500 °C. Cyclohexylidene(trimethylsilyl)methane (90%) was obtained by bulb-to-bulb distillation [120–125 °C (75 mmHg)] and identified by comparison with the reported spectral data.[32]

Pyrolysis of Bis(trimethylsilyl)cyclopentylmethanol (15). Bis(trimethylsilyl)cyclopentylmethanol (0.720 g) was pyrolyzed at 500 °C. Separation of the product mixture by preparative gas chromatography gave allylsilane **16** (48%), *exo*-(trimethylsilyl)cyclopropane **17** (26%), and *endo*-(trimethylsilyl)cyclopropane **18** (9%). Allylsilane **16** was identified by its NMR, IR, and mass spectra: NMR (CCl_4) δ 0.07 (s, 9 H, $SiCH_3$), 1.33–2.00 (m, 4 H), 2.00–2.57 (m, 4 H), 5.37 (t, J = 2 Hz, 1 H, C=CH); IR (neat) 1615 (C=C), 1240 cm^{-1} (SiMe); mass spectrum, m/e 154 (M^+). The allylsilane **16** was desilylated by *p*-toluenesulfonic acid to give 1-methylcyclopentene. *exo*- and *endo*-(Trimethylsilyl)cyclopropanes **17** and **18** were identified by their NMR, IR, and mass spectra and elemental analyses.

exo-(Trimethylsilyl)cyclopropane **17**: NMR (CCl_4) δ –0.65 (t, J = 5 Hz, 1 H, SiCH), –0.10 (s, 9 H, $SiCH_3$), 0.85–1.92 (m, 8 H, aliphatic CH); IR (neat) 1240 cm^{-1} (SiMe); mass spectrum, m/e 154 (M^+). Anal. Calcd for $C_9H_{18}Si$: C, 70.04; H, 11.75. Found: C, 69.91; H, 11.68.

endo-(Trimethylsilyl)cyclopropane **18**: NMR (CCl_4) δ –0.60 (t, J = 9 Hz, SiCH), 0.07 (s, 9 H, $SiCH_3$), 1.13–1.90 (m, 8 H, aliphatic CH); IR (neat) 1245 cm^{-1} (SiMe); mass spectrum, m/e 154 (M^+). Anal. Calcd for $C_9H_{18}Si$: C, 70.04; H, 11.75. Found: C, 70.30; H, 11.91.

Pyrolysis of 1-(Trimethylsilyl)-1-phenylethanol (20). 1-(Trimethylsilyl)-1-phenylethanol (1.20 g) was pyrolyzed at 500 °C. To the pyrolysates was added 0.102 g of *p-tert*-butylphenol and distillation [95–105 °C (160 mmHg)] gave styrene (91%).

Pyrolysis of (Trimethylsilyl)(*o*-methoxyphenyl)methanol (21). A benzene solution of (trimethylsilyl)(*o*-methoxyphenyl)methanol (0.333 g) was pyrolyzed at 600 °C. Separation of the product mixture by preparative gas chromatography gave 2,3-dihydrobenzofuran (28%) and 2,3-benzofuran (16%). Products were identified by comparison with the reported spectral data.[28,33]

Pyrolysis of (Trimethylsilyl)[*p*-(trimethylsilyl)phenyl]methanol (24). A benzene solution of (trimethylsilyl)[*p*-(trimethylsilyl)phenyl]methanol (0.296 g) was pyrolyzed at 600 °C. Separation of the product mixture by preparative gas chromatography gave 1,1-dimethyl-1-silaindan (44%).[9,28]

Pyrolysis of (Trimethylsilyl)(*p-tert*-butylphenyl)methanol (25). A benzene solution of (trimethylsilyl)(*p-tert*-butylphenyl)methanol (0.729 g) was pyrolyzed at 600 °C. Separation of the product mixture by preparative gas chromatography gave 1,1-dimethylindan (22%). 1,1-Dimethylindan was identified by comparison of its NMR and IR spectra with those of authentic sample.[28]

Acknowledgment. We are indebted to the Ministry of Education for financial support of this work through a Grant for Scientific Research (No. 447019). We are pleased to acknowledge a gift of trimethylchlorosilane from the Shinetsu Chemical Co.

