tassium hydroxide in 7.5 mL of 2-propanol in a side-arm test tube were added 0.76 g of 9-fluorobenzanthrone[2a] and 3 mL of benzyl-α-^{13}C cyanide. The mixture was heated to 40–45 °C for 4 h while air was bubbled through it, during which time the color changed to blue and then indigo. The reaction mixture was cooled to room temperature, 2.2 mL of glacial acetic acid was added, and the mixture was allowed to stand overnight. The solid was filtered off, washed with hot methanol, and dried at 90 °C for 1 h, yielding 0.90 g (82%) of crude product, mp 202–205 °C (lit.[2a] mp 224 °C).

4-Benzoyl-9-fluoro-7*H*-benz[*de*]anthracen-7-one-α-^{13}C. A mixture of 1.5 g of anhydrous sodium acetate, 1.35 g of sodium dichromate, 1.0 g of 4-(cyanobenzyl)-9-fluoro-7*H*-benz[*de*]anthracen-7-one-α-^{13}C and 7 mL of glacial acetic acid was heated on a boiling water bath for approximately 3 h and then allowed to cool to room temperature. Upon slow addition of water (7 mL) a yellow solid precipitated which was filtered and washed repeatedly with hot water until the filtrate was colorless. The material was dried in a vacuum oven (55 °C), affording 0.79 g (80%) of product, mp 220 °C (from benzene–petroleum ether).

3-Fluorobenzo[*rst*]pentaphene-5,8-dione-*8*-^{13}C. A mixture of 0.45 g of potassium chloride, 0.45 g of sodium chloride, 5.1 g of *technical*[2b] grade aluminum chloride, and 0.3 g of *m*-nitrobenzoic acid was heated to 125 °C in an Erlenmeyer flask. To the melt was added 0.79 g of 4-benzoyl-9-fluoro-7*H*-benz[*de*]anthracen-7-one-α-^{13}C, and the mixture was maintained at 125 °C for 5 h. The reaction mixture was cooled, and 25 mL of dilute HCl (1:10 v/v) was added dropwise and with stirring. A red solid precipitated which was filtered and dissolved in 35 mL of a boiling mixture of water, hydrochloric acid, and ethanol (5:1:1 v/v/v). After the mixture was filtered and cooled 0.98 g of the red product was collected and air-dried.

3-Fluorodibenzo[*a,i*]pyrene-*8*-^{13}C (3-Fluorobenzo[*rst*]pentaphene-*8*-^{13}C). Aluminum turnings (1.4 g) were dissolved in refluxing cyclohexanol (30 mL) in the presence of a trace of mercury(II) chloride. To the green-black solution was added 0.5 g of 3-fluorobenzo[*rst*]pentaphene-5,8-dione-*8*-^{13}C, and the mixture was heated under reflux for 48 h.

The reaction mixture was worked up as described previously,[20] and the product was purified by chromatography on silica gel: yellow crystals; mp 265 °C (from xylene); yield 40%.

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Registry No. Benzoic acid-^{13}C, 3880-99-7; benzyl-α-^{13}C alcohol, 54522-91-7; benzyl-α-^{13}C chloride, 57742-41-3; benzyl-α-^{13}C cyanide, 73368-35-1; α-phenyl-9-fluoro-7-oxo-7*H*-benz[*de*]anthracene-4-acetonitrile-α-^{13}C, 73368-36-2; 9-fluorobenzanthrone, 61735-79-3; 4-benzyl-9-fluoro-7*H*-benz[*de*]anthracen-7-one-α-^{13}C, 73368-37-3; 3-fluorobenzo[*rst*]pentaphene-5,8-dione-*8*-^{13}C, 73384-25-5; 3-fluorodibenzo[*a,i*]pyrene-*8*-^{13}C, 73384-26-6; 2-*F*-DBP, 73368-38-4; 2,10-F_2-DBP, 61735-78-2; DBP, 189-55-9; 3-*F*-DBP, 61735-77-1; phenyl bromide, 108-86-1.

