J. Org. Chem. 1984, 49, 1997–2001

$(CH_3)_2C_6H_4CO_2H$, 99-64-9; anilinium, 17032-11-0; 3,5-dimethyl-4-nitrophenol, 5344-97-8; 3,5-di-*tert*-butyl-4-nitrobenzoic acid, 67688-81-7; 4-*tert*-butyl-3-nitrobenzoic acid, 59719-78-7; 4-*tert*-butyl-3-(dimethylamino)benzoic acid, 89302-57-8; *N,N,N′,N′*-tetramethyl-1,3-benzenediamine conjugate acid, 82316-53-8; 4,6,*N,N,N′,N′*-hexamethyl-1,3-benzenediamine conjugate acid, 89302-58-9; 4,6-*tert*-butyl-*N,N,N′,N′*-tetramethyl-1,3-benzenediamine conjugate acid, 89302-59-0.

Supplementary Material Available: Extensions of Tables I and II (3 pages). Ordering information is given on any current masthead page.

The Validity of the Revised *F* and *R* Electrical Effect Substituent Parameters

M. Charton

Chemistry Department, Pratt Institute, Brooklyn, New York 11205

Received October 26, 1983

We have examined the revised electrical effect separation recently proposed by Swain, Unger, Rosenquist, and Swain (SURS), *J. Am. Chem. Soc.* **1983**, *105*, 492. Our results include the following: (1) of 17 data sets which meet minimum requirements as test sets (5 or more data points, 3 or more sp^3 hybridized carbon atoms between substituent and active site, 4 or more different types of substituent) 11 gave best fit with σ_I and 2 with F_S, the SURS localized electrical (field/inductive) effect constant. The remaining 4 sets showed no significant difference in goodness of fit. The superiority of the σ_I constants is strikingly demonstrated by weighting the results for the difference in goodness of fit and for the number of data points in the set. (2) The SURS method requires that ionic groups in general and NMe_3^+ in particular be "well behaved", showing no more medium dependence than any other type of group. Our results show that ionic groups have a highly variable localized electrical effect. (3) The σ_I, σ_D separation gives values of C_L, the ratio of transmission of the localized effect from the meta position in benzene to that from the para position. These are in good agreement with values obtained from model systems, field effect calculations, and inductive effect calculations. By contrast, C_L values obtained from correlations with the SURS parameters generally lie outside the range of predicted values. (4) The σ_I values for MZ_n (Z = H or Me) groups are well fit by the equation $\sigma_{IMZ_n} = a_1\chi_M + a_2n_Z + a_0$ whereas F_S values are not. The results demonstrate the failure of the SURS method to achieve an effective separation of electrical effects. Use of the SURS parameters in correlation analysis should therefore be avoided.

Introduction

Some time ago we presented a compendium of localized (field and/or inductive) electrical effect substituent constants, σ_I, together with evidence that they were the best available measures of the localized electrical effect.[1] Recently, Swain and co-workers[2] have published a revised set of *F* values which they infer are the best available set of localized electrical effect substituent constants. In view of the very wide use of electrical effect constants in the application of correlation analysis to chemical reactivities, physical properties, inter- and intramolecular forces and bioactivities, it seemed to use to be of great importance to determine whether σ_I or *F* is a better measure of the localized electrical effect.

Methods

Swain and co-workers[2] (hereafter referred to as SURS) have noted that there are two fundamental assumptions inherent in their method: (1) Electrical effects resulting from a substituent separated from an active site by not less than three saturated carbon atoms are localized effects. An active site is simply an atom or group of atoms at which some quantifiable phenomenon occurs. (2) The trimethylammonia group is free of delocalized (resonance) electrical effects when bonded to a benzene ring.

