Substituent Effects. 10. Critique of the "Improved Evaluation of Field and Resonance Effects" Proposed by Swain et al.

A. J. Hoefnagel, W. Oosterbeek, and B. M. Wepster*

Laboratory of Organic Chemistry, Technische Hogeschool, Delft, The Netherlands

Received September 8, 1983

It is shown that the equation $p = fF + rR + h$ is not satisfactory for the separation of resonance and nonresonance effects or the prediction of substituent effects. Examples include data on the results of steric elimination of resonance, the behavior of charged groups, and gross deviations in substituted phenols and anilinium ions. Some of the reasons behind the failures are indicated.

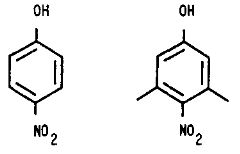
In a recent paper, Swain, Unger, Rosenquist, and Swain[1] presented an "improved evaluation of field and resonance components" in substituent effects, in terms of eq 1. Here

$$p = fF + rR + h \tag{1}$$

F (the nonresonance or "field" constant) and R (the resonance constant) depend on only the substituent while f, r, and h depend on the reaction series but are entirely independent of substituent, and p is the predicted substituent effect; we write Δ for the experimental effect. By a documented statistical procedure the best F and R values were derived for 43 substituents from 220 data points in 14 reaction series, and their applicability was investigated in 32 more data sets.

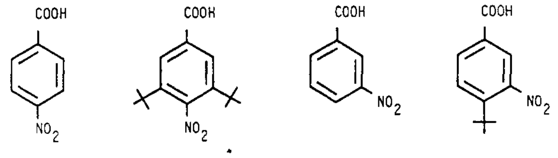
We do not share the evident optimism of Swain et al. with respect to the virtues of eq 1 and wish to give a small selection of our comments in the following three sections. Table I contains statistical results and derived figures obtained when using Swain et al.'s F and R values in eq 1; Table II lists the data sets. In some charts we compare individual experimental data with data calculated with f and r values from Table I.

Chart I



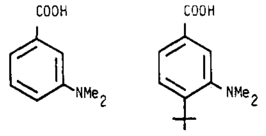
	H_2O	H_2O
Δ-NO_2	2.76	1.85
$f F \rho$	1.03	
$r R \rho$	1.47	

Chart II



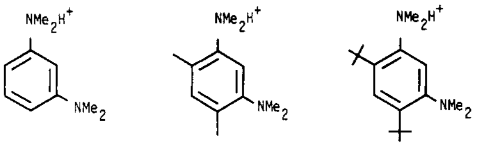
	50E	50E	50E	50E
Δ-NO_2	1.19	1.05	1.07	1.06
$f F$	0.78	0.78	0.90	0.90
$r R$	0.41	0	0.20	0

Chart III



	50E	50E
Δ-NMe_2	-0.14	0.00
$f F$	0.62	0.62
$r R$	-0.76	0

Chart IV



	50E	50E	85E
Δ-NMe_2	-0.57	0.09	0.19
$f F$	1.69		
$r R$	-2.36		

1. Evidence from the Results of Sterically Inhibiting the Resonance. Swain et al. refer to work by Wheland et al.[2] concerning the effects on acid strength of a para nitro group (Δ-4-NO_2) in phenol and 3,5-dimethylphenol (Chart I). The observed decrease of Δ led Wheland to the conclusion that one third to one half of the effect in 4-nitrophenol is attributable to resonance. Swain et al. see this as showing that their scaling of $F = R = 1$ for NO_2 is "appropriate and permits us to compare F with R values rather than only an F with other F's or an R with other R's". We note that the same conclusion could have been drawn for the nitro group in 4-nitroanilinium ion from a much more detailed study of 3-alkyl- and 3,5-dialkyl-4-nitroanilines with varying and known degrees of the reduction of the resonance.[3]

However, these σ_p^- reactions of ArOH or $ArNH_3^+$ do not have a privileged position, and other reaction series give different results. Chart II[4] shows that elimination of the resonance effect of the 4-nitro group in ArCOOH reduces its influence by 0.14 pK units. The same reasoning as above now leads to 100(0.14/1.19) = 12% resonance (12% r), and suggests a scaling of F:R = 0.88:0.12 rather than 1:1. Also, our experimental percent r differs strongly from the 38% r derived by Swain et al. As for the 3-NO_2 group

---

(1) Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492. Cf. Swain, C. G.; Lupton, E. C., Jr. *Ibid.* **1968**, *90*, 4328.