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New Extended Hammett Equation with Donor and Acceptor Resonance Contributions

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It is shown that the equation $Q = \rho_I\sigma_I + \sigma_{R+}\sigma_R^+ + \rho_{R-}\sigma_R^- + h$ effectively copes with wide variations of electronic effects as precisely as the formulation of Ehrenson et al. It is also shown that the Tsuno–Yukawa equation is a mathematical artifact of this equation.

Different substituent constants and different modifications of the original Hammett equation have been derived in order to cope with experimental data involving wide variations in resonance contributions. Mathematical formulations based on a dual-parameter model such as by Ehrenson, Brownlee, and Taft,[2] Yukawa and Tsuno,[3] Swain and Lupton,[4] Hine,[5] and Wepster[6] enjoy high recognition. None of these equations, however, is generally applicable. Recently, Happer and Wright[7] have advanced a complex exponential model to account for these variations. The underlying theme of the most recent work is that no single set of σ_R constants is sufficient to correlate all experimental data. This was demonstrated by Ehrenson et al. using eq 1 (where "σ_R" is different for different

$$\Delta Q = \rho_I\sigma_I + \rho_R\text{"}\sigma_R\text{"} \qquad (1)$$

reaction sites). Usually, for the best fit in a specific practical application, the substituent constants and, eventually, the LFER equation are selected by the method of trial and error. This uncertainty and ambiguity, however, would be eliminated if an equation of universal applicability to electronic effects would be derived with certain fixed sets of substituent constants. Equation 2,

$$Q = \rho_I\sigma_I + \rho_{R+}\sigma_R^+ + \rho_{R-}\sigma_R^- + h \qquad (2)$$

which was introduced by us and tested on various exam-

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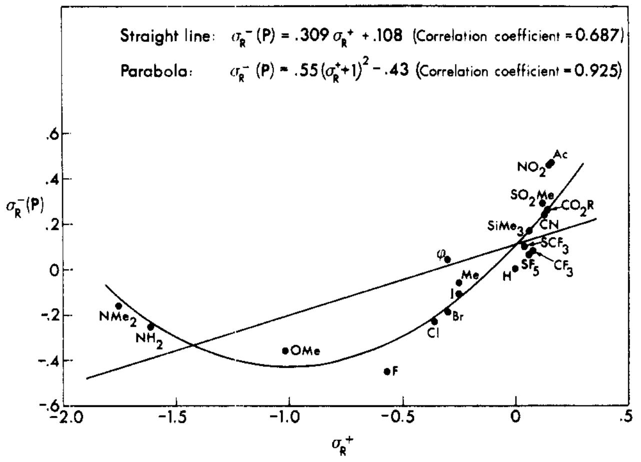

Figure 1. Correlation of σ_R^- vs. σ_R^+.

ples, has proven its universal applicability in this area. σ_I, σ_R^+, and σ_R^- substituent constants are those reported by Ehrenson,[1] the later corresponding to Ehrenson's σ_R^-(P) constant. Whereas Ehrenson et al. sought to cope with variability of resonance effects by introducing a number of σ_R scales and Happer and Wright by introducing a complex exponential equation, our equation represents the resonance effect as a linear combination of σ_R^+ and σ_R^- components. The present work tends to discount the necessity of an equation like Happer and Wright's as being an overparameterization.

As the σ_R^+ constants cover reactions at electron-withdrawing centers strongly interacting with the π system and the σ_R^- constants are similar but for electron-donating centers, the universal character of eq 2 is evident. Thus, for reactions similar to the solvolysis of *tert*-cumyl chlorides, ρ_{R+} is large and ρ_{R-} is essentially zero whereas for reactions similar to dissociation of phenols the situation is reversed. However, for intermediate situations the contribution of both components is comparable; for instance, the weighted percentage of ρ_{R+} effects to total resonance effects is 22 ± 3% for σ_R^-(A), 55 ± 3% for σ_R^0, and 75 ± 2% for σ_R(BA)[8]. Situations where the signs of ρ_{R+} and ρ_{R-} are opposite (e.g., ArSnMe$_3$ + MeO$^-$:[9] ρ_I = +1.843 ± 0.0616, ρ_{R+} = −0.156 ± 0.0240, ρ_{R-} = +1.201 ± 0.084, f = 0.095) are also possible and are indicative of reactions that are more electron donating or withdrawing than the model systems. This particular reaction is also interesting because it is not correlated by any of Ehrenson's σ_R's.