Registry No. 2, 31129-63-2; **3**, 107-46-0; **4**, 770-09-2; **5**, 100-42-5; **6**, 17158-48-4; **7**, 73727-41-0; **10**, 73727-43-2; **11**, 61289-37-0; **12**, 61157-30-0; **13**, 73727-42-1; **14**, 38329-94-1; **15**, 75311-59-0; **16**, 75311-60-3; **17**, 75311-61-4; **18**, 75311-62-5; **20**, 53173-00-5; **21**, 75311-63-6; **22**, 496-16-2; **23**, 271-89-6; **24**, 75311-64-7; **25**, 75311-65-8; **26**, 4912-92-9; **27**, 65609-68-9; **28**, 65609-67-8; *trans*-$Me(CH_2)_7CH{=}CHSiMe_3$, 71779-75-4; *cis*-$Me(CH_2)_7CH{=}CHSiMe_3$, 71779-78-7; *trans*-$Me(CH_2)_5CH{=}CHSiMe_3$, 57365-47-6; *cis*-$Me(CH_2)_5CH{=}CHSiMe_3$, 57365-48-7; *cis*-$PhCH_2CH{=}CHSiMe_3$, 73727-44-3; *trans*-$PhCH_2CH{=}CHSiMe_3$, 58541-15-4; α-bromo(*o*-methoxybenzyl)trimethylsilane, 75311-66-9; α-bromo(*p*-(trimethylsilyl)benzyl]trimethylsilane, 75311-67-0; α-bromo(*p-tert*-butylbenzyl)trimethylsilane, 75311-68-1.

---

(32) Martel, B.; Varache, M. *J. Organomet. Chem.* **1972**, *40*, C53.

(33) Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.; Milwaukee, WI, Vol. VIII p 80.

Separation of Polar and Resonance Substituent Effects. Comparison of Dual Substituent Parameter Equations

Paul R. Young* and Patrick E. McMahon

Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

Received June 26, 1980

Ionization constants for substituted pyridinium ions are analyzed by using the dual substituent parameter equation suggested by Yukawa and Tsuno [$\log k/k_0 = \rho\sigma^n + \rho^r(\sigma^+ - \sigma^n)$]. The results are compared with values obtained from analysis of the same data set by using the Taft equations ($\log k/k_0 = \rho_I\sigma_I + \rho_R\sigma_R$). Approximate free-energy changes due to direct conjugative resonance, estimated by the Yukawa method, are found to be directly proportional to the values estimated by using the Taft equations. A similar direct proportionality is observed for free-energy changes for direct conjugative resonance in the rate and equilibrium benzaldehyde cyanohydrin reactions. The Taft analysis predicts a late, product-like transition state for this reaction. This is consistent with the transition-state structure obtained from the Yukawa analysis and from secondary deuterium isotope effect studies. Assumptions inherent in the simple Yukawa treatment are discussed.

It is well recognized that the Hammett relationship, $\log k/k_0 = \sigma\rho$, is a result of the linear combination of effects arising from both polar and resonance contributions.[1,2] Several correlations have been proposed for the evaluation of these separate polar and resonance terms. The simplest of these is the modified Yukawa equation (eq 1),[3-6] and perhaps the best known is the method described by Taft.[7,8]

For the Yukawa–Tsuno equation, the Gibbs free-energy changes arising from each of the interaction mechanisms can be expressed in the general terms of eq 1,[5] where polar

$$\log k/k_0 = \sigma^n\rho + \sigma^r\rho^r \propto \Delta\Delta G_{\text{polar}} + \Delta\Delta G_{\text{reson}} \quad (1)$$

---

(1) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; p 192.

(2) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, Chapter 3.

(3) Tsuno, Y.; Masami, S.; Takahiro, F.; Yoshihiko, T.; Yasuhide, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3356–3366. Yukawa, Y.; Tsuno, Y.; Sawada, M. *Ibid.* **1966**, *39*, 2277–2286. Yukawa, Y.; Tsuno, Y. *Ibid.* **1959**, *32*, 965–971.

(4) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288–3294; **1978**, *100*, 1228–1235; **1977**, *99*, 8238–8248.

