Registry No.—**19**, 4443-91-8; **20**, 38607-56-6; **21**, 68001-00-3; **22**, 68001-01-4; **24**, 485-46-1; **25**, 68001-02-5; **26**, 61553-76-2; **27**, 68001-03-6; **29**, 31559-49-6; **30**, 68001-04-7; **31**, 68001-05-8; **35a**, 68001-06-9; **36a**, 68001-07-0; **36b**, 68001-08-1; **37**, 68024-31-7; **40**, 68002-09-2; **43**, 68001-10-5; **46**, 68001-11-6; **49**, 68001-12-7; **50**, 68001-13-8; **53**, 239-01-0; dichloromethane, 75-09-2; trimethylsulfoxonium iodide, 1774-47-6; hydroxylamine hydrochloride, 5470-11-1; 4,5-benzo-2,3-homotropone oxime, 68001-14-9; 2,3:5,6-dibenzo[5.1.0]bicycloocta-2,5-dien-4-one oxime, 60070-07-7.

References and Notes

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Substituent Effects. 6.[1-5] Charged Groups: A Simple Extension of the Hammett Equation

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Extensive experimental data show that the Hammett equation fails for charged substituents (poles); variations of σ over more than one σ unit are common. Addition of the Bjerrum field effect term, δ^B, yields the more general equation (8), $\log K - \log K^0 \equiv \Delta = \rho^L\sigma^L + \delta^B$, which holds satisfactorily for poles (at zero ionic strength) as well as for dipoles. In practice, $\rho^L = \rho_{meta}$, i.e., the usual value; $\sigma^L \simeq \sigma^n$ for dipoles, σ^L values for poles have been derived (σ^{Ln}, Table VI); δ^B is the Coulombic term from the classical equations 2–5, characteristically containing the dielectric constant of the solvent, D_s. In section 8 a number of details are discussed, such as the behavior of the series 4-$(CH_2)_nCOO^-$ and 4-$(CH_2)_nNMe_3^+$ and the $\log K$ difference between 4-NMe_3^+ and 4-SO_3^- substituted derivatives. Examples are given where only the Bjerrum term counts ($\Delta = \delta^B$); among these are acidic ester hydrolysis and 4-$CH_2CH_2NMe_3^+$ substitution. Where $\delta^B \simeq 0$ eq 8 reduces to the form of the Hammett equation; with dipoles this holds almost generally (gas-phase data being one of the exceptions), with poles this holds, for instance, for S_N1 reactions and for reactivities at high ionic strengths. Sections 9–14 give a discussion of the data in relation to: the meta/para ratio of the inductive effect; the Kirkwood–Westheimer model; the Hine equation; through-resonance effects (σ^{L+} and σ^{L-}); naphthalene derivatives; and ortho substitution. The applicability of δ^B in aliphatic systems is illustrated and an extended Taft equation is given. The dichotomous eq 8 is compatible with a two-stage model of reactivities. For example, in the first (ionization) stage of the dissociation of XH the XH distance increases to give a pair of ions or a discrete ion pair X^-H^+; in the second stage the proton goes to infinity. The first stage is structure dependent and equally so for poles and dipoles; the second stage is structure independent and D_s is applicable. The Kirkwood–Westheimer cavity model can be parametrized so as to conform with the Bjerrum model. This reevaluation of the cavity model is supported by experimental evidence.

The empirical empire of the Hammett $\rho\sigma$ relation and its extensions is based on our knowledge of substituent effects of uncharged groups, i.e., dipoles. Data on the effects of charged groups, poles, are scarce. Even so, considerable doubt has developed as to the constancy of σ values of poles, although there would seem to be no generally accepted opinion on the question.

In an attempt at clarifying the situation we have studied the substituent effects of a number of positive and negative poles in a number of reaction series. Some results have been given

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Table I. Thermodynamic pK_a* Values of ArCOOH, $ArCH_2COOH$, $ArCH_2CH_2COOH$, and *cis*- and *trans*-ArCH=CHCOOH, in Water and Various Ethanol–Water Mixtures, at 25 °C

compd	registry no.	solvent[a] H_2O	10E	50E	75E
ArCOOH					
3,5-diMe	499-06-9		4.51	5.74	6.52
3-Me	99-04-7		4.44	5.60	6.41
H	65-85-0	4.21	4.37[b]	5.48[b]	6.29[b]
3-F	455-38-9	3.87	4.01	5.04	5.77
3-Cl	535-80-8		3.97	5.01	5.71
3-Br	585-76-2		3.96	4.97	5.69
3-I	618-51-9		4.00	5.05	5.74
3-COMe	586-42-5		3.98	4.90	5.63
3-NO_2	121-92-6		3.59	4.41	5.10
3,5-diNO_2	99-34-3		2.88	3.45	4.02
3-$CH_2NH_3^+Cl^-$	876-03-9	3.62	3.76	4.46	4.97
3-$CH_2NMe_3^+Cl^-$	67688-71-5	3.53	3.62	4.24	4.75
3-$NMe_3^+I^-$	2345-55-3	3.18	3.26	3.77	4.23
3-$NEt_2Me^+I^-$	67711-57-3	3.27	3.35	3.81	4.23
3-$SMe_2^+Tos^-$	34008-77-0	3.06			
4-$CH_2NH_3^+Cl^-$	67688-72-6	3.68	3.81	4.61	5.26
4-$CH_2NMeH_2^+Cl^-$	67688-73-7	3.61	3.73	4.56	5.16
4-$CH_2NMe_2H^+Br^-$	67688-74-8	3.58		4.52	5.09
4-$CH_2NMe_3^+Br^-$	67688-75-9	3.54	3.63	4.37	4.98
4-$CH_2NEt_3^+Br^-$	67688-76-0	3.60	3.67	4.37	4.97
4-$CH_2NBu_3^+Br^-$	67688-77-1	3.58	3.69	4.39	4.93
4-$CH_2CH_2NH_3^+Cl^-$	60531-36-4	3.87	4.01	4.91	5.57
4-$CH_2CH_2NMe_3^+I^-$	67761-86-8	3.87	4.02	4.92	5.59
4-NMe-*t*-Bu	67688-78-2		3.40[c]		
4-$NMe_3^+I^-$	880-00-2	3.23	3.34[b]	3.98[b]	4.56[b]
4-$SMe_2^+Cl^-$	67688-79-3	3.03			
3-$SO_3^-H^+$	121-53-9	4.13	4.32	5.42	6.39
3-$SO_3^-Na^+$	17625-03-5	4.11	4.29	5.41	6.38
4-$SO_3^-K^+$	5399-63-3	4.03	4.21	5.35[b]	6.30[b]
3-*t*-Bu	7498-54-6		4.45	5.72	6.47
3-neopent	67688-80-6			5.78[d]	6.49
3-CEt_3	37872-27-8			5.85	6.51
3-CH_2CN	5689-33-8		4.13	5.14	5.86
3-CH_2Br	6515-58-8			5.29[e]	6.02[e]
3-OH	99-06-9	4.14	4.31	5.45	6.31
4-Me	99-94-5		4.54	5.69	6.50
4-*t*-Bu	98-73-7			5.69	6.45
4-neopent	65687-52-7			5.72[d]	6.44
4-CEt_3	37872-27-8			5.76	6.42
4-CH_2CN	50685-26-2		4.20	5.21	5.96
4-CH_2Br	6232-88-8			5.31[e]	6.01[e]
4-NO_2	62-23-7		3.54	4.29	4.96
4-Cl	74-11-3		4.13	5.07	5.80
ArCOOH					
3,5-di-*t*-Bu	16225-26-6			5.94	6.66
3-Me-4-NO_2	3113-71-1			4.47	
3,5-diMe-4-NO_2	3095-38-3			4.69	
3,5-di-*t*-Bu-4-NO_2	67688-81-7			4.89	
4-Me-3-NO_2	96-98-0			4.62	
4-Me-3,5-diNO_2	16533-71-4			3.64	
4-*t*-Bu-3-NO_2	59719-78-7			4.63	5.30
4-*t*-Bu-3,5-diNO_2	67688-82-8			3.59	
$ArCH_2COOH$[f]					
H[f]	103-82-2	4.31	4.50	5.47	6.20
3,5-diNO_2	67688-83-9		3.81	4.50	5.07
4-NMe_3^+Cl[g]	67688-84-0	3.70	3.87	4.50	5.02
4-$SO_3^-Na^+$	67688-85-1	4.37	4.57	5.57	6.45
$ArCH_2CH_2COOH$[h]					
H[h]	501-52-0	4.67	4.85	5.73	6.50
4-$SO_3^-Na^+$	67688-86-2	4.87	5.05	6.02[b]	6.86[b]
trans-ArCH=CH-COOH					
3,5-diMe	67688-87-3			5.59	6.31
3-Me	14473-89-3	4.44[i]		5.55	6.27
H	140-10-3	4.44[i,j]		5.52	6.22
3-Cl	14473-90-6	4.29[i]		5.24	5.95
3-Br	14473-91-7			5.23	5.93
3-NO_2	1772-76-5	4.12[i]		5.00	5.72
3-$NMe_3^+I^-$	67688-88-4	3.85		4.54	5.02
4-$CH_2NH_3^+Cl^-$	67688-89-5	4.06		4.95	5.50
4-$NMe_3^+I^-$	67711-58-4	3.89		4.70	5.23
4-$SO_3^-Na^+$	67711-59-5	4.50		5.62	6.46
4-NO_2	882-06-4	4.05[i]		4.90	5.64
3,5-di-*t*-Bu	67688-90-8			5.66	6.36
cis-ArCH=CHCOOH					
3-Me	16642-82-3	3.90[k]			
H	102-94-3	3.90[k,l]		5.18	5.88
3-Cl	14290-89-2	3.71[k]		4.94	5.66
3-NO_2	5676-61-9	3.61[k]		4.68	5.42
4-$NMe_3^+I^-$	67688-91-9	3.32		4.20	4.74
4-NO_2	14290-91-6	3.53[k]		4.59	
3,5-di-*t*-Bu	67688-92-0			5.51	6.17

[a] 10E, 50E, and 75E: 10, 50, and 75 volumes of absolute ethanol in 100 volumes of final solution; cf. Experimental Section. [b] Also measured at one-fifth of the usual concentration. The (thermodynamic) pK_a* thus found differs 0.02 or less, and ΔpK_a* 0.01 or less. The same applies to $PhCH_2CH_2COOH$ and its 3- and 4-NMe_3^+ derivatives in 50 and 75% ethanol. [c] pK_a* refers to NMe-*t*-BuH$^+$ as substituent. [d] A. J. M. Reuvers, H. van Bekkum, and B. M. Wepster, *Tetrahedron*, **26**, 2683 (1970). [e] For 3- and 4-CH_2Br the pH of the buffered solutions decreases slowly; the corrections applied are about 0.01 for 50 and 75% ethanol. [f] Other derivatives, ref 4. [g] pK_a* values differ slightly from those obtained with the iodide.[4] [h] Other derivatives, ref 3. [i] J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1008 (1937); J. F. J. Dippy and J. E. Page, *ibid.*, 357 (1938). [j] Present work 4.44, by extrapolation from 10 (4.57), 4 (4.49), and 2% ethanol–water (4.46). [k] From the theses of R. F. J. Nivard and O. I. Matray, Leyden, 1951 and 1956, respectively. [l] Present work, 3.90. Dippy and Lewis, footnote *i*, 3.88.

in previous papers [3,4] and provided support for the thesis that poles do not fit the Hammett equation. Thus, from thermodynamic dissociation constants in water, the σ value of 4-NMe_3^+ appears as 1.8 in the $ArCH_2CH_2COOH$ series[3] and 1.2 in the $ArCH_2COOH$ series,[4] as compared with 0.8 in the $ArNH_3^+$ series.[6] Of course, σ variations of this magnitude should be of help in finding better empirical relationships, and might even provide clues for theoretical interpretation.