Inherent in the SURS method are the further assumptions that ionic groups and hydroxylic groups are well behaved and present no problems. This is in sharp contrast to our conclusion that both ionic groups and to a lesser extent, hydroxylic groups (OH, CO_2H, and CH_2OH), are strongly medium dependent.[1]

We can test the validity of the SURS claims by correlating data for systems with three or more saturated carbon atoms separating substituent X and active site Y with both revised *F* and σ_I constants. As SURS claim that the revised *F* constants are valid for the set of all group types, they must also be valid for any subset. We have therefore restricted the correlations to substituents other than ionic or hydroxylic. If the SURS claim is correct, then the great majority of the data sets studied should give best correlation with the revised *F* values. If the σ_I constants are the better parameters for the localized electrical effect, a preponderence of the data set should give better results with them. We have examined only data sets with five or more data points and with at least four different types of groups. These are groups with significantly different localized effect parameter values. Those data sets which meet these requirements are designated with the prefix T. They are given in Table IS (tables designated S are in the supplementary material).

---

[1] Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119.

[2] Swain, C. G. Unger, S.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492.

0022-3263/84/1949-1997$01.50/0

Table I. Results of Correlations with Eq 1, 2, and 16

set	$f/L/C_L$	h/h^*	r[a]	F[b]	S_{est}[c]	$S_{f/L}$[c]	S_h[c]	S^0[d]	$100r^2$[e]	n[f]
T29F	−0.468	6.292	0.9927	204.0	0.0271	0.0327	0.0182	0.155	98.55	5
T29I	−0.727	6.290	0.9914	171.1	0.0295	0.0556	0.0198	0.169	98.28	5
T31F	−1.05	6.90	0.9597	58.25	0.0964	0.138	0.0801	0.333	92.09	7
T31I	−1.52	6.85	0.9766	103.1	0.0737	0.150	0.0566	0.255	95.37	7
T32F	−0.866	6.95	0.9483	53.61	0.0988	0.118	0.0768	0.366	89.93	8
T32I	−1.38	6.91	0.9888	262.1	0.0466	0.0852	0.0324	0.173	97.76	8
T36RF	−3.24	11.04	0.9692	170.1	0.304	0.248	0.154	0.268	93.02	13
T36RI	−5.05	10.96	0.9934	826.0	0.141	0.176	0.0679	0.125	98.69	13
T37F	−3.29	10.95	0.9982	1121	0.0857	0.0983	0.0577	0.0730	99.64	6
T37I	−5.10	10.94	0.9988	1634	0.0710	0.126	0.0477	0.0601	99.76	6
T38F	−3.26	9.84	0.9963	543.1	0.122	0.140	0.0821	0.105	99.27	6
T38I	−5.05	9.83	0.9969	648.5	0.112	0.198	0.0750	0.0959	99.39	6
T68F	−0.635	0.616	0.9248	82.69	0.0964	0.0699	0.0412	0.407	85.52	16
T68I	−1.11	0.609	0.9895	654.5	0.0367	0.0435	0.0148	0.155	97.91	16
T69F	−0.590	1.008	0.9787	113.9	0.0497	0.0553	0.0334	0.243	95.79	7
T69I	−0.949	1.008	0.9940	412.1	0.0265	0.0467	0.0177	0.130	98.80	7
T96F	−0.825	1.067	0.9918	419.3	0.0467	0.0403	0.0258	0.145	98.36	9
T96I	−1.23	1.057	0.9865	254.2	0.0597	0.0773	0.0326	0.186	97.32	9
T97F	−0.588	0.850	0.9880	285.8	0.0403	0.0348	0.0222	0.175	97.61	9
T97I	−0.881	0.844	0.9871	266.9	0.0417	0.0539	0.0227	0.181	97.44	9
T98F	−0.693	2.089	0.9913	395.5	0.0404	0.0348	0.0223	0.150	98.26	9
T98I	−1.04	2.082	0.9904	359.1	0.0424	0.0548	0.0231	0.157	98.09	9
T100F	−3.06	11.23	0.9365	121.3	0.393	0.278	0.167	0.371	87.71	19
T100I	−5.19	11.16	0.9917	1016	0.144	0.163	0.0569	0.136	98.35	19
T101F	−0.793	6.88	0.9495[g]	36.59[h]	0.0913	0.131[g]	0.0857	0.384	90.15	6
T101I	−1.23	6.87	0.9546[g]	41.11[h]	0.0866	0.192[g]	0.0792	0.365	91.13	6
T102F	−0.868	7.88	0.9327[g]	26.76[g]	0.117	0.168[g]	0.110	0.442	87.00	6
T102I	−1.38	7.88	0.9596[g]	46.46[h]	0.0911	0.202[g]	0.0833	0.345	92.07	6
T9NF	0.692	8.03	0.9749	153.4	0.0720	0.0559	0.0323	0.249	95.04	10
T9NI	1.09	8.02	0.9806	200.6	0.0634	0.0770	0.0287	0.219	96.16	10
T10NF	1.00	1.063	0.9894[g]	93.68[h]	0.0913	0.104[g]	0.0579	0.227	96.90	5
T10NI	1.67	1.016	0.9890[g]	134.5[h]	0.0766	0.144[g]	0.0514	0.191	97.82	5
M31/01	0.865	0.834	0.9813[i]	52.03[i]	0.0720	0.120[i]	0.767[k]	0.272	96.30	4
M40/37	1.07	0.733	0.9997	3712	0.0425	0.0176	0.174[l]	0.0328	99.95	4
T103F	−1.50	5.72	0.9870[g]	113.4[h]	0.122	0.141[g]	0.0964	0.207	97.42	5
T103I	−2.28	5.66	0.9993	1986	0.0295	0.0511	0.0221	0.050	99.85	5