(5) Young, P. R.; McMahon, P. E. *J. Am. Chem. Soc.* **1979**, *101*, 4678–4681.

(6) Young, P. R.; Bogseth, R. C.; Rietz, E. G. *J. Am. Chem. Soc.* **1980**, *102*, 6268–6271.

(7) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. *Prog. Phys. Org. Chem.* **1973**, *10*, 1–80.

(8) Taft, R. W.; Ehrenson, S.; Lewis, I. C.; Glick, R. E. *J. Am. Chem. Soc.* **1959**, *81*, 5352–5361. Taft, R. W.; Lewis, I. C. *Ibid.* **1958**, *80*, 2436–2443; **1959**, *81*, 5343–5352.

0022-3263/80/1945-5290$01.00/0

Table I. Structure–Reactivity Parameters for the Benzaldehyde Cyanohydrin Reaction and for Pyridine Ionization

		Yukawa-Tsuno[a]		Taft[b]		
		ρ	ρ^{r}	ρ_I	$\rho_R{}^m$	$\rho_R{}^p$
benzaldehyde cyanohydrin rxn[c]	K_{add}	0.66	1.12	0.72	0.30	1.08
	k_{fwd}	1.37	0.89	1.38	0.53	1.10
	k_{rev}	0.71	−0.39	0.75	0.28	*d*
pyridinium dissociation[e]	K_a	5.87	1.88	5.153[f]	2.626[f]	2.688[f]

[a] From eq 2. [b] From eq 9. [c] From the data of ref 5. [d] A statistically significant value could not be determined from the data set available. [e] From ref 7. [f] Values calculated in ref 7.

effects[9] are measured by σ^n and resonance effects are measured by σ^r. The constant σ^+ represents a composite effect in which both resonance (σ^r) and inductive (σ^n) effects operate;[10] thus σ^r is proportional to the quantity ($\sigma^+ - \sigma^n$). Substituting and rearranging, one can rewrite eq 1 as eq 2. This equation has the same general form as the

$$\log k/k_0 = \rho(\sigma^n + (\rho^r/\rho)(\sigma^+ - \sigma^n)) \qquad (2)$$

Yukawa–Tsuno equation[3,5] with $r^+ = (\rho^r/\rho)$. It is apparent from this equation that the substituent effect on a reaction can be described by a single parameter as long as the ratio (ρ^r/ρ) is constant. According to this treatment, the free-energy change associated with resonance interaction by a given substituent can be calculated by eq 3.

$$\Delta\Delta G_{reson}/2.3RT \propto \rho^r(\sigma^+ - \sigma^n) \qquad (3)$$

The approach developed by Taft and co-workers[7,8] treats positional dependence (meta or para) as a function of ρ instead of σ, producing distinct treatments for para- and meta-substituted compounds. Additionally, the equations for *each* site are dual parameter, having inductive and resonance terms for both para- and meta-substituted compounds. For para compounds, following σ^+-type reactions

$$\log k/k_0 = \sigma_I\rho_I{}^p + \rho_R{}^p\,\sigma_R{}^+ \propto \Delta\Delta G_{polar} + \Delta\Delta G_{reson} \qquad (4)$$

and for meta compounds

$$\log k/k_0 = \sigma_I\rho_I{}^m + \sigma_R{}^o\,\rho_R{}^m \propto \Delta\Delta G_{polar} + \Delta\Delta G_{reson} \qquad (5)$$

Again, according to the treatment, the free-energy change associated with resonance interactions is given by expressions 6 and 7 for para and meta substituted compounds, respectively.

$$\Delta\Delta G_{reson}(\text{para}) \propto \sigma_R{}^+\rho_R{}^p \qquad (6)$$

$$\Delta\Delta G_{reson}(\text{meta}) \propto \sigma_R{}^o\rho_R{}^m \qquad (7)$$