(2) Wheland, G. W. "Resonance in Organic Chemistry"; Wiley: New York, 1955; pp 367-368. See also: Wheland, G. W.; Brownell, R. M.; Mayo, E. C. *J. Am. Chem. Soc.* **1948**, *70*, 2492.

(3) Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1957**, *76*, 335. Burgers, J.; Hoefnagel, M. A.; Verkade, P. E.; Visser, H.; Wepster, B. M. *Ibid.* **1958**, *77*, 491. Reference 6.

(4) Hoefnagel, A. J.; Hoefnagel, M. A.; Wepster, B. M. *J. Org. Chem.* **1978**, *43*, 4720. Also: Hoefnagel, A. J.; Wepster, B. M. *Ibid.* **1982**, *47*, 2318.

0022-3263/84/1949-1993$01.50/0

Table I.[a] Analysis of Equation 1[b]

no.	series	solv	n	f	r	h	% r	s	C	NMe_3^+ Δ-p	NMe_3^+ F	SO_3^-, Δ-p	types of substituents	
						ArCOOH[c]								
1	meta	H_2O	43[d]	0.57 ± 0.02	0.14 ± 0.01	−0.01 ± 0.01	20	0.02	0.998[d]	0.16[e]	1.82[e]	0.06[e]	DP	S[d]
2		10E	17	0.61 ± 0.03	0.15 ± 0.01	0.00 ± 0.02	20	0.04	0.989	0.17	1.82	0.03	D	
3			19	0.65 ± 0.03	0.15 ± 0.01	−0.01 ± 0.02	19	0.05	0.988				+39 +41	
4		50E	23	0.90 ± 0.05	0.20 ± 0.02	−0.08 ± 0.03	18	0.08	0.982	0.40	1.99	0.09	D	
5			25	0.99 ± 0.05	0.21 ± 0.02	−0.09 ± 0.04	18	0.11	0.978				+39 + 41	
6	para	H_2O	43[d]	0.49 ± 0.03	0.30 ± 0.02	−0.02 ± 0.02	38	0.04	0.994[d]	0.25[e]	2.04[e]	0.07[e]	DP	S[d]
7		10E	12	0.52 ± 0.04	0.33 ± 0.01	−0.01 ± 0.03	39	0.05	0.995	0.24	2.00	0.02	D	
8			14	0.60 ± 0.04	0.33 ± 0.02	−0.04 ± 0.03	35	0.07	0.989				+39 +41	
9		50E	23	0.78 ± 0.03	0.41 ± 0.01	−0.04 ± 0.02	34	0.06	0.995	0.34	1.97	−0.01	D	
10			25	0.86 ± 0.04	0.42 ± 0.01	−0.06 ± 0.03	33	0.08	0.992				+39 +41	
11		75E	23	0.82 ± 0.05	0.45 ± 0.01	0.00 ± 0.03	35	0.08	0.993	0.47	2.11	−0.21	D	
12			25	0.96 ± 0.06	0.45 ± 0.02	−0.05 ± 0.04	32	0.12	0.987				+39 +41	
13		H_2O	5	0.45 ± 0.04	0.24 ± 0.07	0.08 ± 0.04	35	0.01	0.998				5-M	S[d]
14			6	0.41 ± 0.03	0.34 ± 0.01	0.03 ± 0.02	45	0.01	1.000				+NH_2	S[d]
						$ArCH_2COOH$[f]								
15	para	10E	12	0.29 ± 0.04	0.13 ± 0.01	−0.01 ± 0.03	31	0.04	0.977	0.19	2.21	−0.11	D	
16			14	0.40 ± 0.04	0.13 ± 0.02	−0.07 ± 0.03	25	0.06	0.969				+39 +41	
17		50E	12	0.39 ± 0.04	0.18 ± 0.02	−0.01 ± 0.03	32	0.04	0.985	0.38	2.51	−0.17	D	