[a] Correlation coefficient. [b] F test for significance. [c] Standard errors of the estimated slope (f, L, or C_2) and intercept (h or h^*), respectively. [d] S_{est} divided by the root mean square of the data. [e] Percent of the variance of the data accounted for by the correlation equation. [f] Number of data points in the set. [g] 99.0% confidence level (CL). [h] 99.5% CL. [i] 98.0% CL. [j] 97.5% CL. [k] 60.0% CL. [l] 95.0% CL.

Results and Discussion

It is of course necessary to exclude the pK_a's of 4-substituted [2.2.2]bicyclooctane-1-carboxylic acids in 50% aqueous ethanol and of (E)-4-substituted cyclohexanoic acids in water because they are the basis sets used in evaluating the σ_I and F_S values, respectively. We are left with 17 data sets in the literature which meet the requirements for a valid test of the localized electrical effect parameter. The results of correlations by linear regression analysis with the eq 1 and 2 are given in Table I.

$$Q_X = L\sigma_{IX} + h \qquad (1)$$

$$Q_X = fF_{S,X} + h \qquad (2)$$

Of the 17 sets studied, 11 gave best results (higher values of F and $100R^2$ and lowest values of S_{est} and S^0) with σ_I, two with F_S and four showed no significant difference in the quality of correlations. Δ is defined as shown in eq 3. Sets with Δ values less than 0.25 were considered to

$$\Delta \equiv |100R^2{}_I - 100R^2{}_F| \qquad (3)$$

be equally well correlated by σ_I and F_S. Clearly correlation with σ_I value generally gives better results than that with F_S values. In order to establish just how much better the results with σ_I are as compared to those with F_S, it is necessary to include weighting factors for the number of data points in the set, n, and the difference in the goodness of fit. As a measure of the significance of the number of data points we have used the square root of n. This quantity is used to determine the advantage of replication in the reliability of a measurement,[3] a situation somewhat analogous to that of the reliability of a data set. As a weighting factor for goodness of fit we have chosen Δ, defined in eq 3. We then calculate the quantity Γ given by eq 4 for each data set. For the data sets which give

$$\Gamma \equiv n^{1/2}\Delta \qquad (4)$$

significantly better correlation with σ_I, $\Sigma\Gamma = 178$. For those that give significantly better correlation with F_S, $\Sigma\Gamma = 4$.