The correlation of σ_R^- by a linear model vs. σ_R^+ for 19 substituents (Figure 1) has a correlation coefficient of 0.687, whereas the relation $\sigma_R^- = 0.55(\sigma_R^+ + 1.00)^2 - 0.43$ found by trial and error has a correlation coefficient of 0.925. The ratio of their f values as a test recommended by Ehrenson[10] indicates that the linear relationship can be rejected at a 99.9% confidence level. This indicates that only one resonance scale is necessary, but the exact mathematical relationship is still undetermined. Since σ_R^- and σ_R^+ represent the two extremes, they must contain different aspects of this function. For instance, we have shown above that σ_R^- is approximately a quadratic function of σ_R^+; σ_R^- then represents the square term and σ_R^+ the linear term in determining other σ_R scales. A group of reactions which when examined together *appear* to exhibit behavior (in ρ_R^- effects) associated with an isokinetic temperature are the reactions of aqueous H_2SO_4 with Ar_3COH, $Ar_2(C_6H_5)COH$, and $Ar(C_6H_5)_2COH$.[11] The results of these correlations are as follows: Ar_3COH, ρ_I = −11.19 ± 0.194, ρ_{R+} = −9.26 ± 0.082, ρ_{R-} = −2.31 ± 0.199, n = 8, f = 0.0157; $Ar_2(C_6H_5)COH$, ρ_I = −8.11 ± 0.443, ρ_{R+} = −8.06 ± 0.210, ρ_{R-} = +0.584 ± 0.461, n = 6, f = 0.0446; $Ar(C_6H_5)_2COH$, ρ_I = −4.37 ± 0.79, ρ_{R+} = −6.32 ± 0.38, ρ_{R-} = + 2.76 ± 0.83, n = 8, f = 0.129. However, it should be remembered that resonance effects are the composite of ρ_{R+} and ρ_{R-} effects.

This representation of the resonance effect has several analogues. For instance, from the basic concepts of the resonance theory, the electrons of the π system allow polarization in both directions (from and to the reaction site), and, therefore, the substituents should be characterized by both their electron-donating and their electron-withdrawing capabilities. This is analogous to the representation of the resonance state by respective canonic formulas which differ in the direction of the polarization of the π-electron system. Another analogue would be the description of atoms by ionization potentials and electron affinities. In fact, ionization potentials have been correlated by σ^+ constants.[12] Moreover, while there may be a common function relating all resonance scales, the simplicity of this model tends to recommend it over a more precise (and probably more complex) equation.

Two cases from the literature could be found which are similar to eq 2. It was shown by Parsons and Cohen[13] that simultaneous application of σ^+, σ^0, and σ^- substituent constants for one set of experimental data provides an excellent linear correlation. Exner[14] used eq 3 (where d_I

$$\mu_x = \rho_I d_{I,x}\sigma_{I,x} + \rho_R d_{R,x}\sigma_{R,x}{}^{\pm} + \mu_0 \qquad (3)$$

and d_R are distances between charges, and $\sigma_R^{\pm}$ is σ_R^+ for acceptor substituents and σ_R^- for donor substituents) to correlate dipole moment data efficiently. Swain and Lupton attempted a similar formulation, but their results were unsatisfactory because the σ^+ they used did not represent the electronic effects accurately, and possibly the σ's they used were highly correlated against one another and prevented separation.