Experimentally, ρ^r can be determined by the Yukawa approach by plotting the logarithm of $(k/k_0)_{obsd} - (k/k_0)_{calcd}$ against the ($\sigma^+ - \sigma^n$) constant for the substituent under examination.[4-6] The quantity $(k/k_0)_{calcd}$ is readily obtained from $\sigma^n\rho$, where ρ is determined from the best fit of meta substituents. A second, intuitively pleasing method of obtaining ρ^r is by varying the ratio ρ^r/ρ in eq 2 and optimizing the fit of the para data to the line defined by the meta substituents. This fitting procedure is identical with that described by Yukawa et al.[3]

An experimental fit to the Taft equations is not as simple to obtain because an inductive reference line cannot be constructed as it is in the Yukawa method. For a para substituent following the σ^+ constant, the Taft equation can be written as in eq 8.[11] In the analysis, an "effective"

$$\log k/k_0 = \rho_I{}^p(\sigma_I + \lambda\sigma_R{}^+) \qquad \lambda = \rho_R{}^p/\rho_I{}^p \qquad (8)$$

substituent constant must be calculated for each value of λ selected. The ratio λ is then varied and the linear least-squares correlation coefficient calculated. The optimized value of this correlation coefficient is determined, and ρ parameters are calculated. The analysis can be done by hand, although computer analysis is commonly used.[7]

We have previously suggested that isolated resonance parameters may be useful in the diagnosis of transition-state structures where a change in hybridization occurs.[5] Because of this potential, it is necessary to examine the methods available for the determination of the resonance parameters and to explore the assumptions inherent in each. We have therefore reanalyzed three literature data sets by the Yukawa and Taft approaches and herein present a comparison of the results.

Experimental Section

The rearranged form of the Taft equation (eq 9; $i = o, m,$ or p) was used in the following manner: $\log K/K_0$ or $\log k/k_0$ values

$$\log k/k_0 = \rho_I{}^i(\sigma_I + \lambda^i\sigma_R) \qquad \lambda^i = \rho_R{}^i/\rho_I{}^i \qquad (9)$$

were calculated for each substituent. A value of λ^i was arbitrarily selected, and effective substituent constants ($\sigma_I + \lambda^i\sigma_R$) were calculated for each point by using σ_I, $\sigma_R{}^+$ (para substituents), or $\sigma_R{}^o$ (meta substituents), as compiled by Taft and co-workers.[7] A linear regression was performed for each set of data generated by a λ^i value, giving a corresponding slope ($\rho_I{}^i$) and a correlation coefficient. Values for λ^i were varied systematically to determine the data set which gave the highest correlation coefficient. In practice, ρ values were determined with the constraint that $\rho_I{}^m = \rho_I{}^p$, and final values of ρ were determined from consideration of all data points, meta and para. This was done to minimize coincidental fittings associated with the less than minimal basis set recognized for the Taft analysis which was available for the benzaldehyde cyanohydrin reaction.[5] Yukawa parameters ρ and ρ^r were determined from graphical analysis as previously described.[4,5]

Results and Discussion

The substituent effects for the ionization of 3- and 4-substituted pyridinium ions have been analyzed by Taft and co-workers[7] in the terms of eq 9. The most satisfactory fit of the data is obtained by using the $\sigma_R{}^+$ and $\sigma_R{}^o$ scales for the para and meta correlations, respectively. The values of ρ_I, $\rho_R{}^p$, and $\rho_R{}^m$ that have been calculated[7] appear in Table I.

The functional form of the Taft equation clearly outlines two distinct types of resonance-interaction mechanisms. The $\sigma_R{}^+$ scale has been classically applied to those reactions in which the electron-deficient site can come into direct conjugation with the para substituent. When this mechanism is not functional, the $\sigma_R{}^o$ scale is used to measure those resonance contributions unique to meta substituents, or transmitted "through sp^3" centers, such as in the ionization of benzylamines, etc. Total free-energy changes due to resonance interactions are thus seen to be a composite of direct conjugative and nonconjugative ef-

---

(9) van Bekkum, H.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1959**, *78*, 815–823.

(10) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979–4987.

(11) Bromilow, J.; Brownlee, R. T. C. *J. Org. Chem.* **1979**, *44*, 1261–1263.