Table II. Values of $\overline{\sigma}_I$, S and S_{rel}

X	$\overline{\sigma}_I$[a]	σ_I[b]	S[c]	S_{rel}	n[d]
NMe_2^+	0.948	1.07	0.110	3.96	11
CO_2^-	−0.0947	−0.19	0.106	3.81	15
OH	0.283	0.24	0.0564	2.03	21
CH_2OH	0.0888	0.11	0.0429	1.54	8
CO_2H	0.308	0.30	0.0338	1.22	13
Me	0.004	−0.01	0.0174	0.626	15
CO_2Me	0.312	0.32	0.0244	0.878	17
Br	0.467	0.47	0.0292	1.05	30
CN	0.587	0.57	0.0278	1.00	32
OMe	0.310	0.300	0.0449	1.62	15

[a] Arithmetic mean of σ_I. [b] From ref 1. [c] Standard deviation. [d] Number of σ_I values used to obtain $\overline{\sigma}_I$ and S.

---

(3) Wilson, E. B., Jr. "An Introduction to Scientific Research"; McGraw-Hill: New York, 1952; p 252.

Table III. Results of Correlations with Eq 6, 8, and 17

set	a_1/λ	a_2/δ	a_0/h	R[a]	F[b]	r_{12}[c]	S_{est}[d]
501	0.0327	−0.216	0.616	0.9784	56.02	0.181	0.0620
502	0.177	−0.208	0.387	0.8626[i]	10.17[i]	0.428	0.094
511	1.55	−0.275	0.00195	0.9501	115.9	0.092	0.111
512	0.999	3.74	0.0560	0.9681	186.5	0.092	0.307
551	1.03	1.59	−0.0348	0.9959	1028	0.086	0.0437
552	1.18	1.15	0.00966	0.9974	1656	0.239	0.0363
553	1.03	0.966	0.0149	0.9977	1621	0.144	0.0236

set	S_1[d]	S_2[d]	S_h[d]	S^0[e]	$100R^2$[f]	n[g]
501	0.0383[h]	0.0211	0.119[i]	0.261	95.73	8
502	0.107[j]	0.0596[k]	0.333[l]	0.605	74.40	10
501	0.103	0.0726	0.0407[m]	0.330	90.27	28
512	0.285[i]	0.201	0.113[n]	0.265	93.72	28
551	0.0404	0.0450	0.0164[o]	0.0982	99.18	20
552	0.0373	0.0293	0.0144[p]	0.0775	99.49	20
553	0.0248	0.0298	0.0102[q]	0.0743	99.54	18

[a] Multiple correlation coefficient. [b] F test for significance. [c] Partial correlation coefficient of one independent variable with the other. [d] Standard errors of the estimate and the regression coefficients (a_1 or λ, a_2 or δ, a_0 or h). [f] Percent of the variance of the data accounted for by the regression equations. [g] Number of data points in the set. [h] 50.0% CL. [i] 99.0% CL. [j] 60.0% CL. [k] 98.0% CL. [l] 70.0% CL. [m] 0% CL. [n] 30.0% CL. [o] 95.0% CL. [p] 40.0% CL. [q] 80.0% CL. Superscripts indicate the CL of R, F, and the student t tests of the regression coefficients. In the absence of a superscript, the CL is 99.9%. All r_{12} values are significant at less than the 90.0% CL.

Obviously, the results with σ_I are dramatically better than those obtained with F_S.