Table I shows the interrelationships of the various σ scales. The resonance scales of Ehrenson are highly correlated by eq 2 as shown by the high values of the multiple correlation coefficients and the confidence levels (superscripts A through I) from the Student's t test. An interesting point which can be seen in Table I is that the separation of inductive and resonance effects for the aniline type σ's was incomplete. The $\Delta\sigma^{\pm}$ values used for this table were calculated by the equation $\Delta\sigma_R^{\pm} = \sigma_R^{\pm} - \sigma_R^0$, and σ_R^+, σ_R^-, and σ_R^0 were taken from Ehrenson's paper. It was done in this manner to prevent any scaling problems or differences in σ_I contributions. $\Delta\sigma_R^+$ is correlated very well by eq 2 while $\Delta\sigma_R^-$ is only poorly correlated [R(multiple)

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(8) There is reason to believe that the magnitude of the σ values are dependent on the ρ value of the defining reaction. For example, $\sum|\sigma_R^-(P)|/\sum|\sigma_R^+| = \rho_{R-}/\rho_{R+} = 0.55$. This was the central theme in defining σ_n by: Van Bekken, H.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1959**, *78*, 815–50. From a mathematical point of view, the contribution of any independent variable to the dependent variable is equal to that variable's slope multiplied by its value. On this basis, the weighted percentage of ρ_{R+} effects, %R+, is calculated by the formula: $\%R+ = [\sum|\sigma_R^+|\rho_{R+}/(\sum|\sigma_R^+|\rho_{R+} + \sum|\sigma_R^-|\rho_R^-)] \times 100\%$. The error in this quantity, $E_{\%R+}$ is calculated by the formula: $E_{\%R+} = [\sum|\sigma_R^+|\cdot\sum|\sigma_R^-|[E\rho_{R+}{}^2\rho_{R-}{}^2 + E\rho_{R-}{}^2\rho_{R+}{}^2]^{-1/2}/(\sum|\sigma_R^+|\rho_{R+} + \sum|\sigma_R^-|\rho_{R-})^2] \times 100\%$.

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Table I. Correlation[o] of σ Constants by σ_I, σ_R^+, and σ_R^-