18			14	0.58 ± 0.06	0.17 ± 0.03	−0.12 ± 0.05	23	0.09	0.962				+39 +41	
19		75E	12	0.46 ± 0.04	0.22 ± 0.01	−0.01 ± 0.03	32	0.04	0.993	0.48	2.59	−0.33	D	
20			14	0.74 ± 0.08	0.20 ± 0.04	−0.19 ± 0.06	21	0.12	0.959				+39 +41	
						$ArCH_2CH_2COOH$[g]								
21	para	50E	4	0.23 ± 0.01	0.08 ± 0.00	0.00 ± 0.00	26	0.00	1.000	0.32	2.91	−0.32	D	
22			6	0.51 ± 0.10	0.03 ± 0.05	−0.18 ± 0.08	6	0.13	0.955				+39 +41	
23		75E	4	0.32 ± 0.01	0.10 ± 0.00	0.00 ± 0.01	24	0.01	1.000	0.44	2.91	−0.40	D	
24			6	0.69 ± 0.13	0.03 ± 0.06	−0.23 ± 0.10	4	0.17	0.957				+39 +41	
						$ArCH_2CH_2COOEt + OH^-$[h]								
25	para	88E	9	0.37 ± 0.06	0.12 ± 0.01	−0.03 ± 0.04	24	0.05	0.978	0.63	3.24		D	
26			10	0.67 ± 0.12	0.14 ± 0.04	−0.14 ± 0.11	17	0.17	0.937				+41	
						ArOH[i]								
27	para	H_2O	17	0.46 ± 0.03	0.66 ± 0.03	0.05 ± 0.02	59	0.06	0.997	0.03	1.57	0.05	DP	S[d]
28			12	0.47 ± 0.07	0.61 ± 0.05	0.06 ± 0.03	56	0.06	0.993	−0.03	1.51	0.09	D	S[d]
29			9	0.52 ± 0.10	0.65 ± 0.11	−0.01 ± 0.05	56	0.06	0.987	−0.04	1.50	0.20	8-M, H	S[d]
30			9	0.37 ± 0.09	0.12 ± 0.02	−0.07 ± 0.04	24	0.08	0.908	0.62	2.27	0.95	8+M,[j] H	
						$ArNMe_2H^+$[i]								
31	meta	50E	7	2.45 ± 0.08	0.62 ± 0.02	0.10 ± 0.05	20	0.08	0.999	−0.79	1.22		D	
32			8	2.11 ± 0.16	0.59 ± 0.06	0.17 ± 0.13	22	0.24	0.991	−0.34	1.38		+41	
33	para	50E	14	2.94 ± 0.59	1.23 ± 0.16	0.02 ± 0.40	29	0.76	0.946	−1.47	1.04		D	
34			10	1.95 ± 0.23	2.47 ± 0.16	0.32 ± 0.14	56	0.25	0.994	−0.24	1.42		-4+M	
35			10	1.52 ± 0.35	0.71 ± 0.10	−0.12 ± 0.19	32	0.34	0.936	0.86	2.11		9+M,[k] H	
36			5	1.02 ± 0.98	0.55 ± 0.22	−0.20 ± 0.39	35	0.41	0.893	1.71	3.22		4+M, H	
37			4	3.02 ± 0.15	0.48 ± 0.02	−1.66 ± 0.09	14	0.03	0.999	0.09	1.57		4+M	
						$ArCMe_2Cl + H_2O$[d]								
38	para	90A	23	0.34 ± 0.02	0.55 ± 0.01	−0.06 ± 0.01	62	0.04	0.997	−0.25	1.38		DP	S[d]
39			21	0.34 ± 0.02	0.55 ± 0.01	−0.04 ± 0.01	62	0.04	0.998	−0.34	1.32		D	S[d]
40			16	0.37 ± 0.03	0.57 ± 0.01	−0.04 ± 0.01	61	0.03	0.997	−0.55	1.21		15+M, H	S[d]
41			5	0.41 ± 0.12	0.33 ± 0.22	0.05 ± 0.12	45	0.04	0.982	−1.24	0.87		5-M	S[d]
42			6	0.40 ± 0.10	0.41 ± 0.11	0.01 ± 0.03	51	0.03	0.996	−0.99	1.00		+H	S[d]