We have remarked that the σ_I values for ionic groups are highly variable and those for hydroxylic groups somewhat variable due to the effects of the medium. To verify this point we have calculated σ_I values from a large number of data sets for these groups and also for purposes of comparison with a number of ordinary groups. Calculated σ_I values are given in Table IIS; means and standard deviations are given in Table II. The standard deviation of the mean values for σ_I is clearly greatest for the ionic groups NMe_3^+ and CO_2^-. If we define the ratio S_{rel} by eq 5 and choose as X^0 the cyano substituent, we see that S_{rel}

$$S_{rel} = S_X/S_{X^0} \qquad (5)$$

= 3.8 for ionic groups and S_{rel} = 2.0 for OH. Thus, the evidence shows that σ_I values for ionic groups are indeed highly variable. That for OH, and possibly that for OMe as well, are somewhat variable. The value for CO_2H is normal in behavior. The data available for CH_2OH are insufficient to permit any conclusion.

We have shown elsewhere[4,5] that σ_{IX} values where X is MZ_n obey the relationship in eq 6 in which χ_M is the

$$\sigma_{IX} = a_2\chi_M + a_2n_Z + a_0 \qquad (6)$$

Allred–Rochow electronegativity[6] of M. Z is a constant group and n is the number of Z groups bonded to M. This relationship is *not* observed for delocalized electrical effect constants σ_D. We have correlated the F_S constants with eq 6 by means of multiple regression analysis. The sets studied are given in Table IIS. The results are reported in Table III for Z = H or Me. They are somewhat better with σ_I than with F_S when Z = H but vastly better with σ_I when Z = Me (for σ_I $100R^2$ valus are (H) 98.08 and (Me) 98.83).

Furthermore, in the correlations of F_S with eq 6, a_1 is *not* significant whereas in the correlations of σ_I, a_1 is significant.

It is important to note that the χ values used in eq 6 were obtained completely independently from the data used to define σ_I and F_S. Furthermore the n_Z values are pure numbers free from error. Equation 6 has been shown to be applicable to a wide range of groups Z. It is extremely unlikely that eq 6 is a chance relationship. Then if this equation represents a valid relationship between the electronegativity of the atom M, the number of Z groups perturbing that electronegativity, and the localized electrical effect parameter, it follows that F_S is not as good a parameter as is σ_I.

Finally let us consider the value of C_L, the ratio of the localized effect from the meta position to that from the para position in benzene. Thus for eq 7 t indicates the

$$C_{LI}^t = \lambda_m/\lambda_p^t,\ C_{LF}^t = f_m/f_p^t \qquad (7)$$

substituent type: nothing for σ_p, zero for σ_p^0, plus for σ_p^+, and minus for σ_p^-. The values of f_m, f_p, f_p^+, f_p^-, and f_p^0 used are from the correlations reported by SURS;[2] the values of λ_m and λ_p are from our earlier work.[1] Values of λ_p^+, λ_p^-, and λ_p^0 come from correlation with eq 8. The localized

$$\sigma_p^+ = \lambda_p^t\sigma_I + \delta_p^t\sigma_R^t + h \qquad (8)$$

effect generally should not show much variation once substituent position and skeletal group are specified provided that the active site is not separated from the ring by too long a side chain. Thus, for C_L, C_L^0, C_L^+, and C_L^-, we expect about the same magnitude. The data used to obtain λ_p^+, λ_p^- and λ_p^0 are given in Table IIIS; results of correlations with eq 8 are in Table III. Values of C_{LI} and C_{LF} are reported in Table IV. The C_{LF} values show a dramatic variation. The ratio ϕ_F, defined as in eq 9a and 9b, ranges from 0.90 to 1.45. By contrast the range in ϕ_I is 0.85 to 1.00.

$$\phi_F^t = C_{LF}^t/C_{LF} \qquad (9a)$$

$$\phi_I^t = C_{LI}^t/C_{LI} \qquad (9b)$$

There are three methods available for determining C_L values. They can be calculated from the Kirkwood–Westheimer equation.[7] Values calculated by this method are in the range 0.936 to 1.087. Alternatively, values of

---

(4) Charton, M., unpublished results.

(5) Charton, M. In "The Chemistry of Functional Groups, Supplement C" Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; p 269.

(6) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.