set	Q	eq[j]	ρ_I	S_{ρ_I}[k]	ρ_{R^+}	$S_{\rho_{R^+}}$[k]	ρ_{R^-}	$S_{\rho_{R^-}}$[a,k]	h	S_h[k]	$R(\sigma_I, \sigma_{R^+})$[l]	$R(\sigma_I, \sigma_{R^-})$[l]	$R(\sigma_I, \sigma_{R^-})$[l]	R(mult)[m]	f[n]
1-1	σ_R(BA)	2P	−0.0349	0.028[g]	0.464	0.015[a]	0.278	0.033	0.0041	0.013[h]	0.360	0.192	0.687	0.997 24	0.0836
1-2	σ_R(BA)	3P			0.458	0.015[a]	0.281	0.033	−0.0087	0.0077[g]			0.687	0.996 97	0.0848
1-3	σ_R(BA)	2A	−0.0702	0.023[b]	0.420	0.015[a]	0.302	0.028	0.0030	0.010[h]	0.360	0.328	0.821	0.998 19	0.0677
1-4	σ_R(BA)	3A			0.412	0.019[a]	0.297	0.034	−0.0214	0.0083[d]			0.821	0.997 07	0.0834
1-5	σ_R^0	2P	−0.0056	0.036[i]	0.252	0.019[a]	0.383	0.041	−0.0198	0.016[g]	0.360	0.192	0.687	0.991 35	0.148
1-6	σ_R^0	3P			0.251	0.018[a]	0.384	0.040	−0.0218	0.0092[d]			0.687	0.991 33	0.143
1-7	σ_R^0	2A	−0.0540	0.030[e]	0.193	0.020[a]	0.412	0.037	−0.0208	0.014[f]	0.360	0.328	0.821	0.993 74	0.126
1-8	σ_R^0	3A			0.187	0.021[a]	0.408	0.039	−0.0396	0.0095[a]			0.821	0.992 41	0.134
1-9	σ_R^-(A)	2P	0.118	0.040[b]	0.141	0.022[a]	0.935	0.046	0.0018	0.018[i]	0.360	0.192	0.687	0.994 38	0.119
1-10	σ_R^-(A)	3P			0.161	0.025[a]	0.923	0.056	0.0452	0.013[b]			0.687	0.991 07	0.145
1-11	$\Delta\sigma_R^-$(A)	2P	0.168	0.044[b]	−0.122	0.024[a]	0.550	0.050	0.0002	0.0208[i]	0.360	0.192	0.687	0.953 25	0.340
1-12	$\Delta\sigma_R^-$(A) ($w/o\phi$, NH_2)	2P	0.188	0.029[a]	−0.159	0.018[a]	0.575	0.033	0.0150	0.014[g]	0.301	0.154	0.681	0.982 32	0.214
1-13	$\Delta\sigma_R^-$(A)	3P			−0.093	0.030[b]	0.534	0.068	0.0621	0.0168[b]			0.687	0.904 71	0.464
1-14	$\Delta\sigma_R^-$(A)	2A	0.0983	0.036[c]	−0.205	0.024[a]	0.589	0.044	−0.0008	0.0176[i]	0.360	0.328	0.821	0.967 20	0.286
1-15	$\Delta\sigma_R^-$(A) ($w/o\phi$, NH_2)	2A	0.112	0.029[b]	−0.230	0.021[a]	0.599	0.034	−0.0110	0.013[g]	0.301	0.284	0.793	0.982 37	0.214
1-16	$\Delta\sigma_R^-$(A)	3A			−0.194	0.028[a]	0.596	0.052	0.0334	0.013[c]			0.821	0.951 00	0.337
1-17	$\Delta\sigma_R^-$(P)	2P	0.0056	0.036[i]	−0.252	0.019[a]	0.616	0.041	0.0198	0.016[g]	0.360	0.192	0.687	0.971 09	0.269
1-18	$\Delta\sigma_R^-$(P)	3P			−0.251	0.018[a]	0.616	0.040	0.0218	0.0092[d]			0.687	0.971 04	0.260
1-19	$\Delta\sigma_R^+$	2P	0.0056	0.036[i]	0.748	0.019[a]	−0.383	0.041	0.0198	0.016[g]	0.360	0.192	0.687	0.996 78	0.0902
1-20	$\Delta\sigma_R^+$	3P			0.749	0.018[a]	−0.384	0.040	0.0218	0.0092[d]			0.687	0.996 78	0.0874
1-21	$\Delta\sigma_R^+$	2A	0.0540	0.030[e]	0.806	0.020[a]	−0.412	0.037	0.0208	0.014[f]	0.360	0.328	0.821	0.997 67	0.0767
1-22	$\Delta\sigma_R^+$	3A			0.813	0.021[a]	−0.408	0.039	0.0396	0.0095[a]			0.821	0.997 18	0.0818

[a] Confidence level (CL) by Student's test is 99.9%. [b] CL 99.0–99.9%. [c] CL 98–99%. [d] CL 95–98%. [e] CL 90–95%. [f] CL 80–90%. [g] CL 50–80%. [h] CL 20–50%. [i] CL < 20%. [j] Equation 2: $Q = \rho_I\sigma_I + \rho_R^+\sigma_R^+ + \rho_R^-\sigma_R^- + h$. Equation 3: $Q = \rho_{R^+}\sigma_R^+ + \rho_{R^-}\sigma_R^- + h$. Equation 2A or 3A: σ_R^- is σ_R^-(A). Equation 2P or 3P: σ_R^- is σ_R^-(P). [k] Standard deviation of estimate of ρ_I, ρ_{R^+}, ρ_{R^-}, and h. [l] Partial correlation coefficient. [m] Multiple correlation coefficient. [n] f is the root mean square of the deviations (SD) divided by the root mean of the data (RMS). (See Discussion for details.) [o] For 19 substituents except where substituents are withdrawn from the data set, in which case, the number of substituents is 19 minus the number of substituents withdrawn.