The present paper gives most of our results on pole substituents, along with literature data. They have been analyzed in terms of the classical ideas developed by G. N. Lewis and N. Bjerrum and recently revived by Palm and his co-workers.[7] The outcome is that the Hammett equation needs only a simple extension to cover the effects of both dipoles and poles. The extended equation is evaluated and its impact on several topics is outlined.

Results

In previous papers we gave thermodynamic dissociation constants in the series $ArCH_2COOH$,[4] $ArCH_2CH_2COOH$,[3] and $ArCMe_2CH_2COOH$,[3] including those involving the substituents 3- and 4-NMe_3^+ and 3- and 4-$CH_2NH_3^+$. Table I lists our data in the series ArCOOH and *cis*- and *trans*-ArCH=CHCOOH and additional data in the other series. Table II gives the reaction constants ρ and other statistical data of the series mentioned, and also of some related series. The Hammett equation is written here in the form

Table II. Reaction Constants and Other Statistical Data[a]

reaction	solvent[b]	ref	$\rho \pm s_\rho$	s	R	int	substituents
ArCOOH	H_2O	*c*	1.054 ± 0.043	0.028	0.997	−0.004	2,3,4,5,6,9
	10E	*d*	1.092 ± 0.010	0.013	1.000	−0.010	1–10
	50E	*d*	1.516 ± 0.038	0.049	0.998	−0.054	1–10
	75E	*d*	1.672 ± 0.025	0.033	0.999	−0.025	1–10
$ArCH_2COOH$	H_2O	*e*	0.486 ± 0.022	0.011	0.998	−0.007	3,5,7,9
	10E	*f,d*	0.525 ± 0.015	0.019	0.998	−0.026	1,2,3,4,5,6,9,10
	50E	*f,d*	0.740 ± 0.028	0.037	0.995	−0.063	1,2,3,4,5,6,7,9,10
	75E	*f,d*	0.837 ± 0.016	0.021	0.999	−0.028	1,2,3,4,5,6,7,9,10
$ArCH_2CH_2COOH$	H_2O	*g*	0.24				
	10E	*h,f*	0.268 ± 0.009	0.009	0.999	−0.003	3,9,10
	50E	*h,f*	0.385 ± 0.019	0.025	0.994	−0.033	1,2,3,5,6,9,10
	75E	*h,f*	0.448 ± 0.007	0.009	0.999	−0.006	1,2,3,5,6,9,10
$ArCMe_2CH_2COOH$	50E	*h,f*	0.377 ± 0.043	0.021	0.988	−0.014	3,5,6,9
	75E	*h,f*	0.448 ± 0.047	0.024	0.989	−0.015	3,5,6,9
trans-ArCH=CHCOOH	H_2O	*i*	0.418 ± 0.034	0.021	0.993	0.009	2,3,5,9
	50E	*d*	0.723 ± 0.011	0.008	1.000	0.007	1,2,3,5,6,9
	50E	*j*	0.676 ± 0.010	0.006	1.000	0.004	2,3,4,5,6,9
	75E	*d*	0.725 ± 0.015	0.011	0.999	−0.005	1,2,3,5,6,9
cis-ArCH=CHCOOH	H_2O	*k*	0.400 ± 0.036	0.023	0.992	0.022	2,3,5,9
	50E	*d*	0.703 ± 0.037	0.019	0.999	−0.007	3,5,9
	50E	*j*	0.634 ± 0.010	0.005	1.000	−0.002	3,5,9
	75E	*d*	0.647 ± 0.035	0.018	0.999	−0.007	3,5,9
$ArCOOEt + OH^-$	85E	*l*	2.541 ± 0.077	0.056	0.998	−0.025	1,2,3,5,6,9
ArCOO(*l*-menthyl) + OMe^-	MeOH	*m*	2.643 ± 0.050	0.032	0.999	0.032	2,3,5,6,9
$ArCH_2COOEt + OH^-$	85E	*n,f*	1.245 ± 0.038	0.019	0.999	−0.013	3,5,7,9
$ArCH_2CH_2COOEt + OH^-$	88E	*o,f*	0.635 ± 0.016	0.010	0.999	0.004	2,3,4,5,9
trans-ArCH=CHCOOEt + OH^-	88E	*p*	1.264 ± 0.050	0.025	0.999	0.010	3,5,9
	85E	*q*	1.270 ± 0.030	0.015	1.000	−0.006	3,5,9
$ArCOOH + Ph_2CN_2$	EtOH	*r*	0.945 ± 0.047	0.029	0.998	0.002	2,3,5,9
	2-Me-2-BuOH	*r*	1.412 ± 0.057	0.035	0.998	0.019	2,3,5,9
$ArCH_2COOH + Ph_2CN_2$	EtOH	*s,f*	0.400 ± 0.016	0.010	0.998	0.011	2,3,5,9
	EtOH	*t*	0.446				
	2-Me-2-BuOH	*s,f*	0.741 ± 0.021	0.013	0.999	0.004	2,3,5,9
$ArCH_2CH_2COOH + Ph_2CN_2$	EtOH	*t*	0.241				3,5
	EtOH	*t*	0.238				
trans-ArCH=CHCOOH + Ph_2CN_2	EtOH	*t*	0.404 ± 0.003	0.001	1.000	0.001	3,5,9

[a] ρ, reaction constant, at 25 °C unless indicated otherwise; s_ρ, standard deviation of ρ; s, standard deviation of the experimental points; R, correlation coefficient; int, intercept regression line with ordinate ($\sigma = 0$); substituents, actual substituents in the compounds involved in the calculation of ρ, identified according to their number and with standard σ values:[3] (1) 3,5-diMe, −0.098; (2) 3-Me, −0.069; (3) H, 0; (4) 3-F, 0.337; (5) 3-Cl, 0.373; (6) 3-Br, 0.391; (7) 3-I, 0.352; (8) 3-COMe, 0.376; (9) $3\text{-}NO_2$, 0.710; (10), $3,5\text{-diNO}_2$, 1.379. [b] Solvent: water or ethanol–water mixtures unless indicated otherwise; the composition is specified in Table I and in the footnotes. [c] W. Ostwald, *Z. Phys. Chem. Stoechiom. Verwandschaftsl.*, **3**, 369 (1889). These results are presented to pay homage to this classic work. The 13 pK_a values common to Ostwald's work and that of Dippy et al. (see ref 3) give $\rho = 1.010 \pm 0.032$, $s = 0.038$, $R = 0.995$, int = 0.016. [d] Present work. [e] J. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, 161, 1888 (1934); J. F. J. Dippy and R. H. Lewis, *ibid.*, 644 (1936). [f] Reference 4. [g] By linear extrapolation of ρ in 50 and 10% ethanol vs. percent ethanol; this procedure holds good for ArCOOH and $ArCH_2COOH$. [h] Reference 3. [i] Note *i* of Table I. [j] 50% Ethanol v/v, i.e., 44% w/w; R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **31**, 3423 (1966). [k] Note *k* of Table I. [l] 84.6% ethanol w/w; B. Jones and J. Robinson, *J. Chem. Soc.*, 3845 (1955). See also ref 1. [m] Temperature 30 °C; R. W. Taft, M. S. Newman, and F. H. Verhoek, *J. Am. Chem. Soc.*, **72**, 4511 (1950). [n] 85.4% ethanol w/w; J. G. Watkinson, W. Watson, and B. L. Yates, *J. Chem. Soc.*, 5437 (1963). [o] Temperature 30 °C; 87.8% ethanol v/v, i.e., 85% w/w; R. Fuchs and J. A. Caputo, *J. Org. Chem.*, **31**, 1524 (1966). [p] Temperature 30 °C; 87.8% ethanol v/v, i.e., 85% w/w; J. J. Bloomfield and R. Fuchs, *J. Org. Chem.*, **26**, 2991 (1961). [q] 85% ethanol v/v, i.e., 81.6% w/w; K. K. Satpathy, P. L. Nayak, and M. K. Rout, *Indian J. Chem.*, **9**, 680 (1971). [r] Temperature 30 °C; A. Buckley, N. B. Chapman, M. R. J. Dack, J. Shorter, and H. M. Wall, *J. Chem. Soc. B*, 631 (1968). Other ρ values in ethanol 0.916 and 0.979, see ref 1. [s] Temperature 30 °C; N. B. Chapman, J. R. Lee, and J. Shorter, *J. Chem. Soc. B*, 769 (1969). [t] Temperature 30 °C; K. Bowden, N. B. Chapman, and J. Shorter, *Can. J. Chem.*, **42**, 1979 (1964). The regression line of log k of $ArCH_2COOH$ for H, 4-Me, 4-Br, and $4\text{-}NO_2$ in ethanol vs. those of footnote *s* has slope 1.114, $R = 1.000$. The product of this slope and the first ρ value of $ArCH_2COOH$, 0.400, gives the second ρ value. The regression line of log k of $ArCH_2CH_2COOH$ for H, 4-Me, 3-Cl, and $4\text{-}NO_2$ in ethanol vs. those of $ArCH_2COOH$ of note *s* has slope 0.595, $R = 0.995$. The product of this slope and the first ρ value of $ArCH_2COOH$ gives the second ρ value of $ArCH_2CH_2COOH$. Similar ρ values are obtained from R. A. More O'Ferrall and S. I. Miller, *J. Am. Chem. Soc.*, **86**, 4016 (1964).

$$\Delta = \rho\sigma \tag{1}$$

where Δ is the substituent effect ($\log K_Y - \log K_H$ or $\log k_Y - \log k_H$), $\rho \equiv \rho_m$ is the reaction constant obtained with our usual set of standard meta σ values (specified in Table II), and σ is the substituent parameter which may be either the "normal" value, σ^n, in the absence of mesomeric para interaction,[1,4,5] or an exalted value.[1]

The σ values derived from our data on carboxylic acids are part of Table III which, in addition, contains figures pertaining to the analysis given in the Discussion. Tables IV and V are similarly composed from, mainly, literature data on equilibria and rates, respectively. Some further data from this laboratory have been included in Table IV. Most of these are second dissociation constants of compounds the first dissociation constant of which has been reported;[3,4] thus, the second dissociation constant of 4-hydroxyphenylacetic acid yields the substituent effect of the $4\text{-}CH_2COO^-$ group in the phenol series. Tables IX and X give substituent effects in sodium chloride solutions; Table XI contains our data on dilute acid hydrolysis of methyl benzoates.