(7) Kirkwood, J. G.; Westheimer, F. H. *J. Chem. Phys.* **1938**, *6*, 506. Westheimer, F. H.; Kirkwood, J. G. *Ibid.* **1938**, *6*, 513. Westheimer, F. H.; Shookhoff, M. W. *J. Am. Chem. Soc.* **1939**, *61*, 555. Westheimer, F. H. *Ibid.* **1939**, *61*, 1977.

Table IV. Values of C_L and ϕ

t^a	$C_{LF}{}^t$	$\phi_F{}^t$	$C_{LI}{}^t$	ϕ_{LI}
R	1.16	1.00	0.999	1.00
RP	1.24	1.07	0.970	0.97
RM	1.68	1.45	0.847	0.85
RZ	1.04	0.90	0.970	0.97

[a] Substituent type. R = σ_p, RP = $\sigma_p{}^+$, RM = $\sigma_p{}^-$, RZ = $\sigma_p{}^0$.

C_L may be obtained from model systems of suitable geometry free of delocalized (resonance) electrical effects. Finally, the improved inductive effect model of Exner and Fiedler[8] can be used. As this last method is applicable only to saturated systems it too involves the use of appropriate model systems.

In order to avoid a choice of any particular substituent constant in obtaining C_L values we derive a relationship which gives this quantity directly. For the system which models the meta substituted benzenes we may write

$$Q_{mX} = L_m\sigma_{LX} + h_m \qquad (10)$$

and for the corresponding para system

$$Q_{pX} = L_p\sigma_{LX} + h_p \qquad (11)$$

In eq 10 and 11 σ_L is the true localized electrical effect parameter, which is here presumed unknown, and Q is some measured quantity such as pK_a or log k. Then

$$(Q_{mX} - h_m)/L_m = (Q_{pX} - h_p)/L_p = \sigma_L \qquad (12)$$

and

$$Q_{mX} - h_m = (L_m/L_p)(Q_{pX} - h_p) \qquad (13)$$

or

$$Q_{mX} = (L_M/L_p)Q_{pX} - (L_m/L_p)h_p + h_m \qquad (14)$$

Then as L_m as $\rho\lambda_m$ and $L_p = \rho\lambda_p{}^1$ it follows from eq 7 that

$$Q_{mX} = C_LQ_{pX} - C_Lh_p + h_m \qquad (15)$$

Thus,

$$Q_{mX} = C_LQ_{pX} + h \qquad (16)$$

We have correlated data for model systems with eq 16. The data used are reported in Tables IS; results of the correlations are in Table I (sets designated by the prefix M). The C_L values obtained are 0.865 ± 0.120 for the 3-substituted adamantane-1-carboxylic acid (**3-A**)/4-substituted bicyclo[2.2.2]octane-1-carboxylic acid (**4-O**) model and 1.07 ± 0.0176 for the 3-substituted quinuclidinium (**3-Q**)/4-substituted quinuclidinium (**4-Q**) model. Values of C_L for these model systems calculated from the Kirkwood–Westheimer equation are 0.806 for **3-A**/**4-O** and 1.05 for **3-3A**/**4-Q**. The Exner–Fiedler method gives C_L values of 1.00 for the **3-A**/**4-O** model and 0.893 for the **3-O**/**4-O** model. These values of C_L obtained from the three methods are generally in better agreement with the C_{LI} values than they are with the C_{LF} values. The model systems combined with the Kirkwood–Westheimer calculations indicate that C_L lies in the range 0.865 to 1.087. All of the C_{LI} values are in this range. All but one of the C_{LF} values lie outside it. Thus, both the magnitude and the variability of C_{LF} show that the revised F_S and R_S parameters are not valid localized and delocalized electrical effect substituent constants.