Table II. Distribution of Data Sets by Ehrenson's Statistical Test of the Ratio of f Values[a]

	no. of rejects for eq 2								no. of rejects for either eq at less	no. of rejects for eq 1							
eq tested	99.9%	99.5%	99%	97.5%	95%	90%	75%	50%	than 50%	50%	75%	90%	95%	97.5%	99%	99.5%	99.9%
Benzoic Acid Reaction Type																	
2A			1		5	2	7	3	5	4	3	4	2	2		1	
2P		1	1	3	1	3	5	3	8	2	2	4	3	3			
σ^0 Reaction Type																	
2A		2	1	1	3		2	1		5	1	1	2	2	1		1
2P	2	1	1	1	1	2	1		2	2	3	2	2	1	1		1
σ^- Reaction Type																	
2P	1				1	3	4	1	4	3	4	2	3	1		1	
σ^+ Reaction Type																	
2P								8	7	5	3	3	2	2	1		1
Meta Reaction Type																	
2P					2	1	2	1	2	1	1		1				
Miscellaneous Reaction Type																	
2P						1		3	1	2		1					1
Ortho Reaction Type																	
2P						1	3	2	2	2	2	2			1		
Total																	
2P	3	2	2	4	5	11	15	18	26	17	15	14	11	7	3	1	3

[a] Sixteen reactions reject eq 2 at greater than the 95% CL, 116 between the 95% CL limits of both equations, and 25 reject eq 1 at greater than the 95% CL (total of 157 reactions). Of the 16 reactions which reject eq 2 at greater than the 95% CL, three at 99.9% and one at 99% can be disqualified because they are used to define the σ_R's used to correlate them.

Table III. Comparison[a] of Eq 2 with Ehrenson's Method

type	Σn_i[b]	eq 1[b]	Σn_i[c]	eq 1[c,d]	eq 2P[c,e]
benzoic acid[f]	199	0.0686	203	0.0705	0.0759
σ^0 [g]	159	0.0985	163	0.120	0.144
σ^- [h]	108	0.0780	117	0.113	0.107
σ^+ [i]	102	0.0896	111	0.110	0.0902
meta[j]	152	0.0887	150	0.111	0.116
miscellaneous[k]	42	0.137	44	0.175	0.0743
ortho[l]	57	0.172	61	0.282	0.303

[a] The experimental data was taken from Ehrenson's article.[2] [b] As recorded in Ehrenson's article for the same data sets. [c] This is different from Ehrenson's because H is considered as a substituent, and not all the substituents Ehrenson used can be used because either σ_R^+ or σ_R^- was not defined. [d] Ehrenson's equation but with a fitted intercept and with all calculations done identically with eq 2P. [e] $Q = \rho_I\sigma_I + \rho_R^+\sigma_R^+ + \rho_R^-\sigma_R^-(P) + h$. [f] Data sets 1, 2, 6-15, 26, 28, 29, 31, 35, 37, 38, 40, and 42 in Table II in Ehrenson's article. [g] Data sets 3, 8, 9, 11-16, 18, 19, 21, 22, 23, 24, and 26 in Table VIII in Ehrenson's article. [h] Data sets 1, 7, 11-15, 22, and 26-28 in Table VI in Ehrenson's article. [i] Data sets 1, 3, 6, 8, 10, 11, 12, 19, 21, 24, and 25 in Table XIII in Ehrenson's article. [j] Contains all data sets in Table XI in Ehrenson's article. [k] Data sets 4, 7, 8, and 9 in Table XXIX,f in Ehrenson's article. [l] Data sets 2, 5, 6, and 9-12 in Table XXIX,g in Ehrenson's article.

= 0.95]. It appears that the reason for this poor correlation is either the variability or the poor definition of the values for donor substituents [i.e.: $\Delta\sigma_R^-(A)$, NMe_2 = +0.18; $\Delta\sigma_R^-(A)$, NH_2 = 0.0]. Neglect of the phenyl and amino substituents improved the correlation slightly [R(multiple) = 0.98]. The question now presents itself as to which is the better equation, the Tsuno–Yakawa equation or the method of Ehrenson, Brownlee, and Taft. Since an inductive effect is a more fundamental property (being based on substituted acetic acid ionization, substituted bicyclo[2.2.2]octanecarboxylic acid ionization, etc.) than σ^0, it should provide a clearer indication of what is actually happening. In terms of resonance effects in the Tsuno–Yakawa equation, part of this effect (σ_R^0 in the σ^0 term) must have the same slope as the inductive effects which cannot give accurate results. Furthermore, whether this particular combination of resonance terms ($\Delta\sigma_R^\pm$) can be considered specifically as cross conjugation is doubtful. While it is shown that the σ constants of the Tsuno–Yakawa equation are equivalent to the resonance terms in eq 2, the restrictions of their formulation do not make it as general as eq 2.