Discussion

1. Ionic Strength Effects. The Debye–Hückel and Brønsted theories give a quantitative description of the variation with concentration of equilibrium and rate "constants", respectively. The dependence on the charges of reactants and products or transition state implies that substituent effects of charged and uncharged substituents as measured at even relatively low concentrations are not suitable for direct comparison, but should be corrected to zero ionic strength, $I = 0$.

The consequences of the above with respect to σ values have been demonstrated (and applied) quite clearly by Zollinger.[8] However, they are neglected so often that it would seem useful to emphasize that correction to $I = 0$ is vital and that the effects on σ become quite large if the dielectric constant of the solvent and ρ are low. A good example is provided by the alkaline hydrolysis of ethyl 4-NMe_3^+-β-phenylpropionate in 88% ethanol at an ionic strength $I = 0.05$. The observed $\Delta \log k$ yields $\sigma = 0.84$;[4] the correction to $I = 0$ is 0.63 $\log k$ units and yields $\sigma = 1.84$, a value that is reassuringly close to $\sigma = 2.08$ for the thermodynamic pK_a^* of the corresponding acid in 75% ethanol obtained from measurements at $I = 0.004$. Figure 16 provides further illustrations.

Accordingly, we have applied corrections for ionic strength to literature data where necessary and will consider Δ at $I = 0$ only, unless indicated otherwise. We note that part of these corrections cannot be satisfactory. In many cases the concentrations used cannot be inferred with certainty or with accuracy from the data given, or the concentration and the solvent composition are beyond the region for which activity coefficients can be calculated with confidence. The consistency of the results (as in the above example) causes us to believe that most of our corrections are sufficiently accurate.

In contrast, work by Palm et al. indicates that data at very high ionic strength ($I = 1$–4) are also highly significant with respect to the problems of the present paper. This aspect will be discussed in section 8.g.1.

2. σ Values. The present data give a clear answer as to whether charged substituents fit the Hammett $\rho\sigma$ relation: they do not. The Tables III–V contain a multitude of examples, only part of which can be discussed. Figure 1 provides some visual aid as to the variation of σ, and gives occasion to the following comments: (a) 4-NMe_3^+ and 4-$CH_2NH_3^+$ vary over about one σ unit; (b) the ratio 4-NMe_3^+/4-$CH_2NH_3^+$ varies from 1.1 to 2.2; (c) 4-SO_3^- varies over one σ unit, in a way opposite to that of the positive poles; (d) 4-SO_3^- and 4-$CH_2NH_3^+$ have about the same positive value for $ArNH_3^+$, but differ more than two σ units for $ArCH_2CH_2COOH$.

The general conclusion from Figure 1 and the other data is that the variation of σ values is so large that it makes no sense to average σ values of poles, or to assign special significance to values observed for benzoic acids in water. Hence, the behavior of poles must be described by an expression differing from Hammett's, preferably one which is also applicable to dipoles.

A more specific conclusion is that at least two effects are needed for describing the behavior of poles. One of these is, almost inescapably, the Coulomb field effect of the charge and it is especially the oppositeness of the trends for positive and negative poles as in Figure 1 which forms a formidable argument. Since, however, positive σ values are observed for 4-SO_3^- (and other negative poles), at least one other effect must play a part and, often, this is the more important part.

The distinction of two effects in the (nonconjugative) substituent influences is, of course, by no means new. Coulomb effects of charges were already considered by Ostwald,[9] and Lewis[10] emphasized a transmission through the chain. Our data rather emphatically suggest the importance of more than one effect, and, therefore, a short discussion of the latitude and limitations of these classical approaches would seem pertinent.

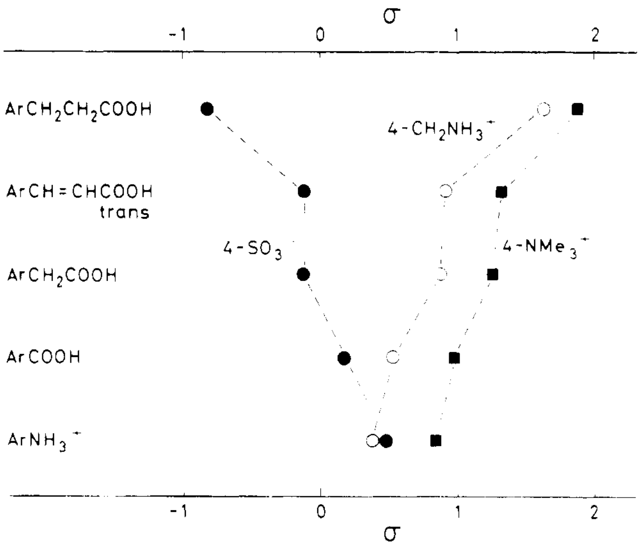


Figure 1. Examples of the variation of σ values of charged substituents in water. Some of the values for 4-SO_3^- contain a through-resonance component, but this represents <0.2 σ unit (cf. section 12 and ref 4).

3. Lewis's Model of the Inductive Effect. This model is characterized by the following features:[10] (a) "a displacement of electrons at one end of a chain proceeds throughout the whole chain"; (b) "it becomes less marked the greater the distance"; and (c) "it becomes less marked the more rigid the constraints which hold the electrons in the intervening atoms". Of these, (a) describes a general mechanism, (b) and (c) give qualifications which allow a parametrization in terms of a "falloff factor" or "attenuation factor" which is dependent on structural factors such as the presence of heteroatoms and double bonds. Thus, this model is able to account for regularities as to be observed in Table II. The ρ values of the systems $Ar(CH_2)_nCOOX$ are in the ratio 4:2:1 for $n = 0, 1, 2$, irrespective as to whether a dissociation constant is involved or alkaline ester hydrolysis with a negatively charged reagent, or a reaction with a neutral reagent as diphenyldiazomethane, and irrespective of the solvent.[11] Again, the near equality of the ρ values of cis and trans isomeric systems is natural, and the similarity of the ρ values of the cinnamic acids and the arylacetic acids can be rationalized on the basis of the falloff factor being closer to unity in the former case (0.7 for $-CH{=}$) than in the latter (0.5 for $-CH_2-$), reflecting the larger polarizability of the double bond.

Successful as these concepts may be with regard to the Hammett equation, the mechanism contains nothing to differentiate between poles and dipoles. Therefore, induction through the chain cannot be the only factor at work.

The authors are aware that the Lewis model has been criticized severely from a quantitative point of view: an effect "passing through the molecule atom by atom" [10] would be vanishingly small beyond two bonds.[12] Whether this view is correct or not, the chain mechanism does not constitute the only route by which polarity may be transmitted. In fact, a quantitative electrostatic model developed by Dr. C. F. Wilcox,[13] presenting a more sophisticated treatment of the electron displacements induced in the polarizable matter present and taking account of molecular structure, yields strong evidence that induction within the molecule is of importance.[14] However this may be, those frowning at the Lewis chain mechanism may substitute it with the mechanism(s) which determine the abovementioned Lewis–Hammett regularities for dipoles but do not (fully) mirror the effect of poles.

Table III.[a] Analysis of Substituent Effects in Carboxylic Acid Dissociation Constants: σ and σ^L, and Deviations of Calculated from Experimental Values of the Present Work

compd	registry no.	solvent	δ^B	$\Delta - \delta^B$	σ	σ^L	dev
ArCOOH							
3-Cl[b,c]		H_2O	0.02	0.35	0.37	0.35	0
(5.9)		10	0.02	0.38	0.37	0.35	0.00
		50	0.03	0.44	0.31	0.29	−0.09
		75	0.04	0.54	0.35	0.32	−0.05
3-NO_2[d,e]		H_2O	0.05	0.66	0.71	0.66	0
(6.5)		10	0.05	0.73	0.71	0.67	0.01
		50	0.07	1.00	0.71	0.66	0.00
		75	0.10	1.09	0.71	0.65	−0.01
4-Cl[b]		H_2O[f]	0.02	0.21	0.23	0.21	
(6.7)		50	0.03	0.38	0.27	0.25	
		75	0.04	0.45	0.29	0.27	
4-NO_2[d]		H_2O[f]	0.05	0.73	0.78	0.73	
(7.5)		50	0.07	1.12	0.78	0.74	
		75	0.09	1.24	0.80	0.74	
3-$CH_2NH_3^+$		H_2O	0.45	0.14	0.59	0.14	−0.04
(6.9)		10	0.48	0.13	0.56	0.12	−0.07
		50	0.67	0.35	0.67	0.23	0.08
		75	0.92	0.40	0.79	0.24	0.10
3-$CH_2NMe_3^+$		H_2O	0.45	0.23	0.68	0.23	−0.07
(6.9)		10	0.48	0.27	0.69	0.25	−0.06
		50	0.67	0.57	0.82	0.38	0.12
		75	0.92	0.62	0.92	0.37	0.12
3-NMe_3^+		H_2O	0.49	0.54	1.03	0.54	−0.05
(6.3)		10	0.52	0.59	1.02	0.54	−0.05
		50	0.73	0.98	1.13	0.65	0.09
		75	1.00	1.06	1.23	0.63	0.07
3-NEt_2Me^+		H_2O	0.49	0.45	0.94	0.45	−0.09
(6.3)		10	0.52	0.50	0.93	0.46	−0.09
		50	0.73	0.94	1.10	0.62	0.12
		75	1.00	1.06	1.23	0.63	0.16
3-SMe_2^+		H_2O	0.47	0.68	1.15	0.68	−0.08
(6.6)							
4-$CH_2NH_3^+$		H_2O	0.40	0.13	0.53	0.13	−0.05
(7.9)		10	0.42	0.14	0.51	0.13	−0.06
		50	0.58	0.29	0.57	0.19	0.02
		75	0.80	0.23	0.62	0.14	−0.07
4-$CH_2NMeH_2^+$		H_2O	0.40	0.20	0.60	0.20	−0.01
(7.9)		10	0.42	0.22	0.59	0.20	−0.01
		50	0.58	0.34	0.61	0.22	0.02
		75	0.80	0.33	0.68	0.20	−0.02
4-$CH_2NMe_2H^+$		H_2O	0.40	0.23	0.63	0.23	−0.04
(7.9)		50	0.58	0.38	0.63	0.25	−0.03
		75	0.80	0.40	0.72	0.24	−0.05
4-$CH_2NMe_3^+$		H_2O	0.40	0.27	0.67	0.27	−0.05
(7.9)		10	0.42	0.32	0.68	0.29	−0.03
		50	0.58	0.53	0.73	0.35	0.04
		75	0.80	0.51	0.78	0.30	−0.03
4-$CH_2NEt_3^+$		H_2O	0.40	0.21	0.61	0.21	−0.07
(7.9)		10	0.42	0.28	0.64	0.26	−0.03
		50	0.58	0.53	0.73	0.35	0.11
		75	0.80	0.52	0.79	0.31	0.05
4-$CH_2NBu_3^+$		H_2O	0.40	0.23	0.63	0.23	−0.06
(7.9)		10	0.42	0.26	0.62	0.24	−0.06
		50	0.58	0.51	0.72	0.34	0.07
		75	0.80	0.56	0.81	0.33	0.08
4-$CH_2CH_2NH_3^+$		H_2O	0.33	0.01	0.34	0.01	−0.02
(9.3)		10	0.35	0.01	0.33	0.01	−0.02
		50	0.49	0.08	0.38	0.05	0.03
		75	0.67	0.05	0.43	0.03	0.00
4-$CH_2CH_2NMe_3^+$		H_2O	0.33	0.01	0.34	0.01	−0.02
(9.3)		10	0.35	0.00	0.32	0.00	−0.03
		50	0.49	0.07	0.37	0.05	0.02
		75	0.67	0.03	0.42	0.02	−0.02
4-NMe-*t*-BuH^+	67711-60-8	10	0.46	0.51	0.89	0.47	0
(7.2)							
4-NMe_3^+		H_2O	0.43	0.55	0.98	0.55	0.02
(7.2)		10	0.46	0.57	0.94	0.52	−0.01
		50	0.63	0.87	0.99	0.57	0.07
		75	0.87	0.86	1.03	0.51	−0.03