We have presented a considerable body of evidence which shows that F_S and R_S are not "pure" localized and delocalized electrical effect parameters. What then are they? If they are not "pure" electrical effect parameters they must be composite electrical effect parameters. Any composite electrical effect parameter can be resolved into its localized and delocalized effect components by correlation with an equation which is analogous to eq 8. In eq 17 represents the composite substituent constant. We have

$$\sigma_{TX} = \lambda\sigma_{IX} + \delta\sigma_{DX} + h \qquad (17)$$

correlated F_S and R_S values with this equation. The data used are reported in Table IIS; the results of the corelations are in Table III. We may conveniently interpret the results by means of the percent delocalized effect, P_D, defined by eq 18 and the electrical effect composition ratio

$$P_D = (|\delta|\cdot 100)/(|\lambda| + |\delta|) \qquad (18)$$

ϵ, defined by eq 19. Values of P_D and of ϵ are given in

$$\epsilon = \delta/\lambda \qquad (19)$$

Table V. It is interesting to note that ϵ for F_S is negative.

Table V. Values of P_D and ϵ

	P_D	S_P	ϵ	S
F_S	15.1	4.11	−0.177	0.0483
R_S	78.9	7.19	3.74	1.09

Our results show that F_S and R_S are indeed composite substituent parameters. Though predominantly a function of the localized electrical effect F_S includes a delocalized (resonance) contribution of about 15%. R_S is largely a function of the delocalized effect but includes a localized effect contribution of about 20%. If the only purpose of correlation analysis were to develop equations for predicting chemical, physical, or biological properties as a function of structural variation F_S and R_S, or any other pair of composite electrical effect parameters of different composition, would suffice. Another more important purpose of correlation analysis is the provision of a quantitative separation of electrical effects to aid in mechanistic interpretation of chemical reactivities and the nature of electrical effects upon physical properties and biological activities. For this purpose the revised F and R parameters are unacceptable.

Conclusions

Our results lead inexorably to the following conclusions: (1) A study of systems which all workers in the field agree are as free of delocalized (resonance) electrical effects as it is possible to be shows that σ_I is a very much better localized electrical effect parameter than is F_S. (2) Ionic groups have highly variable localized effect parameters. The OH and perhaps the OMe groups have somewhat variable parameters, the CO_2H group seems to behave normally. The extensive work of Wepster and his group supports our conclusions regarding the variability of substituent constants for ionic groups.[9] (3) The results obtained with eq 6 cast further doubt on the validity of the F_S constants as a "pure" measure of the localized electrical effect. (4) The $C_{LF}{}^t$ values show that (a) There is far too much variability in C_{LF} for the SURS electrical effect separation to be valid. (b) The C_{LF} values, except for $C_{LF}{}^0$ lie outside the range of the C_L values obtained from the Kirkwood–Westheimer equation or from model systems.

---

[8] Exner, O.; Fiedler, P. *Collect. Czech. Chem. Commun.* **1980**, *45*, 1251.

[9] Hoefnagel, A. J.; Hoefnagel, M. A.; Wepster, B. M. *J. Org. Chem.* **1978**, *43*, 4720; van de Graaf, B.; Hoefnagel, A. J.; Wepster, B. M. *Ibid.* **1981**, *46*, 653. Hoefnagel, A. J.; Wepster, B. M. *Ibid.* **1982**, *47*, 2318.

As the F_S parameters are not true localized electrical effect parameters it follows that the treatment of SURS does not constitute a successful separation of electrical effects. No valid conclusions concerning the nature of substituent effects may be drawn from correlations with the revised F and R constants, and therefore the use of these constants serves no practical or useful purpose. That this is the case is hardly surprising in view of the large body of data which has accumulated[1] indicating that the NMe$_3^+$ group, contrary to the statements of SURS, has a significant electron donor delocalized effect.

Supplementary Material Available: Tables of test and model data, calculated values of σ_I, and data correlated with eq 6, 8, and 17 (6 pages). Ordering information is given on any current masthead page.