On this basis, the various experimental data sets, including F NMR chemical shifts, C NMR chemical shifts, acidities, and nucleophilic and electrophilic substitutions, that Ehrenson et al.[2] correlated were recorrelated with eq 2 and the results compared. The data sets were classified as in Ehrenson's article in seven types, e.g., benzoic acid type, σ^0 type, etc. This comparison was accompanied in two ways. Since the confidence levels from the ratio of the f values can be determined in spite of the number of data points, all data sets can be used for this comparison. Any equation is simply a representation or summary of data, and Ehrenson's test[10] simply states whether both representations are equivalent for a particular data set and, if not, to what degree (CL) they are not. Table II shows the distribution of data sets by this method. Of the 157 experimental data sets, only 16 are significantly (>95% CL) better represented by eq 1, and of these 16, 4 are used to define the σ's used to correlate them. That is, less than 10% of the reactions studied are significantly better correlated by eq 1. The explanation for this is that the more specific or limited a LFER is, the higher the precision; this has been discussed thoroughly by Exner[15] and more recently by Wold and Sjöström.[16] For those cases where eq 1 is significantly better, the data sets are very similar to the model reaction upon which the particular σ_R is defined.

Since f values are the root mean square of the deviations divided by the root mean square of the data, a comparison of the sum of these values would indicate the general quality of the correlations. Because of the mathematical variations caused by a large number of independent variables and a small number of data points, only data sets with eight or more points were used. The results for each type were summed by the equation $F = (\sum n_i f_i^2/\sum n_i)^{1/2}$, where f_i is the f value for each individual data set and n_i is the number of points for that data set. These values are slightly different from those of Ehrenson in three ways. (1) The equation Ehrenson used was forced through zero, and our equation has a fitted intercept, and, therefore, the deviations are somewhat different.[17] (2) The number of data points in each particular case could be different because not all substituent constants (σ_R^+ or σ_R^-) were defined, and Ehrenson did not consider the unsubstituted compound as a data point. (3) Ehrenson used $(\sum_i(Y_i - Y_h)^2/n)^{1/2}$ for the root mean square of the data where Y_h is the value of the unsubstituted compound whereas we used $(\sum_i(Y_i - \bar{Y})^2/n)^{1/2}$ where $\bar{Y}$ is $\sum_i Y_i/n$. Table III shows these differences in the calculational method and also shows that eq 1 and eq 2 have the same precision.

The arguments and statistical data presented in this article demonstrate that eq 2 is a Hammett equation that represents all types of electronic effects precisely.

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(15) Exner, O. *Collect. Czech. Chem. Commun.* **1975**, *40*, 2781–91.

(16) Wold, S.; Sjöström, M. In "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; Chapter 1.

(17) Many authors question whether forcing the equation through zero as Ehrenson does is justified since this gives the value of the unsubstituted compound infinite weight. Since the data correlated were ΔQ values, the fitted intercept has a value of $Q_H - Q_0$ and this was tested by the Student's t test. Most authors fit Q values, which in turn give a fitted intercept of Q_0 which almost invariably has a confidence level of 99.9% by the Student's test. This method is incorrect because all that it says is that Q_0 is significantly different from zero. There were 80 data sets with eight or more points. For eq 1, the number of data sets with the indicated confidence levels for the intercept are as follows: 99.9%, 0; 99%, 0; 98%, 0; 95%, 3; 90%, 3; 80%, 13; 50%, 22; 20%, 21; <20%, 18. For eq 2P (see footnote j of Table I): 99.9%, 0; 99%, 0; 98%, 1; 95%, 2; 90%, 5; 80%, 10; 50%, 30; 20%, 20; <20%, 12. Since a 95% confidence level is generally chosen as the limit of meaningfulness, it is clearly seen that only in three data sets is the use of an intercept of any importance.