Table III *(continued)*

compd	registry no.	solvent	δ^B	$\Delta - \delta^B$	σ	σ^L	dev
4-SMe_2^+		H_2O	0.41	0.77	1.18	0.77	0
(7.6)							
3-SO_3^-		H_2O	0.45	0.53	0.08	0.53	0.04
(6.9)		10	0.48	0.53	0.05	0.49	−0.01
		50	0.66	0.72	0.04	0.47	−0.02
		75	0.91	0.81	−0.06	0.48	−0.01
4-SO_3^-		H_2O	0.39	0.57	0.18	0.57	0.06
(8.0)		10	0.41	0.57	0.15	0.52	0.01
		50	0.57	0.70	0.09	0.46	−0.07
		75	0.79	0.78	−0.01	0.47	−0.07
3-CH_2CN		10			0.22		
		50			0.22		
		75			0.26		
3-CH_2Br		50			0.13		
		75			0.16		
4-CH_2CN		10			0.16		
		50			0.18		
		75			0.20		
4-CH_2Br		50			0.11		
		75			0.17		
$ArCH_2COOH$							
3-$CH_2NH_3^+$	67711-61-9	H_2O	0.38	0.10	0.99	0.21	0.01
(8.1)		10	0.41	0.10	0.97	0.19	0.01
		50	0.56	0.26	1.11	0.35	0.13
		75	0.78	0.33	1.33	0.39	0.18
3-NMe_3^+	67688-93-1	H_2O	0.42	0.23	1.34	0.47	−0.06
(7.5)		10	0.44	0.26	1.33	0.50	−0.05
		50	0.61	0.54	1.55	0.73	0.10
		75	0.85	0.60	1.73	0.72	0.11
4-$CH_2NH_3^+$	67688-94-2	H_2O	0.37	0.06	0.88	0.12	−0.03
(8.4)		10	0.39	0.08	0.90	0.15	−0.01
		50	0.55	0.15	0.95	0.20	0.02
		75	0.75	0.16	1.09	0.19	0.01
4-NMe_3^+		H_2O	0.43	0.18	1.26	0.37	−0.08
(7.3)		10	0.45	0.18	1.20	0.34	−0.10
		50	0.62	0.35	1.31	0.47	−0.04
		75	0.86	0.32	1.41	0.38	−0.12
4-SO_3^-		H_2O	0.39	0.33	−0.12	0.68	0.08
(8.0)		10	0.41	0.34	−0.13	0.65	0.07
		50	0.57	0.47	−0.14	0.64	0.09
		75	0.79	0.54	−0.30	0.65	0.11
$ArCH_2CH_2COOH$							
3-$CH_2NH_3^+$	67688-95-3	H_2O	0.34	0.11	1.88	0.46	0.07
(9.3)		10	0.36	0.13	1.83	0.49	0.08
		50	0.49	0.18	1.74	0.47	0.11
		75	0.68	0.30	2.19	0.67	0.22
3-NMe_3^+	67688-96-4	H_2O	0.36	0.14	2.08	0.58	0.00
(8.7)		10	0.38	0.16	2.01	0.60	0.00
		50	0.52	0.33	2.21	0.86	0.10
		75	0.72	0.42	2.54	0.94	0.16
4-$CH_2NH_3^+$	67688-97-5	H_2O	0.31	0.08	1.63	0.33	0.04
(10.1)		10	0.33	0.10	1.60	0.37	0.05
		50	0.45	0.08	1.38	0.21	0.01
		75	0.62	0.13	1.67	0.29	0.05
4-NMe_3^+	67688-98-6	H_2O	0.33	0.12	1.88	0.50	−0.01
(9.3)		10	0.35	0.13	1.79	0.48	−0.01
		50	0.49	0.18	1.74	0.47	−0.02
		75	0.68	0.25	2.08	0.56	0.01
4-SO_3^-		H_2O	0.31	0.11	−0.83	0.46	−0.01
(10.1)		10	0.33	0.13	−0.75	0.48	−0.01
		50	0.45	0.16	−0.75	0.42	−0.04
		75	0.62	0.26	−0.80	0.58	0.03
$ArCMe_2CH_2COOH$							
4-NMe_3^+	67688-99-7	H_2O^g	0.33	0.11	1.83	0.46	−0.02
(9.3)		50	0.49	0.28	2.04	0.74	0.08
		75	0.68	0.31	2.21	0.69	0.07
trans-ArCH=CHCOOH							
3-NMe_3^+		H_2O	0.35	0.24	1.41	0.57	−0.01
(8.8)		50	0.52	0.46	1.35	0.64	0.03
		75	0.72	0.48	1.66	0.66	0.05
4-$CH_2NH_3^+$		H_2O	0.31	0.07	0.91	0.17	−0.01
(10.1)		50	0.45	0.12	0.79	0.17	−0.01

Table III *(continued)*

compd	registry no.	solvent	δ^B	$\Delta - \delta^B$	σ	σ^L	dev
		75	0.62	0.10	0.99	0.14	−0.03
4-NMe_3^+		H_2O	0.33	0.22	1.32	0.53	0.00
(9.5)		50	0.48	0.34	1.13	0.47	−0.04
		75	0.66	0.33	1.37	0.46	−0.05
4-SO_3^-		H_2O	0.30	0.24	−0.14	0.57	0.01
(10.3)		50	0.44	0.34	−0.14	0.47	−0.03
		75	0.61	0.37	−0.33	0.51	0.00
4-NO_2		H_2O^h			0.93		
		50			0.86		
		75			0.86		
cis-ArCH=CHCOOH							
4-NMe_3^+		H_2O	0.46	0.12	1.45	0.30	−0.09
(6.7)		50	0.68	0.30	1.39	0.43	−0.07
		75	0.94	0.20	1.76	0.31	−0.14
4-NO_2		H_2O^i			0.93		
		50			0.84		

[a] Compound: indicated are reaction series, substituent, and (in parentheses) the distance r between charge on substituent (or dipole) and dissociating proton used in the calculation of δ^B (for geometrical details see Supplementary Material and section 8.e); counterions are given in Table I and in ref 3 and 4. Solvent: 10, 50, and 75 stand for 10%, 50%, and 75% ethanol–water (Table I). δ^B, absolute value of δ^B (eq 2–5), using dielectric constants for water, 78.5; 10%, 73.9; 50%, 53.4; 75%, 38.6 (G. Åkerlöf, *J. Am. Chem. Soc.*, **54,** 4125 (1932)). Δ, thermodynamic pK_a* parent compound *minus* thermodynamic pK_a* substituted compound (Table I and ref 3 and 4). $\sigma = \Delta/\rho$ (ρ from Table II). $\sigma^L = (\Delta - \delta^B)/\rho$. dev, deviation, i.e., $\Delta - \Delta$(calcd), Δ(calcd) from eq 8, using the average σ^{Ln} values of Table VI. Dev 0 indicates single or defining data. [b] μ = 1.5 D. [c] θ = 40 °. [d] μ = 4.0 D. [e] θ = 35°. [f] pK_a values in water taken from J. F. J. Dippy, *Chem. Rev.*, **25,** 151 (1939). [g] In water, pK_a 4.54; $PhCMe_2CH_2COOH$ in water, pK_a 4.98, by extrapolation of pK_a* vs. 1/D for 10 (5.16), 4 (5.04), and 2% (5.03) ethanol–water mixtures. The value of ρ was equated to that of $ArCH_2CH_2COOH$, 0.24. [h] Dippy et al., footnote *i*, Table I. [i] Nivard, footnote *k*, Table I.

4. Bjerrum's Electrostatic Model; the Field Effect. In his discussion of the first and second dissociation constants of aliphatic dicarboxylic acids in water, Bjerrum[15] used Coulomb's law to calculate the work involved in removing the second proton to infinity against the field of the COO^- group. The general expression obtained for the substituent effect of a charge can be written in terms of log K or log k units as:

$$\pm\delta^B = Ne^2 z_A z_B / 2.3RTD_s r \qquad (2)$$

where N = Avogadro's number, e = electronic charge, z_A and z_B = charge number, R = gas constant, T = absolute temperature, D_s = dielectric constant of the solvent, and r = distance between the charges involved; the superscript of δ^B refers to Bjerrum, who used D_s consistently. With $z_A = z_B$ = 1, and r in units of angstroms, at 25 °C in water:

$$\pm\delta^B = 3.1/r \qquad (3)$$

The ± signs in eq 2 and 3 (and later equations) are attached to δ^B in order to draw attention to a sign problem: $+\delta^B$ gives the correct sign for a contribution to Δ for the dissociation constant K_a of a protonic acid; $-\delta^B$ gives the correct sign when bimolecular reactions are involved. This can be traced back to the reaction being viewed as an association process instead of as the "conjugate reaction", i.e., the dissociation of the transition state. We do not propose a formal solution here (like using K_b and a negative sign), since we feel that this would add to the confusion. Instead we suggest the application of common sense in assigning the algebraic sign to δ^B.