no.	input H-NH$_2$	solvent	*n*	*f*	*r*	*h*	% *r*	*s*	*C*	NMe$_3^+$ Δ-*p*	NMe$_3^+$ *F*	NH$_2$, Δ-*p*	types of substituent
	Δ-NH$_2$					ArCMe$_2$Cl + H$_2$O[d]							
A	−0.6	90A	6	0.42 ± 0.07	0.32 ± 0.01	0.06 ± 0.04	43	0.03	0.9988	−1.36	0.83	−0.0001	5-M, NH$_2$
B	−0.9		6	0.38 ± 0.07	0.42 ± 0.01	0.01 ± 0.04	53	0.03	0.9992	−0.85	1.05	0.0009	
C	−1.2		6	0.34 ± 0.08	0.51 ± 0.01	−0.03 ± 0.05	60	0.04	0.9993	−0.39	1.29	0.0018	
D	−1.5		6	0.30 ± 0.09	0.61 ± 0.02	−0.08 ± 0.06	67	0.04	0.9993	0.11	1.63	0.0028	
E	−1.8		6	0.26 ± 0.10	0.70 ± 0.02	−0.12 ± 0.07	73	0.05	0.9992	0.58	2.03	0.0037	
F	−2.1		6	0.22 ± 0.12	0.80 ± 0.02	−0.17 ± 0.08	78	0.06	0.9992	1.09	2.63	0.0047	
	R-NH$_2$												
G	−2.5		6	0.32 ± 0.08	0.55 ± 0.02	−0.05 ± 0.05	63	0.04	0.9993	−0.15	1.43	0.0022	
H	−4		6	0.40 ± 0.07	0.37 ± 0.01	0.04 ± 0.04	48	0.03	0.9995	−1.13	0.92	0.0003	

[a] Solvent: 10E, 10% ethanol, etc., 90A, 90% acetone; *n*, number of data in set; *f*, *r*, and *h* were evaluated by nonlinear least squares (Hamilton, W. C. "Statistics in Physical Science"; Ronald Press: New York, 1964), (multiple) correlation coefficients, *C*, standard deviations, *s*, and errors are defined as usual (Shorter, J. "Correlation Analysis of Organic Reactivity"; Research Studies Press: Chichester, 1982); $\%r = 100\ r/(f + r)$ as in ref 1; Δ, observed substituent effect; *p*, substituent effect calculated from eq 1; $F = (\Delta - h)/f$, and $F = (\Delta/\rho - h)/f$ for ArOH and ArCMe$_2$Cl (see ref 1); substituents coded as DP, dipoles and poles, D, dipoles only, 39, SO$_3^-$, 41, NMe$_3^+$, 5-M, five π-acceptor dipoles CF$_3$, COOH, COOEt, CN, NO$_2$), *n*-M, *n* π-acceptor dipoles, 4+M, four π-donors (NMe$_2$, NHAc, OH, OMe), *n*+M, *n* π-donor dipoles; Δ-NH$_2$, input data for effect NH$_2$, *R*-NH$_2$, input resonance parameter NH$_2$. [b] Further data on meta series and on meta and para ArNH$_3^+$ in supplementary material. [c] Part of the data in ref 4. [d] Reference 1; *C* of ArCOOH in water has been defined differently. [e] Based on data in ref 4, using *f*, *r*, and *h* from set 1 or 6. [f] Reference 10. [g] Hoefnagel, A. J.; Monshouwer, J. C.; Snorn, E. C. G.; Wepster, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 5350. [h] Fuchs, R.; Caputo, J. A. *J. Org. Chem.* **1966**, *31*, 1524; for NMe$_3^+$ see ref 4, Table V. [i] Part of the data for +M groups in ref 8. [j] 8+M: Me, *t*-Bu, NH$_2$, NMe$_2$, OH, OMe, F, Br. [k] 9+M: Me, *t*-Bu, NMe$_2$, NHAc, OH, OMe, F, Cl, Br.

our data indicate (formally) 1% *r* as compared with 20% *r* derived by Swain. Twisting is also found to be ineffective when comparing Δ-3-NO$_2$ in anilinium- and 4-*tert*-butylanilinium ion.[5]

Such discrepancies are not limited to the nitro group. Charts III and IV give data for the 3-NMe$_2$ group in ArCOOH[5] and ArNMe$_2$H$^+$.[5,6] In either case both the resonance and the nonresonance appear as strongly overestimated by the approach of Swain et al.; the experimental substituent effect of a "perpendicular" NMe$_2$ group is invariably small.