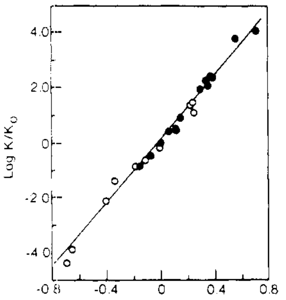

Figure 1. Plot of log K/K_0 for the ionization of 3-substituted (●) and 4-substituted (○) pyridinium ions against the quantity $\sigma^n + (\rho^r/\rho)(\sigma^+ - \sigma^n)$ using the ratio $\rho^r/\rho = 0.32$. The ionization constants are from ref 7.

fects. For a given reaction, if the changes in nonconjugative resonance effects for para substituents are proportional to changes in nonconjugative resonance effects for the meta substituents ($\sigma_R{}^o\rho_R{}^p \propto (\sigma_R{}^o\rho_R{}^m)$), a value can be calculated for the free-energy change for *direct* conjugative resonance by eq 10. The degree to which this equation correctly

$$\Delta\Delta G_{\text{dir}}{}^p = 2.3RT(\sigma_R{}^+\rho_R{}^p - q(\sigma_R{}^o\rho_R{}^m)) \qquad (10)$$

describes the direct conjugative resonance free-energy change is a function of the constant q which describes the relationship between nonconjugative effects from both the meta and para positions. If $q = 1$, the free-energy change would be accurately predicted by the simple subtraction of the appropriate products of the $\sigma\rho$ values for a given substituent. It is probable, however, that q is not equal to one and most likely that it is *less than* one in most cases, as evidenced by the large number of data sets containing meta- and para-substituted compounds which closely follow σ^n, with $\sigma^n < \sigma_{\text{meta}}$. Free-energy changes for conjugative resonance which are calculated in this manner are therefore expected to be somewhat exaggerated.

In the modified Yukawa–Tsuno treatment, resonance contributions for para substituents appear as positive or negative deviations from the correlation line defined by meta substituents and the σ^n scale.[3-5] The relative sizes of these deviations from the values predicted by the σ^n scale for that particular para substituent are proportional to the free-energy change associated with the resonance contribution. Since the "normal" (σ^n) scale is defined on the basis of ionizations of benzyl-type compounds,[2,9] any contribution arising from "through-sp^3" nonconjugative resonance is contained in the σ^n constant, and the deviations thus represent *conjugative* resonance effects.

The degree to which the deviations accurately reflect free-energy changes associated with direct resonance effects will depend on the type of reaction under consideration. The more closely the rate or equilibrium under consideration resembles sp^3 geometry at the benzyl position, the better the correlation can be expected to be.

Pyridinium compounds do not possess sp^3 geometry at the ionizing site. Nevertheless, the data for 3-substituted pyridines give a linear plot against meta substituent constants with systematic negative deviations for 4-substituted compounds plotted at their σ^n values. The magnitudes of these negative deviations are proportional to the quantity $(\sigma^+ - \sigma^n)$ for each substituent, and eq 2, with the ratio $\rho^r/\rho = 0.32$, gives a linear plot with a correlation coefficient of 0.994 (Figure 1). The values of ρ and ρ^r that are obtained by this treatment are given in Table I.

It is most likely that the free-energy changes that are calculated from the deviations in this plot are less than the "true" free-energy change associated with conjugative resonance. This is because the ionization of pyridinium compounds is not attenuated by an intervening sp^3 center as is the ionization of benzylamine, which follows σ^n. It is, therefore, not clear if the 4-substituted compounds should be plotted according to σ^n or to the meta substituent constant. Since $\sigma^n < \sigma_{\text{meta}}$, a larger negative value of $\Delta\Delta G_{\text{reson}}$ would be calculated if the data were plotted at the σ_{meta} values. The data calculated according to the σ^n constants are probably *proportional* to the "true" conjugative resonance effects but are most likely lower limits.