Linear Solvation Energy Relationships. 28. An Analysis of Swain's Solvent "Acity" and "Basity" Scales

R. W. Taft,* Jose-Luis M. Abboud,* and Mortimer J. Kamlet*

Department of Chemistry, University of California, Irvine, California 92717, Departement de Chimie, Universite Cadi Ayyad, Marrakech, Morocco, and Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland 20910

Received December 14, 1983

From a computer correlation involving 1080 data sets for 61 solvents and 77 reactions and physicochemical properties, Swain and co-workers have concluded that all solvent effects can be rationalized in terms of two solvent property scales, A, measuring anion solvating ability or "acity", and B, measuring cation solvating ability or "basity". On this basis they assert that, in the three parameter Taft–Abboud–Kamlet correlations, the hydrogen bond acceptor (HBA) basicity parameter, β, is superfluous. It is shown that of Swain's 77 properties, 71 involve non-hydrogen bond donor (non-HBD) solutes and the other 6 involve only very weak or non-HBA solvents, so that conditions necessary for applicability of β are not met. For properties which do involve HBD solutes and HBA solvents, correlations with A/B are shown to be of substantially poorer quality than corresponding π^*/β correlations. Rather than being a "basity" measure, B is shown to measure solvent dipolarity/polarizability.

Swain, Swain, Powell, and Alluni (SSPA) have recently[1] described the formulation of two new solvent property scales: A, represented as a measure of anion-solvating ability or "acity" and B, represented as a measure of cation solvating ability or "basity". These scales were arrived by at least-squares fitting of the data for 77 reactions and physicochemical properties (for a total of 61 solvents) to equations of the form of eq 1, where A and B characterize

$$P = P_0 + aA + bB \tag{1}$$

the solvent and P, P_0, a and b depend only on the reaction or property. They reported that the two unrelated parameters (A and B) alone account for over 98% of the effects from changing solvent in the set of 1080 typical rates, equilibria, and spectral energies that they examined. By any standards their effort represents a prodigious computational undertaking.

SSPA also reported comparisons of their correlations with those obtained for 18 of their reactions and properties using the present authors' (TAK)[2,3] solvatochromic parmeters π^*, δ, α, and β in equations of the generalized form of eq 2. Generally the regression eq 1 and 2 were said to

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta \tag{2}$$

be of comparable quality in spite of noninclusion of many data by TAK; 365 data gave an overall correlation coefficient, r, of 0.987 for the 18 SSPA correlations, while 279 data gave an overall r value of 0.984 for the same 18 TAK correlations. The TAK correlations in the above comparisons were with π^* and α, and addition of the β term was said not to improve the fits.

That the two-parameter SSPA correlations showed slightly better goodness of fit than the TAK correlations, despite the fact that TAK were said to have the option of using any or all of four different solvent constants in eq 2, and despite the fact that TAK were said to have omitted from important reactions many solvents that SSPA retained, was cited as further evidence of the superiority of the A–B parameters over the π^*–δ–α–β parameters. Further, based on the above comparison, SSPA concluded that three or more solvent constants were superfluous in correlating solvent effects since the fits with two constants were already satisfactory ($r > 0.98$) and additional constants yielded no improvement. They concluded specifically that correlations of reactions with the β parameter are generally unsatisfactory and that the β parameter is superfluous.

We wish now to record our complete and unreserved agreement that, insofar as SSPA's 77 data sets are concerned, the β parameter which is the solvatochromic measure of solvent hydrogen bond acceptor (HBA) basicity, indeed, is superfluous. The reasons are as follows. Despite misconceptions set forth by SSPA, the solvatochromic parameters of TAK follow a quite rigid set of rules. Wherever solutes are hydrogen bond donor acids, (or certain nonprotonic Lewis acids) and solvents are HBA bases, the TAK correlations have always shown significant dependences on the β parameter. When these conditions are not fulfilled, the TAK correlations never included

---

[1] Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* **1983**, *105*, 502.

[2] Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 1080.

[3] Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

0022-3263/84/1949-2001$01.50/0