2. Charged Substituents. Contrary to what Swain et al. believe, the effects of charged substituents (poles) do not fit eq 1. This is illustrated in Table I in several ways. Firstly, if the dipole substituent data give a satisfactory fit, addition of data pertaining to NMe$_3^+$, or NMe$_3^+$ and SO$_3^-$, usually affects the values of *f* and *r* and causes serious damage to *s*, to *C*, and to the uncertainty in *f* and *r* (e.g., sets 19–20, 25–26, and 31–32). Secondly, considerable differences are found between Δ observed for NMe$_3^+$ and SO$_3^-$ and the values of *p* calculated when using *f*, *r*, and *h* from the dipole correlation. Thirdly, the values of *F* of NMe$_3^+$ required to fit the dipole regression plane are far from constant, varying from roughly 1 to 3 in the para series.

The variation of *F* values for NMe$_3^+$ is, not surprisingly, parallel with the variation of the Hammett $\sigma = \Delta/\rho_m$ values discussed at some length in a previous paper[4,7] in that the lower ρ values yield the higher σ and *F* values. A seeming exception forms the near equality of the *F* values in meta and para ArCOOH (ρ = 1) and para ArOH (ρ = 2.2), where Swain et al. data give *F* = 1.6, 1.7, and 1.6, respectively. The anomaly was found to be a consequence of the use of nonthermodynamic p*K* values for the benzoic acids; thermodynamic values[4] give *F* = 1.8–2.1.

3. Through-Resonance Effects. Swain et al. state that "*the apparently enhanced* or abnormally important *resonance*, formerly thought to operate with NH$_2$ or OH in the σ_p^+ reaction or with CN or NO$_2$ in the σ_p^- reaction, *was only an artifact or illusion*.... ." This would imply that the efforts by Yukawa and Tsuno, Hine, or Taft and others to deal with such through-resonance effects would be superfluous; there would be no such thing as a sliding scale of σ values. Once more, we disagree.

Chart V gives some data from the para ArOH series;[8] Chart VI illustrates the para ArNMe$_2$H$^+$ series.[8,3] The main point is that the deviations are entirely unacceptable with a gross overestimation of the resonance contribution. The satisfactory fit obtained by Swain et al. for para ArOH can be traced back to their set containing only the +M groups Me, *t*-Bu, and Br; it was mentioned explicitly that the value for OMe was deleted with two other "dubious data".[9] The disastrous effects on the values of *f* and *r* and on the fit, when changing the selection of substituents, has been illustrated for para ArOH (sets 29–30), ArNMe$_2$H$^+$ (sets 33–37), and ArNH$_3^+$ (sets 62–71).

The failure of eq 1 noticed here is due to the weight of the para S$_N$1 standard σ_p^+ reaction in the parametrization. This, of course, is the counterpart of the situation sketched

---

(5) Unpublished work from this laboratory.

(6) "Steric Effects in Conjugated Systems", Proceedings of a Chemical Society Symposium, Hull 1958; Butterworths: London, 1958; pp 82–92.

(7) Accordingly, the equation $p = fF + rR + \delta^B + h$, where δ^B is the Bjerrum term, with *F* = 1.0 for NMe$_3^+$ removes most of the deviations. However, we do not recommend this approach because of the other defects of eq 1.

(8) Hoefnagel, A. J.; Hoefnagel, M. A.; Wepster, B. M. *J. Am. Chem. Soc.* **1976**, *98*, 6194. Chart V is based on set 27, Chart VI on set 34.

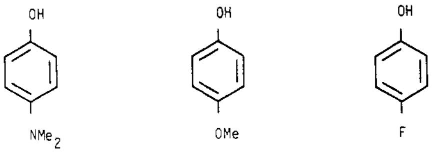
(9) Reference 1, Table II, footnote *e*.