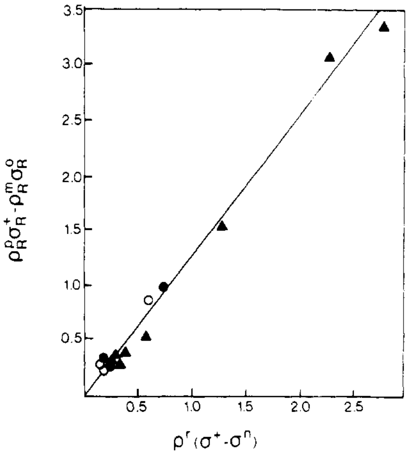

Figure 2. Plot of the "resonance term" from the Yukawa–Tsuno equation (eq 3) against the comparable "direct conjugative resonance" term from the Taft equation (eq 10; $q = 1$) for the ionization of 4-substituted pyridinium ions (▲), the equilibrium addition of HCN to benzaldehydes (●), and the forward rate constants for the addition of NC^- to benzaldehydes (○).

Thus, allowing some assumptions, one can isolate a free-energy term associated with conjugative resonance from both the Taft and Yukawa–Tsuno treatments. In Figure 2, $\rho^r(\sigma^+ - \sigma^n)$, the "resonance term" from the Yukawa–Tsuno approach, is plotted against $(\rho_R{}^p\sigma_R{}^+ - \rho_R{}^m\sigma_R{}^o)$, the resonance contribution calculated by the Taft approach for the ionization of substituted pyridinium ions (triangles). The fit is quite satisfactory, and the slope of the correlation is about 1.2. The fact that this slope is not unity is consistent with the prediction that the free-energy changes would be *underestimated* by the Yukawa treatment and slightly *overestimated* by the Taft treatment. The important conclusion is that comparable estimates of free-energy changes associated with conjugative resonance can be obtained from *both* methods.

We have recently shown that changes in hybridization from sp^2 to sp^3 which occur in the transition state for the addition of cyanide anion to benzaldehydes can be diagnosed by examining the changes in "conjugative resonance" that are observed for the kinetic process relative to the equilibrium value.[5] As a measure of conjugative resonance in the above experiment, we compared the values of $\rho^r{}_{\text{rate}}$ (for the forward reaction) and $\rho^r{}_{\text{eq}}$ that were obtained from treatment of the data according to the modified Yukawa–Tsuno equation. The ratio that was obtained (0.79) was experimentally indistinguishable from the ratio of kinetic and equilibrium secondary deuterium isotope effects (0.83), a more classical method for estimating hybridization changes.[12] It was suggested that ρ^r ratios may therefore provide a useful alternate or supplement to isotope effects in the characterization of transition-state structures.[5]

---

[12] Bilkodi, Z.; de Lorimier, R.; Kirsch, J. F. *J. Am. Chem. Soc.* **1975**, *97*, 3417–3422. do Amaral, L.; Bastos, M. P.; Bull, H. G.; Cordes, E. H. *Ibid.* **1973**, *95*, 7369–7374. Shiner, V. J., Jr. In "Isotope Effects in Chemical Reactions"; Collins, C., Bowman, W. S., Eds.; Van Nostrand: Princeton, NJ, 1970.

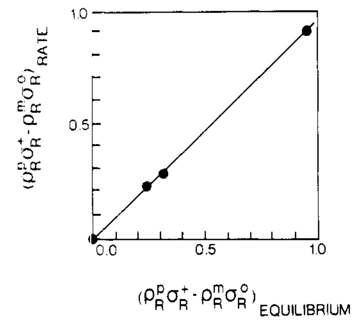

Figure 3. Plot of the "direct conjugative resonance" terms from the Taft equation (eq 10; $q = 1$) for the kinetic and equilibrium additions of HCN to substituted benzaldehydes. The slope is 0.88; the data are from ref 5.

The fact that the free-energy changes for conjugative resonance interactions that are calculated by the Taft and Yukawa methods are proportional (Figure 2) suggests that conjugative resonance effects, calculated by the Taft method, may also be useful in estimating transition-state structures. The data set which was used for the benzaldehyde cyanohydrin experiment is not large enough to allow an unambiguous determination of $\rho_R{}^p$, $\rho_R{}^m$, and ρ_I. However, approximate values have been determined for the rate and equilibrium processes (Table I). The free-energy changes calculated for these data are shown as the circles in Figure 2 (open circles are k_{fwd}, closed circles are K_{add}). Again, both the Taft and Yukawa methods give proportional values. In Figure 3, the free-energy changes for direct resonance interaction, as estimated by the Taft approach and eq 9, for the kinetic process (k_{fwd}) are plotted against the comparable data for the equilibrium addition. The slope of this plot is 0.88, slightly larger than the 0.79 value estimated by using the Yukawa equation and the 0.83 value obtained from isotope methods.[5] The slight overestimation that is observed is consistent with the prediction that $q < 1$ for these types of reactions, although the data set is far too limited to explore this difference quantitatively.

