7 kcal/mol in 4-nitrophenolate anion. Such data and similar ones involving transition states[5] are of obvious importance, for instance, for mechanistic studies, comparisons with quantum-mechanical calculations,[16] or in judging (changes in) rotational barriers.[17]

The eq 10 and 12 do not contain terms representing solvent effects. These are probably not very large, but discussion is beyond the scope of this paper. Again, temperature effects are not always covered by the $2.3RT$ term,[18] and it is, therefore, well to remember that the $\Delta\sigma_R$ values and ω_p have been derived from experimental data in water and more or less comparable solvents, and at room temperature. Although incorporation of these factors will have to await future experimental and theoretical work, this does not detract from the fact that eq 10 and 12, when handled with care, should be of fairly wide applicability and should provide good service in many problems.

On the basis of the present considerations, the extended Hammett equation covering through-resonance can now be written in order of decreasing sophistication as in eq 13–16

$$\log K/K^0 = \tau[\sigma^n(X_1) - \sigma^n(X_2)]\sigma^n(Y) + 2.4\Delta\sigma_R{}^\pm(Y)\Delta\Delta\sigma_R{}^\mp(X_1,X_2) \tag{13}$$

$$\log K/K^0 = \rho\sigma^n(Y) + 2.4\Delta\sigma_R{}^\pm(Y)\Delta\Delta\sigma_R{}^\mp(X_1,X_2) \tag{14}$$

$$\log K/K^0 = \rho\sigma^n(Y) + \rho r^\pm\Delta\sigma_R{}^\pm(Y) \tag{15}$$

$$\log K/K^0 = \rho\sigma^n(Y) + \rho[\sigma(Y) - \sigma^n(Y)] \tag{16}$$

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(11) The most general form, in which $\sigma_Y{}^R$ is replaced by $(\sigma_{Y_1}{}^R - \sigma_{Y_2}{}^R)$, can be left out of consideration here since we refer to hydrogen as the "other" substituent.

(12) See also S. I. Miller, *J. Amer. Chem. Soc.*, 81, 101 (1959).

(13) Data from P. D. Bolton and F. M. Hall, *Aust. J. Chem.*, 21, 939 (1968); *J. Chem. Soc. B*, 259 (1969); *cf.* 1247 (1970); also unpublished work from this laboratory; *cf.* ref 1 for other data.

(14) J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 77, 491, 509 (1958).

(15) The relation between τ_p and ω_p for this case should be $\tau_p\sigma_{NO_2}{}^R \cdot \sigma_{NH_2}{}^R = \omega_p\Delta\sigma_R^-(NO_2)\Delta\sigma_R^+(NH_2)$. The actual values are in satisfactory agreement: 3.50 × 0.56 × (−0.72) ≈ 2.4 × 0.45 × (−1.23), or 1.41 ≈ 1.33.

(16) For the correspondence of $\Delta\Delta G_p$ and $\Delta\Delta H_{int}$, see L. G. Hepler, *J. Amer. Chem. Soc.*, **85**, 3089 (1963); also P. D. Bolton and F. M. Hall, ref 13.

(17) *Cf.* F. A. L. Anet and M. Ahmad, *J. Amer. Chem. Soc.*, **86**, 119 (1964); F. A. L. Anet and D. Wong, unpublished work.

(18) In the ArOH series, in water at 10–55°, $\Delta\Delta G_p$ for the 4-nitro derivative does indeed increase linearly with T, and ρ is constant (*cf.* P. D. Bolton, F. M. Hall, and I. H. Reece, *J. Chem. Soc. B*, 709 (1967); G. F. Allen, R. A. Robinson, and V. E. Bower, *J. Phys. Chem.*, **66**, 171 (1962); L. G. Hepler, ref 16). In the $ArNH_3^+$ series, in water at 10–50°, $\Delta\Delta G_p$ for the 4-nitro derivative is independent of temperature, and ρ is proportional to $1/T$ (*cf.* Bolton, *et al.*, ref 13). The latter behavior is accounted for by eq 10′, $-\Delta\Delta G_p = \omega_p{}'\Delta\sigma_R{}^\pm(Y)\Delta\Delta\sigma_R{}^\mp(X_1,X_2)$, with $\omega_p{}' = 3.3$ kcal/mol.