Table II. Observed Substituent Effects[a]

1 reference 1 || **2** 1 .18 3 .39 6 .41 8 -.08 11 .40 12 .68 15 .11
17 -.07 18 .36 19 .0 20 .06 21 .37 24 .12 25 -.07 28 .76 30 .78 40
.45 || **3** 39 .08 41 1.11 || **4** 1 .23 3 .58 5 -.08 6 .51 8 -.24 11
.47 12 .99 15 .07 17 -.17 18 .44 19 .0 20 .03 21 .43 24 .11 25
-.12 28 1.03 30 1.07 32 .16 33 .02 37 -.33 40 .59 42 -.22 43 -.14
|| **5** 39 .07 41 1.71 || **6** reference 1 || **7** 1 -.03 3 .52 11 .24
12 .72 17 -.15 18 .07 19 .0 20 -.39 24 -.29 25 -.17 28 .75 30 .83
|| **8** 39 .16 41 1.03 || **9** 1 -.07 3 .67 5 -.79 6 .42 8 -.21 11 .41
12 1.03 15 -.34 17 -.22 18 .23 19 .0 20 -.53 21 .37 24 -.31 25
-.21 28 1.09 30 1.19 32 -.02 33 .03 37 -.37 40 .78 42 -.01 43 -.92
|| **10** 39 .13 41 1.50 || **11** 1 -.11 3 .73 5 -.90 6 .54 8 -.16 11
.49 12 1.14 15 -.34 17 -.20 18 .30 19 .0 20 -.60 21 .50 24 -.32 25
-.21 28 1.16 30 1.33 32 -.02 33 .08 37 -.31 40 .87 42 .06 43 -.93
|| **12** 39 -.01 41 1.73 || **13**-**14** reference 1 || **15** 1 .06 6 .14 11
.13 12 .39 18 .07 19 .0 20 -.09 21 .14 24 -.05 25 -.07 30 .45 32
.0 || **16** 39 -.07 41 .61 || **17** 1 .04 6 .19 11 .19 12 .52 18 .11 19
.0 20 -.12 21 .22 24 -.06 25 -.09 30 .61 32 .03 || **18** 39 -.10 41
.96 || **19** 1 .02 6 .24 11 .25 12 .62 18 .14 19 .0 20 -.19 21 .25 24
-.10 25 -.12 30 .69 32 .04 || **20** 39 -.25 41 1.15 || **21** 5 -.10 12
.26 19 .0 30 .31 || **22** 39 -.29 41 .67 || **23** 5 -.12 12 .36 19 .0
30 .41 || **24** 39 -.36 41 .93 || **25** 5 -.211 11 .188 15 -.089 18 .128
19 .0 24 -.080 25 -.079 30 .507 43 -.170 || **26** 41 1.166 || **27**-**29**
reference 1 || **30** 5 -.28 6 .28 8 -.14 18 .05 19 .0 20 -.14 24 -.12
25 -.14 43 -.17 || **31** 8 -.23 11 1.70 19 .0 24 .38 25 -.21 30 3.19
43 -.57 || **32** 41 3.08 || **33**-**37** 1 -.02 3 3.28 6 1.20 8 -.34 11 1.07
12 4.00 18 .19 19 .0 20 -1.19 24 -.80 25 -.51 28 3.96 30 5.05 43
-1.39 || **38**-**42** reference 1 || **A**-**H** reference 1 ||.

[a] Substituents are numbered as in ref 1: 1 NHAc, 3 COMe; 5 NH_2; 6 Br; 8 *t*-Bu; 11 Cl; 12 CN; 15 OEt; 17 Et; 18 F; 19 H; 20 OH; 21 I; 24 OMe; 25 Me; 28 SO_2Me; 30 NO_2; 32 OPh; 33 Ph; 37 CH_2SiMe_3; 39 SO_3^-; 40 CF_3; 41 NMe_3^+, 42 $SiMe_3$; 43 NMe_2. The underlined reaction number is followed by pairs of figures; the first refers to the substituent, the second gives the observed substituent effect Δ in log units (set 30 $\Delta/\rho_m = \Delta/2.203^4$) with leading and trailing zeros omitted. The end of a set is followed by ||. Unless indicated otherwise the data are from this laboratory (see text).