It would be useful at this point to explore the limiting conditions inherent in the Yukawa approach as compared to those of the more general Taft equations. (1) In the Yukawa approach, a single scale (σ^n) is used to plot "normal" values for para substituents as well as meta substituents. Since these σ^n constants are composites containing both resonance and inductive terms, they can be represented in the Taft nomenclature[7] by expression 11. A correlation against σ^n is therefore expected to be

$$\sigma^n \propto (\sigma_I + (\rho_R{}^i/\rho_I{}^i)\sigma_R{}^o) \qquad i = \text{meta or para} \qquad (11)$$

useful only in those cases where the ratio $\rho_R{}^i/\rho_I{}^i$ for the reaction under consideration is the same as the ratio observed in the reference reaction defining the σ^n scale. Fortunately, for a large number of cases, Taft[7] has reported that the ratio $\rho_R{}^i/\rho_I{}^i$ is approximately constant at 0.5. (2) In the Yukawa approach, a single slope is used to define inductive substituent effects at both the para and the meta positions. This is only valid if, in the Taft nomenclature, $\rho_I{}^m = \rho_I{}^p$. For aqueous solutions and for low percentages of organic solvents in aqueous mixtures, Taft[7] has found that these inductive ρ values are indeed equal, so that $\rho_I{}^i$ can be simply expressed as ρ_I. This equality is not rigorously observed in the pyridinium data shown in Figure 2 and Table I where $\rho_I{}^m/\rho_I{}^p = 1.17$. This inequality may contribute to the nonunit slope that is observed in Figure 2.

If the approximate equalities outlined above are valid for a given system, then

$$\rho \propto \rho_I$$

$$\sigma^n \propto (\rho_I + (\rho_R{}^m/\rho_I)\sigma_R{}^o)$$

and based on Figure 2

$$\rho^r(\sigma^+ - \sigma^n) \propto (\rho_R{}^p\sigma_R{}^+ - \rho_R{}^m\sigma_R{}^o)$$

Substitution into the rearranged form of the generalized Taft equation[13] (eq 12) gives the simple Yukawa–Tsuno equation (eq 2).

$$\log k/k_0 = \rho_I[(\sigma_I + (\rho_R{}^m/\rho_I)\sigma_R{}^o) + 1/\rho_I(\rho_R{}^p\sigma_R{}^+ - \rho_R{}^m\sigma_R{}^o)] \quad (12)$$

In summary, approximate values for free-energy changes associated with conjugative resonance can be obtained by either the Taft or the modified Yukawa–Tsuno approach. Both equations require assumptions to be made regarding the importance of nonconjugative resonance participation. The free-energy changes that are calculated for both equations are proportional for pyridinium ionization and for the addition of cyanide anion to benzaldehydes. It is reasonable to assume that other reactions will display similar proportionality. A comparison of the free energies for conjugative resonance changes in the addition of cyanide anion to benzaldehydes for the rate and the equilibrium processes gives an estimate of transition-state hybridization that is close to the estimate obtained from isotope-effect studies for both methods. Theoretical rigor and versatility appear to favor the Taft approach, although the experimental simplicity, the smaller data set requirement, and the intuitive appeal of the modified Yukawa–Tsuno equation argue for its general use for those reactions which would be expected to follow the simple σ^n scale.

Acknowledgment. We gratefully acknowledge the National Science Foundation (CHE80-00054) for support of this work.

---

(13) Addition and subtraction of the quantity $\rho_R{}^m\sigma_R{}^o$ to the para form of the Taft equation (eq 8), followed by the factoring of the inductive ρ subject to the condition that the meta and para values are equal, yields the rearranged equation (eq 12). The expression is applicable to meta substituents as well if the last term in the equation, representing the direct conjugative free-energy contribution, is taken as zero.