Equation 3 gave quite reasonable results for glutaric acid and the higher members of the series, but failed increasingly for the lower members. The relative success and failure of eq 2 and 3 for systems as studied in the present paper follows similar lines and is illustrated for the substituent 4-NMe_3^+ in Figure 2. In systems like $ArCH_2CH_2COOR$ δ^B comes close to the substituent effect Δ, also in solvents as 85% ethanol. In systems like ArCOOMe, ArOH, $ArNH_2$, and $ArNMe_2$ eq 2 fails convincingly as shown by the "vertical" set of points at $\delta^B \simeq$ 0.5. The similar effect of moving the charge of a para substituent away from the benzene ring is exemplified by the alkaline hydrolysis of methyl 4-$(CH_2)_n NMe_3^+$-benzoates (cf. Figure 14). Another and very direct demonstration of a failure of the Bjerrum approach is found with the effects of 3-PO_3^{2-} and 3-SO_3^- in ArOH. For 3-PO_3^{2-} Δ = −0.88, so that the ef-

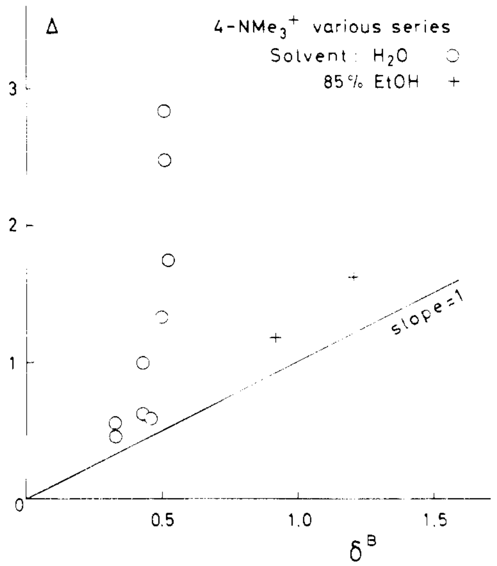


Figure 2. Substituent effects of 4-NMe_3^+, illustrating the relative success and failure of the Bjerrum and Kirkwood–Westheimer approaches (sections 4 and 10). The circles, in order of decreasing Δ, pertain to the systems $ArNMe_2H^+$, $ArNH_3^+$, ArOH, ArCOOMe (+OH^-), ArCOOH, $ArCH_2COOH$, *cis*- and *trans*-ArCH=CHCOOH, and $ArCH_2CH_2COOH$. The crosses pertain to the alkaline hydrolysis of $ArCH_2COOEt$ and $ArCH_2CH_2COOEt$. Only for the longer side chains is Δ close to δ^B. The compounds with δ^B = 0.50–0.52 should represent cavities with practically the same effective dielectric constant.

fect of the singly charged 3-SO_3^- group should be −0.44; its actual value, however, is $\Delta = +0.59$.

An interpolation would seem in order here. Bjerrum's δ^B relates to mathematical point charges. In the case of the symmetrical dibasic acids the experimental quantity which is most suitable to confront δ^B with is $\log K_1/4K_2$ (four is the statistical factor), in which nonmathematical effects such as those due to the presence of the heteroatoms cancel,[16] at least approximately. Of course, such a comparison is not generally possible, and the usual comparison of, e.g., 4-SO_3^--benzoic acid with benzoic acid corresponds with the comparison of, e.g., $2K_2$ of glutaric acid with K of n-butyric acid.

After the advent of the theory of dipole moments, Waters,[17] Eucken,[18] and Schwarzenbach and Egli[19] derived an (approximate) expression for the field effect of dipole substituents on $\log K$ and $\log k$:

$$\pm\delta^B = Nez_A\mu \cos\theta/2.3RTD_sr^2 \qquad (4)$$

where μ = dipole moment and θ = angle between the dipole and the line of length r joining the center of the dipole and the reaction center (the proton in the dissociation of protonic acids). With $z_A = 1$, μ in Debye units, and r in angstroms, at 25 °C in water, eq 5 holds.

$$\pm\delta^B = 0.65\mu \cos\theta/r^2 \qquad (5)$$

Of course, the dipoles can also be treated as compounded of two point charges using eq 2 or 3.

Equations 4 and 5 give δ^B values which are only a small fraction of Δ. Thus, for 3-nitrobenzoic acid in water $\Delta = 0.71$ and $\delta^B = 0.05$.

Two extreme views present themselves. First, it can be assumed that only the field effect is of importance. Then, if the forms of eq 2 and 4 are to be retained, concurrence of Δ and δ^B can only be obtained by replacing D_s by a much smaller empirical "effective dielectric constant", ${}^eD_E$. This line of thought was first discussed by Eucken[18] who observed that ${}^eD_E = 5$ serves well for the dissociation constants of meta dipole-substituted benzoic acids in water. The differences between D_s (78.5) and ${}^eD_E$ were explained as the result of the lines of force passing in part through the molecule, causing ${}^eD_E$ to be in between that of the solvent and that of a hydrocarbon ($D \simeq 2$). Some years later Kirkwood and Westheimer[20] presented a much more refined treatment in which a theoretical effective dielectric constant, ${}^tD_E$, is *calculated* by electrostatic theory from the parameters of the cavity formed by the molecule in the solvent. This model will receive further attention in section 10.

The other extreme view starts from the assumption that δ^B does represent the field effect, at least approximately, and that the discrepancy between Δ and δ^B must be ascribed to some other factor(s). When accepting δ^B as correct for point charges and point dipoles in the solvent, $\Delta - \delta^B$ appears as representing effects *due to the presence of the molecule* with all its implications as to dependence on chemical structure. We shall pursue this view in what follows.

5. Inductive and Field Effects as Additive Quantities; an Extended Hammett Equation. In the above notes on the inductive and field effects an effort was made to discuss one almost to the exclusion of the other, and this is what one meets often in recent papers. Yet, in most classical papers the (nonconjugative) substituent effect is considered as composite. Lewis, who is usually quoted as advocating the through-the-chain effect only, was also considering a through-space factor.[21] Bjerrum was convinced that an effect "durch die Atomkette" is operative,[22] and, unable to calculate this effect, investigated the virtues of his single-factor equation 3. Eucken[18] divided the work A needed to remove a proton in two parts. The first part, A_1, is the work needed to transform the X–H bond into X^-H^+ without changing the nuclear distance. The second part, A_2, is needed to bring H^+ to infinity against the field of X^- and other charges or dipoles in the rest of the system. In his further discussion of eq 2–5 Eucken assumed A_1 to be constant in a series of related compounds, and concentrated on A_2. Explicit attempts to treat the substituent effect quantitatively as the sum of inductive and field effects have been made by Ebert[23] as early in 1925, and by Schwarzenbach and Egli in 1934.[19] Recently, Palm and his co-workers have investigated the value of the concept in a number of papers.[7]

These ideas can be summarized as:

$$\Delta = \delta^L + \delta^E \qquad (6)$$

or

$$\Delta = \delta^L + \delta^B \qquad (7)$$

where δ^L represents the effect through or due to the molecule (the superscript referring to Lewis), δ^E is the electrostatic effect holding if D_E is applicable (the superscript referring to Eucken), and δ^B is the Bjerrum effect of eq 2–5. Equation 7 will be explored in the present paper. Equation 6 is more flexible, but carries all problems relating to D_E with it; some details will be discussed in section 10.

With respect to quantification of δ^L, the correspondence of the Hammett equation and the Lewis concept (see section 3), suggests an expression of the ρ–σ type, so that eq 7 can be written as:

$$\Delta = \rho^L\sigma^L + \delta^B \qquad (8)$$

where δ^L is a σ value free from Bjerrum field effects and ρ^L is a reaction constant based on such (meta) σ^L values.

Equation 8 is a simple extension of the Hammett equation (eq 1), and, in the absence of through-conjugation, should represent the substituent effects of dipoles as well as poles. This equation will now be considered in detail, and put to the test on the basis of the data of Tables I–V.

6. Equation 8 and Dipole Substituents. Formally, eq 8 requires a redefinition of ρ and σ values, and the obvious choice is to start from the definition $\rho^L \equiv 1$ for the benzoic acids in water at 25 °C. Then, for 3-NO_2 and 3-Cl, with $\Delta = 0.71$ and 0.37 and $\delta^B = 0.05$ and 0.02, we obtain $\sigma^L = 0.66$ and 0.35, respectively (Table III).

It can be easily verified that the smallness of δ^B and the rough parallel between μ and σ implies that we can generally take:

$$\rho^L = \rho \qquad (9)$$

and that for dipoles

$$\rho\sigma \simeq \rho^L\sigma^L + \delta^B \qquad (10)$$

Hence, eq 8 is not in conflict with adherence of dipole-substituent effects to the Hammett equation (eq 1). However, the data in question cannot serve, conversely, as a test of eq 8; in this connection we note that eq 9 and 10 would also hold if the field-effect terms were, say, twice as large (corresponding with $D_E = 0.5D_s$; cf. section 10). Thus, even if eq 8 is better in principle, its advantages for dipole-substituent effects in solvents with high D_s are certainly not in proportion to its pretentiousness (for gas-phase data see section 16). Our conclusion is that eq 8 does not compel us to effect the above redefinitions and that it allows using eq 1 with dipole substituents.

7. Equation 8 and Pole Substituents; (Normal) σ^{Ln} Values. In judging and discussing the quality of eq 8 for poles and the improvement over the Hammett equation (eq 1), plots of Δ and $\Delta - \delta^B$ vs. ρ are helpful; Figures 3, 4, 5–10,[24] and 17 are examples. From such plots we can read: (a) the δ^B value as the vertical distance between corresponding points, and its

Table IV.[a] **Analysis of Substituent Effects: σ and σ^L, and Deviations of Calculated from Experimental Values of Various Acid–Base Equilibria**