Chart V

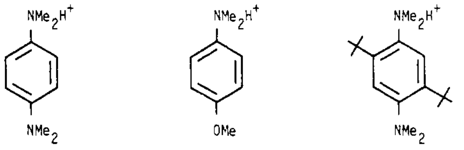


	H_2O	H_2O	H_2O
Δ-4-Y	-0.37	-0.26	0.10
f F ρ	0.71	0.55	0.76
r R ρ	-5.61	-2.47	-0.88

in the first section. There we found that incorporation of the π-acceptors in a σ_p^- reaction led to overestimation of resonance effects of π-acceptors in ArCOOH. Here we find an overestimation of the resonance effects of π-donors in the absence of through-resonance.

It would seem appropriate at this stage to make a remark of more general interest. Inspection of the tabulated *F* and *R* values reveals that the 9 dipole substituents with reputed −M effects span much smaller ranges than the 23 +M dipoles; *F* from 0.44 to 1.00 and −0.19 to 0.90, respectively, *R* from 0.45 to 1.07 and −0.04 to −3.81, respectively. Again, the difference $(F - R)$ ranges over 0.9 units for the −M groups, as against 4.3 units for the +M groups. This observation is not restricted to the *F* and *R* values. It is also found, e.g., with the Yukawa–Tsuno equations, as illustrated by $\Delta\sigma_R^- - NO_2 = 0.45$ and $\Delta\sigma_R^+ - NH_2 = -1.23$.[10] Moreover, it should be borne in mind that what really counts is the corresponding free energy differences involved; these amount to 1.4 (ArOH) and 8 kcal/mol, respectively. In this connection it is instructive to note that the resonance factor for 4-NO_2 in ArOH is equalled energetically by that of the relatively weak donors Me and F in the σ_p^+ reaction.

Chart VI



	50E	50E	85E
Δ-4-Y	-1.39	-0.80	0.02
f F	1.35	1.05	
r R	-9.41	-4.15	

Apparently, nature has endowed us with a nice variation of easily accessible π-donors, whereas the common π-acceptors form a cluster-like group with less discriminating abilities with respect to linear free energy relationships relating to the usual reactivities. This, then, explains why para $ArCMe_2Cl$, with data on a satisfactory mixture of +M and −M substituents (NH_2 and OH as well as CN and NO_2), can fit eq 1. The fit is determined by the +M groups; the −M groups follow obediently.

These points have been illustrated numerically in Table I for the S_N1 reaction in various ways: (a) Sets 38–40 show that deleting −M groups and/or poles causes little change. (b) Using only the 5 available −M groups yields different and highly uncertain *f* and *r* values (set 41); addition of H gives already a considerable improvement (set 42). (c) In sets A–F the combination of the data for the 5 −M groups with a strongly varying input for NH_2 ($-\Delta/4.54 = -0.6$ to -2.1; Swain et al. −1.3) causes *f* and *r* to vary strongly but has little effect on *s* and *C*, whereas *p* of NO_2 is found to vary only from 0.80 to 0.85. (d) Sets G and H illustrate the same for varying input of the *R* value of NH_2 (Swain et al. −2.52). (e) In the sets A–H the "synthetic" figures for NH_2 contribute virtually nothing to the standard deviation; $\Delta - p$ is vanishingly small. Swain et al. consider the agreement between predicted and "experimental" values for NH_2, NO_2, etc. in the σ_p^+ reaction as favoring their view that one resonance parameter suffices; we believe the above shows this agreement to be trivial.

Our conclusion is that the scope of eq 1 is more limited than its authors suggest. The illusion of almost general validity has been the result of an insufficient selection of data and a deletion or disregard of published substituent effects, disguising serious failures with respect to its predictive power and, in particular, its separation in resonance and nonresonance effects. In our opinion, the nature and size of the deviations are such that the use of this approach cannot be recommended.

Registry No. PhOH, 108-95-2; *p*-$NO_2C_6H_4OH$, 100-02-7; *p*-$NO_2C_6H_4CO_2H$, 62-23-7; *m*-$NO_2C_6H_4CO_2H$, 121-92-6; *m*-N-

---

(10) Hoefnagel, A. J.; Wepster, B. M. *J. Am. Chem. Soc.* **1973**, *95*, 5357.

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