Provided all substituent parameters are known, eq 13 does not need any experimental data for the calculation (prediction) of log K/K^0 and $\Delta\Delta G_p$; eq 14 requires only an experimental determination of ρ; eq 15 in addition relies on the experimental determination of (at least) one exalted σ value to evaluate r; eq 16 only separates "normal" and through-resonance effects, and provides $\Delta\Delta G_p$ values only as far as the exalted σ values are determined experimentally. Which of these equations is most profitable depends on the specific problem involved; the accuracy of the results obtained will, of course, increase from eq 13 to eq 16.

Returning, finally, to the systems I, these are rather exceptional in that the reaction center is the same in all series, in that this reaction center is mesomerically insulated from the aromatic ring, and in that no charged substituents are involved in the comparisons.[5,6] As to eq 3, holding for these systems, the above treatment would suggest that the term $\Delta\sigma_R^+(XCH_3)$ should be replaced by $[\Delta\sigma_R^+(XCH_2COOH) - \Delta\sigma_R^+(XCH_2COO^-)]$. The applicability of eq 3 then means that these two quantities are proportional, which would seem to be not unreasonable. Further details of the behavior of the systems I are discussed in a separate paper [2]

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Nucleophilic Substitution Reactions Involving Sulfenic Acids and Sulfenyl Derivatives. The Nucleophile- and Acid-Catalyzed Oxygen-18 Exchange of Phenyl Benzenethiolsulfinate[1a,2]

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Abstract: The acid- and nucleophile-catalyzed oxygen-18 exchange of phenyl benzenethiolsulfinate-^{18}O has been studied in 60% dioxane using *n*-butyl sulfide, bromide ion, and chloride ion as the nucleophilic catalysts. Comparison of the rates for the exchange with the rates for the acid- and nucleophile-catalyzed racemization of (+)-PhS(O)SPh under the same conditions shows that benzenesulfenic acid (PhSOH) is orders of magnitude more reactive than water as a nucleophile toward reactive sulfenyl derivatives such as PhSCl, PhSBr, or $PhSS^+R_2$. The rapidity with which PhSOH performs a nucleophilic substitution on such sulfenyl compounds explains why sulfenic acids are never isolated as hydrolysis products of sulfenyl halides and related compounds. The relatively high reactivity of sulfenic acids as nucleophiles in displacements at dicoordinate sulfur would appear to have other significant ramifications for a number of aspects of sulfur chemistry.

Sulfenic acids, RSOH, are thought to be important intermediates in a variety of organosulfur reactions,[3-6] but only in a few very special cases have they proved capable of actual isolation.[7,8] One typical example of their elusiveness is the following. Although sulfenic acids are almost certainly produced during the hydrolysis of arylsulfenyl chlorides, ArSCl, Vinkler and Klivenyi found[9] that the first isolable product of the hydrolysis of such sulfenyl halides was invariably not the sulfenic acid but the corresponding sulfenic anhydride (or thiolsulfinate), ArS(O)SAr. Clearly, because of their probable importance as intermediates in many organic sulfur reactions, it is desirable for us to learn as much as we can about the chemical behavior and reactivity of sulfenic acids, but clearly also, since one is seldom going to be able to isolate a sulfenic acid and study its chemistry directly, almost all of this information is going to have to be derived in an indirect manner.

Ever since the pioneering review by Foss[10] sulfur chemists have recognized that reactions involving nucleophilic substitution at sulfur play a central role in organic sulfur chemistry and, in particular, that much of the chemistry of sulfenyl derivatives can be understood in terms of reactions, or reaction sequences, involving nucleophilic displacements at dicoordinate sulfur, which can be represented in a generalized sense as shown in eq 1.

$$Nu^- + R\text{-}S\text{-}Y \longrightarrow R\text{-}S\text{-}Nu + Y^- \qquad (1)$$

The studies described in the present paper, which are

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