compd	solvent	ref	Δ	*r*	δ^B	$\Delta - \delta^B$	σ	σ^L	dev
$ArCOOH$[b]									
3-$NMe_3^+Cl^-$	H_2O	*c*	0.99	6.3	0.49	0.50	0.99	0.50	−0.09
4-$NMe_3^+Cl^-$		*c*	0.96	7.2	0.43	0.53	0.96	0.53	0.00
3-$N_2^+BF_4^-$		*d*	1.65	6.3	0.54	1.11	1.65	1.11	0
4-$N_2^+BF_4^-$		*d*	1.79	7.2	0.47	1.32	1.79	1.32	0
3-$SMe_2^+Tos^-$		*e*	1.06	6.6	0.47	0.59	1.06	0.59	−0.17
4-$SMe_2^+Tos^-$		*e*	0.96	7.6	0.41	0.55	0.96	0.55	−0.22
3-COO^-		*f*	−0.10	6.6	0.46	0.36	−0.10	0.36	0.12
	50E	*g*	−0.23		0.67	0.44	−0.15	0.29	0.08
4-COO^-	H_2O	*f*	0.04	7.9	0.39	0.43	0.04	0.43	0.17
	50E	*g*	−0.17		0.58	0.41	−0.11	0.27	0.02
3-PO_3H^-	H_2O	*h*	−0.17	7.1	0.44	0.27	−0.17	0.27	0.03
4-PO_3H^-		*h*	−0.09	8.2	0.38	0.29	−0.09	0.29	0
3-$SO_3^-Na^+$		*i*	0.00	6.9	0.45	0.45	0.00	0.45	−0.04
4-$SO_3^-Na^+$		*i*	0.03	8.0	0.39	0.42	0.03	0.42	−0.09
$ArCH_2COOH$[j]									
4-$N_2^+BF_4^-$	H_2O	*d*	1.07	7.3	0.43	0.64	2.20	1.32	0.00
$ArB(OH)_2$[k]									
3-COO^-	25E	*k*	−0.19	6.1	0.59	0.40	−0.09	0.18	−0.12
4-COO^-		*k*	0.04	7.1	0.51	0.55	0.02	0.25	−0.02
$ArPO_3H^-$[h]									
3-COO^-	H_2O	*h*	−0.30	7.2	0.43	0.13	−0.27	0.12	−0.14
	50E	*h*	−0.45		0.64	0.19	−0.39	0.16	−0.09
4-COO^-	H_2O	*h*	−0.16	8.3	0.37	0.21	−0.14	0.19	−0.08
	50E	*h*	−0.43		0.55	0.12	−0.37	0.10	−0.18
$ArOH$[l]									
2-$CH_2CH_2NMe_3^+I^-$	H_2O	*m*	0.43	4.5	0.69	−0.26			
		n	0.55			−0.14			
3-$CH_2NMe_3^+I^-$		*m*	1.11	5.8	0.53	0.58	0.50	0.26	−0.08
		n	1.16			0.63	0.53	0.29	−0.03
4-$CH_2NMe_3^+I^-$		*m*	1.25	6.6	0.47	0.78	0.57	0.35	0.07
		n	1.29			0.82	0.59	0.37	0.11
3-$CH_2CH_2NMe_3^+I^-$		*m*	0.57	7.6	0.41	0.16	0.26	0.07	0
4-$CH_2CH_2NMe_3^+I^-$		*m*	0.20	8.1	0.38	−0.18	0.09	−0.08	−0.25
		n	0.49			0.11	0.22	0.05	0.04
3-$(CH_2)_3NMe_3^+I^-$		*m*	0.36	8.9	0.35	0.01	0.16	0.00	0
4-$(CH_2)_3NMe_3^+I^-$		*m*	0.20	9.0	0.34	−0.14	0.09	−0.06	−0.01
3-$NMe_3^+Tos^-$		*e*	2.01	5.2	0.60	1.41	0.91	0.64	0.11
3-$NMe_3^+I^-$		*o*	2.03			1.43	0.92	0.65	0.13
3-$NMe_3^+Cl^-$		*c*	2.02			1.42	0.92	0.64	0.12
3-$NMe_3^+I^-$		*m*	1.88			1.28	0.85	0.58	−0.02
3-$NMe_3^+Cl^-$		*p*	1.94			1.34	0.88	0.61	0.04
4-$NMe_3^+Tos^-$		*e*	1.72	6.0	0.52	1.20	0.78	0.54	0.03
4-$NMe_3^+I^-$		*o*	1.85			1.33	0.84	0.60	0.16
4-$NMe_3^+Cl^-$		*c*	1.80			1.28	0.82	0.58	0.11
4-$NMe_3^+I^-$		*m*	1.70			1.18	0.77	0.54	0.01
4-$NMe_3^+Cl^-$		*p*	1.65			1.13	0.75	0.51	−0.04
4-$NMe_3^+I^-$	49E	*q*	2.16		0.77	1.39	0.80	0.52	−0.03
4-$N_2^+BF_4^-$	H_2O	*d*	6.60	6.0	0.52	6.08	2.99	2.76	3.17
3-$SMe_2^+BrC_6H_4SO_3^-$		*e*	2.39	5.5	0.57	1.82	1.08	0.83	0.14
3-$SMe_2^+I^-$		*o*	2.39			1.82	1.08	0.83	0.14
4-$SMe_2^+BrC_6H_4SO_3^-$		*e*	2.75	6.3	0.49	2.26	1.25	1.02	0.56
4-$SMe_2^+I^-$		*o*	2.75			2.26	1.25	1.02	0.56
3-CH_2COO^-		*n*	−0.28	7.0	0.44	0.16	−0.13	0.07	0.14
3-CH_2COOEt		*n*	0.27				0.12		
4-CH_2COO^-		*n*	−0.35	7.0	0.44	0.09	−0.16	0.04	0.07
4-CH_2COOMe		*n*	0.15				0.07		
3-$CH_2CH_2COO^-$		*n*	−0.43	8.2	0.38	−0.05	−0.20	−0.02	0.08
3-CH_2CH_2COOEt		*n*	0.05				0.02		
4-$CH_2CH_2COO^-$		*n*	−0.43	8.8	0.35	−0.08	−0.20	−0.04	0.01
4-CH_2CH_2COOEt		*n*	−0.05				−0.02		
4-$CMe_2CH_2COO^-$		*n*	−0.37	8.8	0.35	−0.02	−0.17	−0.01	0
4-$CH_2CH(COO^-)_2$		*n*	−0.69		0.83	0.14	−0.31	0.06	0
4-$CH{=}C(COO^-)_2$		*n*	0.18		0.84	1.02	0.08	0.46	0
3-COO^-		*n*	0.04	5.7	0.54	0.58	0.02	0.26	0.05
		r	0.13		0.54	0.67	0.06	0.30	0.14
	49E	*q*	−0.24		0.80	0.56	−0.09	0.21	−0.08
4-COO^-	H_2O	*n*	0.62	6.6	0.47	1.09	0.28	0.49	0.52
		r	0.68		0.46	1.14	0.31	0.52	0.57

Table IV (*continued*)

compd	solvent	ref	Δ	*r*	δ^B	$\Delta - \delta^B$	σ	σ^L	dev
	49E	*q*	0.26		0.69	0.95	0.10	0.35	0.25
4-COOMe	H_2O	*n*	1.65				0.75		
3,5-diMe-4-COO^-		*n*	−0.35	6.6	0.47	0.12	−0.16	0.05	0
3,5-diMe		*s*	−0.18				−0.08		
3-O^-		*t*	−1.09	5.1	0.61	−0.48	−0.49	−0.22	0.14
		u	−1.22			−0.61	−0.55	−0.28	0
4-O^-		*t*	−1.81	5.9	0.53	−1.28	−0.82	−0.58	−0.29
		u	−1.51			−0.98	−0.68	−0.45	0
		v	−1.63		0.52	−1.11	−0.74	−0.50	−0.12
		w	−1.57			−1.05	−0.71	−0.48	−0.06
3-$SO_3^-Na^+$		*i*	0.68	5.8	0.53	1.21	0.31	0.55	0.13
		n	0.59			1.12	0.27	0.51	0.04
4-$SO_3^-Na^+$		*i*	1.02	6.7	0.46	1.48	0.46	0.67	0.36
		n	0.94			1.40	0.43	0.63	0.28
3-PO_3^{2-}		*h*	−0.88	6.0	1.04	0.16	−0.40	0.07	0
4-PO_3^{2-}		*h*	−0.58		0.90	0.32	−0.26	0.15	0.06
ArSH[x]									
3-$NMe_3^+BrC_6H_4SO_3^-$	48E	*e*	2.32	5.4	0.85	1.47	0.88	0.56	−0.08
4-$NMe_3^+Tos^-$		*e*	2.13	6.3	0.73	1.40	0.81	0.53	0.01
4-$NMe_3^+Cl^-$	49E	*q*	2.18		0.73	1.45	0.89	0.59	0.10
$ArNH_3^+$ [y]									
3-$CH_2NH_3^+$	H_2O	*n*	1.10	5.8	0.53	0.57	0.37	0.19	0.04
	50E	*n*	1.32		0.78	0.54	0.37	0.15	−0.10
4-$CH_2NH_3^+$	H_2O	*n*	1.12	6.7	0.46	0.66	0.38	0.22	0.13
	50E	*n*	1.31		0.68	0.63	0.37	0.18	−0.01
4-$CH_2NMe_2H^+$	H_2O	*n*	1.47	6.7	0.46	1.01	0.50	0.34	0.22
4-$CH_2CH_2NMe_3^+$		*n*	0.50	8.2	0.38	0.12	0.17	0.04	0.03
	50E	*n*	0.62		0.56	0.06	0.17	0.02	−0.05
	75E	*n*	0.79		0.77	0.02		0.01	−0.10
3-NH_3^+	H_2O	*z*	2.06	5.2	0.59	1.47	0.70	0.50	−0.06
		n	2.12			1.53	0.72	0.52	0
4-NH_3^+		*z*	1.63	6.0	0.51	1.12	0.55	0.38	−0.03
		n	1.66			1.15	0.56	0.39	0
3-$NMe_3^+Cl^-$		*c*	2.62	5.2	0.59	2.03	0.89	0.69	0.29
4-$NMe_3^+Cl^-$		*c*	2.46	6.0	0.51	1.95	0.84	0.66	0.39
4-$N_2^+BF_4^-$		*d*	9.33	6.0	0.51	8.82	3.17	3.00	4.94
4-COO^-		*n*	0.76	6.7	0.48	1.24	0.26	0.42	0.48
4-$CH_2SO_3^-Na^+$		*n*	0.00	7.1	0.44	0.44	0.00	0.15	0.06
	50E	*n*	−0.30		0.64	0.34	−0.08	0.10	−0.12
3-$SO_3^-Na^+$	H_2O	*i*	0.75	5.9	0.53	1.28	0.26	0.44	−0.16
		aa	0.84			1.37	0.29	0.47	−0.07
		n	0.89			1.42	0.30	0.48	−0.02
4-$SO_3^-Na^+$		*i*	1.23	6.8	0.46	1.69	0.42	0.57	0.19
		aa	1.35			1.81	0.46	0.62	0.31
		n	1.40			1.86	0.48	0.63	0.36
4-CH_2COOMe	50E	*bb*	0.15				0.04		
4-CH_2CH_2COOMe		*cc*	−0.16				−0.04		
4-CMe_2CH_2COOMe		*cc*	−0.13				−0.04		
$ArNMeH_2^+$ [dd]									
3-PO_3H^-	H_2O	*h*	0.07	6.1	0.51	0.58	0.02	0.19	−0.14
$ArNEtH_2^+$ [dd]									
3-PO_3H^-	H_2O	*h*	0.29	6.1	0.51	0.80	0.10	0.27	0.08
$ArNMe_2H^+$ [ee]									
4-$CH_2NH_3^+$	H_2O	*n*	1.30	6.7	0.46	0.84	0.37	0.24	0.20
	50E	*n*	1.44		0.68	0.76	0.34	0.18	−0.01
3-NMe_2H^+	H_2O	*n*	2.71		0.59	2.12	0.76	0.60	0
4-NMe_2H^+		*ff*	2.68	6.0	0.51	2.17	0.74	0.60	0.14
		n	2.51		0.51	2.00	0.71	0.56	0
3-$NMe_3^+Cl^-$		*c*	2.91	5.2	0.59	2.32	0.80	0.64	0.18
		n	2.81		0.59	2.22	0.79	0.62	0.12
	50E	*n*	3.08		0.87	2.21	0.72	0.52	−0.32
4-$NMe_3^+Cl^-$	H_2O	*c*	2.84	6.0	0.51	2.33	0.78	0.64	0.41
		n	2.82			2.31	0.79	0.65	0.42
	50E	*n*	3.08		0.76	2.32	0.72	0.54	0.05
4-COO^-	H_2O	*n*	1.01	6.7	0.48	1.49	0.28	0.42	0.57
$ArCH_2NH_3^+$ [gg]									
3-CH_2COO^-	H_2O	*n*	−0.38	7.5	0.41	0.03	−0.34	0.03	0.02
	50E	*n*	−0.72		0.61	−0.11	−0.56	−0.08	−0.12
4-CH_2COO^-	H_2O	*n*	−0.34	8.0	0.39	0.05	−0.30	0.04	0.04
	50E	*n*	−0.62		0.57	−0.05	−0.48	−0.04	−0.06
4-CH_2COOMe		*n*	0.10				0.08		

Table IV (*continued*)

compd	solvent	ref	Δ	r	δ^B	$\Delta - \delta^B$	σ	σ^L	dev
3-$CH_2CH_2COO^-$	H_2O	*n*	−0.36	9.6	0.32	−0.04	−0.32	−0.04	0.06
	50E	*n*	−0.64		0.47	−0.17	−0.49	−0.13	−0.05
4-$CH_2CH_2COO^-$	H_2O	*n*	−0.33	9.5	0.32	−0.01	−0.29	−0.01	0.04
	50E	*n*	−0.56		0.48	−0.08	−0.43	−0.06	−0.03
trans-4-$CH{=}CHCOO^-$	H_2O	*n*	−0.07	9.7	0.32	0.25	−0.06	0.22	0.01
	50E	*n*	−0.22		0.47	0.25	−0.17	0.19	−0.02
3-COO^-	H_2O	*n*	−0.19	7.0	0.44	0.25	−0.17	0.22	−0.02
	50E	*n*	−0.49		0.65	0.16	−0.38	0.12	−0.15
4-COO^-	H_2O	*n*	−0.13	7.2	0.43	0.30	−0.12	0.27	0.01
	50E	*n*	−0.29		0.63	0.34	−0.22	0.27	0.00
4-COOMe		*n*	0.64				0.49		
4-Me	H_2O	*n*	−0.14				−0.12		
	50E	*n*	−0.14				−0.11		
$ArSO_2NH_2$[hh]									
4-PO_3^{2-}	H_2O	*h*	−0.64	7.9	0.78	0.14	−0.57	0.12	0
$ArNHSO_2Ph$[ii]									
4-COO^-	H_2O[ii]	*jj*	0.35	6.7	0.46	0.81	0.19	0.43	0.32
	80MCS	*kk*	−0.20		1.14	0.94	−0.07	0.32	0.18
$Ar_3C^+ + H_2O \rightleftharpoons Ar_3COH + H^+$[ll]									
4,4′,4″-tri$NMe_3^+ClO_4^-$	H_2O	*ll*	8.11	6.5	1.44	6.67	0.69	0.57	0.46

[a] Compound: indicated are reaction series and substituent; counterions are given when present in the preparations used. The reactions have been ordered as in H. H. Jaffé, *Chem. Rev.*, **53,** 191 (1953), and ref 1. Solvent [dielectric constants, in parentheses, from G. Åkerlöf, *J. Am. Chem. Soc.*, **54,** 4125 (1932)]: H_2O (20 °C, 80.4; 25 °C, 78.5; 30 °C, 76.7; 80 °C, 61; 90 °C, 58); 25E, 48E, 49E, 50E, and 75E represent percentages of ethanol in ethanol–water mixtures (67, 53, 54, 53, and 38.6 at specified temperatures); 80 MCS, 80% methylcellosolve–water (32, footnote *kk*). Temperature 25 °C; for exceptions see footnotes *c, d, q, r, t, u, ff, ii.* Δ, r, δ^B, σ, σ^L, and dev as in Table III; Δ has been corrected statistically where applicable. [b] In water at 0 °C, $\rho = 1$; pK_a(PhCOOH) 4.20 at 25 and 0 °C. [c] A. V. Willi, ref 6. $ArNMe_2H^+$ at 20 °C. [d] E. S. Lewis and M. D. Johnson, *J. Am. Chem. Soc.*, **81,** 2070 (1959). ArCOOH, temperature 0 °C. All data for N_2^+ uncorrected for ionic strength effects. [e] F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **78,** 87 (1956). [f] B. J. Thamer and A. F. Voigt, *J. Phys. Chem.*, **56,** 225 (1952); B. J. Thamer, *ibid.*, **59,** 450 (1955). The estimated uncertainties given by Thamer and Voigt correspond with a range in σ^L of 0.28–0.42 for 3-COO^- and of 0.29–0.54 for 4-COO^-. [g] C. F. Wilcox and J. S. McIntyre, *J. Org. Chem.*, **30,** 777 (1965). [h] H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Am. Chem. Soc.*, **75,** 2209 (1953). $ArPO_3H^-$: H_2O, $\rho = 1.121$; 50E, $\rho = 1.153 \pm 0.196$, $s = 0.10$, $R = 0.97$ (ref 4). $I = 0.13$–0.23. Some ionic strength corrections, e.g., for 3-PO_3^{2-}-phenol, are as high as 0.68 pK units. [i] H. Zollinger, W. Büchler, and C. Wittwer, *Helv. Chim. Acta*, **36,** 1711 (1953). [j] $\rho = 0.486$ (Table II). [k] B. Bettman, G. E. K. Branch, and D. L. Yabroff, *J. Am. Chem. Soc.*, **56,** 1865 (1934); $\rho = 2.177$ (ref 1). [l] Reference 1: H_2O, $\rho = 2.205$; 49E, $\rho = 2.687$. PhOH, pK_a in water: 25 °C, 10.00 (except ref *m*: 9.89); 20 °C, 10.07; 30 °C, 9.93 [for temperature variation see P. D. Bolton, F. M. Hall, and J. Kudrynski, *Aust. J. Chem.*, **21,** 1541 (1968); P. D. Bolton, F. M. Hall, and I. H. Reece, *Spectrochim. Acta*, **22,** 1149 (1966)]. [m] J. Epstein, R. E. Plapinger, H. O. Michel, J. R. Cable, R. A. Stephani, R. J. Hester, C. Billington, and G. R. List, *J. Am. Chem. Soc.*, **86,** 3075 (1964). $I = 0.1$; pK found for PhOH, 9.78. [n] This laboratory. [o] S. Oae and C. C. Price, *J. Am. Chem. Soc.*, **80,** 3425 (1958). [p] H. C. Ko, W. F. O'Hara, T. Hu, and L. G. Hepler, *J. Am. Chem. Soc.*, **86,** 1003 (1964). [q] Temperature 20–22 °C: G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, **22,** 360 (1939). [r] Temperature 20 °C: B. Jones and J. C. Speakman, *J. Chem. Soc.*, 19 (1944). [s] D. T. Y. Chen and K. J. Laidler, *Trans. Faraday Soc.*, **58,** 480 (1962). [t] Temperature 30 °C: C. T. Abichandani and S. K. K. Jatkar, *J. Indian Inst. Sci.*, **A21,** 417 (1938). [u] Temperature 20 °C: J. Sunkel and H. Staude, *Ber. Bunsenges. Phys. Chem.*, **72,** 567 (1968). $I = 0.1$, [v] J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.*, **49,** 1140 (1953). $I = 0.65$. [w] C. A. Bishop and L. K. J. Tong, *J. Am. Chem. Soc.*, **87,** 501 (1965). $I = 0.375$. [x] Reference 1: 48E, $\rho = 2.624$; 49E, $\rho = 2.453$. [y] Reference 1: H_2O, $\rho = 2.941$. In 50E, $\rho = 3.574$; 75E, ρ taken as 4; pK_a* ($PhNH_3^+$): H_2O, 4.62; 50E, 4.04; 75E, 3.78 (unpublished). Our measurements on *m*- and *p*-phenylenediamine at $I = 0.04$. [z] A. V. Willi, *Z. Phys. Chem. (Frankfurt am Main)*, **27,** 233 (1961). [aa] R. O. MacLaren and D. F. Swinehart, *J. Am. Chem. Soc.*, **73,** 1822 (1951); R. D. McCoy and D. F. Swinehart, *ibid.*, **76,** 4708 (1954). [bb] Reference 4. [cc] Reference 3. [dd] $\rho = 3$ (estimated); pK_a-($PhNMeH_2^+$) 4.86; pK_a ($PhNEtH_2^+$) 5.27 (unpublished). [ee] Reference 1: H_2O, 25 °C, $\rho = 3.557$. In H_2O, 20 °C, $\rho = 3.62$ (cf. ref 2, footnote 18). pK_a* ($PhNMe_2H^+$): in H_2O, 25 °C, 5.16; in 50E, 25 °C, 4.16; ρ in 50E, 4.281 (unpublished). Our measurements on tetramethyl-*m*- and -*p*-phenylenediamines at $I = 0.04$. [ff] Temperature 20 °C: A. V. Willi, *Helv. Chim. Acta*, **40,** 2019 (1957). [gg] H_2O: $\rho = 1.129$, pK_a ($PhCH_2NH_3^+$) 9.39. 50E: $\rho = 1.297$, pK_a* ($PhCH_2NH_3^+$) 8.64 (unpublished). [hh] $\rho = 1.13$ [from H and 3-NO_2 at 20 °C, reported by A. V. Willi, *Helv. Chim. Acta*, **39,** 46 (1956)]; pK_a ($PhSO_2NH_2$) 10.04 at 25 °C after temperature correction (cf. footnote *l*). [ii] Temperature 20 °C, H_2O: $\rho = 1.89$ (from H and 3-NO_2 as in footnote *hh*). 80% MCS: $\rho = 2.918$ (ref 1). [jj] A. V. Willi, footnote *hh*. [kk] W. Simon, A. Mörikofer, and E. Heilbronner, *Helv. Chim. Acta*, **40,** 1918 (1957). [ll] Temperature 25 °C: M. J. Cook, N. L. Dassanayake, C. D. Johnson, A. R. Katritzky, and T. W. Toone, *J. Am. Chem. Soc.*, **97,** 760 (1975); $\rho = 3.90 \pm 0.27$; $s = 0.46$; $R = 0.993$ (H, 3,3′,3″-triCl, 4-NO_2, 4,4′-diNO_2, and 4,4′,4″-triNO_2). The data at 80 °C give $\sigma^L = 0.52$, at 90° $\sigma^L = 0.58$. Dielectric constants were taken equal to those of water.

variation due to the variation of r and D_s; (b) the variation of the fraction that δ^B is of Δ, mostly between 20 and 80%; (c) $\sigma = \Delta/\rho$ and $\sigma^L = (\Delta - \delta^B)/\rho$ as the slope of the line from the origin to the point in question; (d) the variation of σ and σ^L. The individual σ and σ^L values have been included in Tables III–V.

We regard the general picture provided by these figures as highly satisfactory with respect to eq 8: the $\Delta - \delta^B$ points conform to a straight line through the origin as well as could be hoped for, i.e. σ^L is reasonably constant. This qualification gains in weight when it is considered that $\Delta - \delta^B$ contains the combined uncertainties in two experimental equilibrium or rate constants, their (different) Debye–Hückel–Brønsted corrections, the distance r (for conformational problems see section 8.e), and the (effective) dielectric constant, quite apart from the intrinsic limitations of $\rho\sigma$ relations. An extreme example is the alkaline hydrolysis of 4-$NMe_3^+C_6H_4CH_2COOEt$ in 85% ethanol: at $I = 0.1$, $\Delta = 0.88$, from which is calculated $\Delta = 1.61$ at $I = 0$, giving $\Delta - \delta^B = 0.40$. In view of the magnitude of these "manipulations", the corresponding point in Figure 3 at $\rho = 1.25$ is surprisingly well in line with the other data.

Table V.[a] Analysis of Substituent Effects: σ and σ^L, Deviations of Calculated from Experimental Values, and Literature Data on Reaction Rates

reaction and substituent	solvent	temp, °C	Δ^{obsd}	Δ	r	δ^B	$\Delta - \delta^B$	σ	σ^L	dev
$ArCOOMe + OH^-$										
$4\text{-}NMe_3^+I^-$	H_2O[b]	25		1.323[b]	6.2	0.50	0.82	0.81	0.50	−0.04
$4\text{-}CH_2NMe_3^+I^-$			0.704	0.966	6.9	0.45	0.52	0.59	0.32	0.00
$4\text{-}(CH_2)_2NMe_3^+I^-$			0.180	0.442	8.4	0.37	0.07	0.27	0.04	0.02
$4\text{-}(CH_2)_3NMe_3^+I^-$			0.003	0.265	9.3	0.34	−0.08	0.16	−0.05	0.02
$4\text{-}(CH_2)_4NMe_3^+I^-$			−0.101	0.161	10.7	0.29	−0.13	0.10	−0.08	0
$4\text{-}CH_2NMe_2$			−0.017					−0.01		
$4\text{-}CH_3$			−0.285					−0.17		
$ArCOOEt + OH^-$										
$3\text{-}COO^-$	60A[c]	25	0.378	−0.070	6.0	0.92	0.85	−0.03	0.34	0.26
$4\text{-}COO^-$			0.406	−0.042	6.9	0.80	0.76	−0.02	0.31	0.12
$4\text{-}O^-$			−2.521	−2.969	6.2	0.88	−2.09	−1.20	−0.85	−0.98
$ArCH_2COOEt + OH^-$										
$3\text{-}NMe_3^+I^-$	60A[d]	25	1.315	1.557	6.8	0.81	0.75	1.72	0.83	0.22
$4\text{-}NMe_3^+I^-$			1.070	1.312	6.7	0.82	0.49	1.45	0.54	0.01
$4\text{-}NMe_3^+I^-$	85E[e]	25	0.878	1.612	6.7	1.21	0.40	1.29	0.32	−0.26
$ArCH_2CH_2COOEt + OH^-$										
$3\text{-}NMe_3^+I^-$	88E[f]	30	0.738	1.364	7.9	0.98	0.38	2.15	0.60	0.01
$4\text{-}NMe_3^+I^-$			0.540	1.166	8.4	0.92	0.25	1.84	0.39	−0.09
$ArOCOMe + OH^-$										
$3\text{-}COO^-$	60A[g]	15	0.199	−0.239	7.3	0.74	0.50	−0.16	0.33	0.14
$4\text{-}COO^-$			0.290	−0.148	7.5	0.72	0.57	−0.10	0.38	0.18
$ArOCOPh + OH^-$										
$3\text{-}NMe_3^+I^-$	H_2O[h]	25		1.072	7.0	0.44	0.63	0.96	0.57	−0.03
$4\text{-}NMe_3^+I^-$				0.973	6.8	0.45	0.52	0.88	0.47	−0.07
$3\text{-}COO^-$				−0.123	7.3	0.43	0.31	−0.11	0.28	0.04
$4\text{-}COO^-$				−0.011	7.5	0.41	0.40	−0.01	0.36	0.11
$3\text{-}O^-$				−0.828	7.0	0.44	−0.39	−0.75	−0.35	−0.08
$4\text{-}O^-$				−0.717	6.8	0.45	−0.27	−0.65	−0.24	0.23
$4\text{-}SO_3^-$				0.113	7.6	0.41	0.52	0.10	0.47	−0.05
$ArOSO_2C_6H_4Me + OH^-$										
$3\text{-}NMe_3^+I^-$	H_2O[i]	50		1.738	8.6	0.37	1.37	0.89	0.70	0.21
$4\text{-}NMe_3^+I^-$				1.515	8.4	0.38	1.14	0.77	0.58	0.10
					5.7	*0.57*	*0.95*		*0.48*	*−0.09*
$4\text{-}SO_3^-$				0.647	9.1	0.35	1.00	0.33	0.51	0.00
					6.4	*0.50*	*1.15*		*0.59*	*0.15*
$3\text{-}COO^-$		60		−0.223	9.2	0.35	0.13	−0.12	0.07	−0.32
$4\text{-}COO^-$				−0.123	9.0	0.36	0.24	−0.07	0.13	−0.25
$3\text{-}O^-$				−1.538	8.6	0.38	−1.16	−0.82	−0.62	−0.64
$4\text{-}O^-$				−1.309	8.4	0.39	−0.92	−0.70	−0.49	−0.08
$4\text{-}NO_2$				1.542				0.82		

[a] Δ^{obsd} is log k observed for substituted compound *minus* log k observed for parent compound. Other headings as in Tables III and IV. 60A: 60% acetone–water. [b] J. H. Smith and F. M. Menger, *J. Org. Chem.*, **34,** 77 (1969). Their tabulated log k value for $4\text{-}NMe_3^+$ is five times that of the value measured in 0.0400 M NaOH (private communication, Dr. Menger). Accordingly, the value in 0.04 M NaOH was corrected for salt effects, and then brought to the 0.2 M level. $\rho = 1.63$ from H and $4\text{-}NO_2$. [c] S. Tommila and E. Tommila, *Ann. Acad. Sci. Fenn., Ser. A,* **59,** No. 5 (1942); E. Tommila, A. Nurro, R. Murén, S. Merenheimo, and E. Vuorinen, *Suom. Kemistil. B,* **32,** 115 (1959). $I = 0.10$; $\rho = 2.468$ (ref 1); $D = 44.4$. [d] R. O. C. Norman and P. D. Ralph, *J. Chem. Soc.*, 5431 (1963). $\rho = 0.903$ (ref 4); $D = 44.4$. Initial concentrations: ester, 0.0089 M; NaOH, 0.0089 M (private communication, Dr. Norman). [e] See Table II; $D = 30.1$. Initial concentrations: ester, 0.05 M; NaOH, 0.05 M. [f] See Table II; $D = 31.1$. Initial concentrations: ester, 0.023 M; NaOH, 0.030 M (private communication, Dr. Fuchs). [g] E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938). $I = 0.10$; $\rho = 1.509$ (ref 1); $D = 46.8$. [h] T. O. Püssa, V. M. Nummert (Maremäe), and V. A. Palm, *Reakts. Sposobn. Org. Soedin.*, **9,** 697 (1972). English summary, 727–728; ref 30b, 7f. $\rho = 1.111 \pm 0.145$; $s = 0.073$; $R = 0.992$ (H, 3-Cl, $3\text{-}NO_2$). [i] V. M. Maremäe and V. A. Palm, *Reakts. Sposobn. Org. Soedin.*, **1,** 85 (1964), English summary, 100–102; ref 28a, 28b, 7c, 30a. At 50 °C: $\rho = 1.959 \pm 0.086$; $s = 0.054$; $R = 0.998$ (H, 3-Me, 3-Cl, $3\text{-}NO_2$); $D = 69.9$. At 60 °C: $\rho = 1.871 \pm 0.066$; $s = 0.042$; $R = 0.999$ (H, 3-Me, 3-Cl, $3\text{-}NO_2$); $D = 66.6$. The italicized figures relate to the "late" transition state with the negative charge on the phenolic oxygen as assumed by Palm et al.; the other figures relate to an "early" transition state with the negative charge 4 Å away from the phenolic oxygen (see Chart for geometrical details[24]). The use of r of the late transition state and the corresponding high value of δ^B is, however, not justified (see section 16). The exaltation of $4\text{-}NO_2$, small at best, is not in favor of the late transition state; $\Delta^1 = 0.87$ (see section 8.a) is close to $\Sigma|\delta^B| = 0.73$.

The points for Δ confirm and extend the large variations in σ illustrated in Figure 1. Figure 3, for example, shows that the whole range of σ for $4\text{-}NMe_3^+$, 0.7–2.2, is "continuously" populated. We note that the Δ values are not chaotic but approach a line parallel to that representing σ^L. This is caused by the fact that in most cases $\delta^B = 0.3$–0.6. In those cases where δ^B is almost the same the Δ line is at that distance from the ($\Delta - \delta^B$) line. The three points for $3\text{-}SO_3^-$ in water (Figure 4) have δ^B values from −0.45 to −0.53; accordingly, the Δ points are approximately on a straight line parallel to the σ^L line and 0.5 pK_a units below it.

Average values of "normal" [1] σ^L values, to be denoted as σ^{Ln},

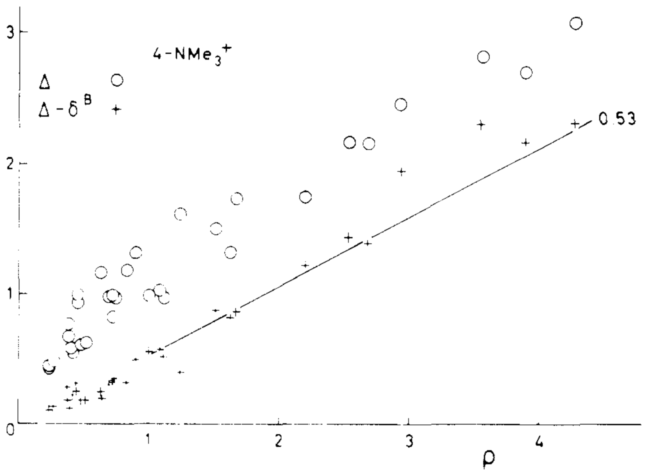


Figure 3. Δ and $\Delta - \delta^B$ of 4-NMe_3^+ vs. ρ. The line drawn has the slope of the average σ^L value, 0.53. The regression line through the origin for $\Delta - \delta^B$ has slope 0.56, $s = 0.12$, $R = 0.992$, $n = 33$ (for $\rho \geq 1$ slope $= 0.57$, $s = 0.16$, $R = 0.994$, $n = 14$). Individual σ^L values range from 0.30 to 0.74; σ values from 0.69 to 2.21.

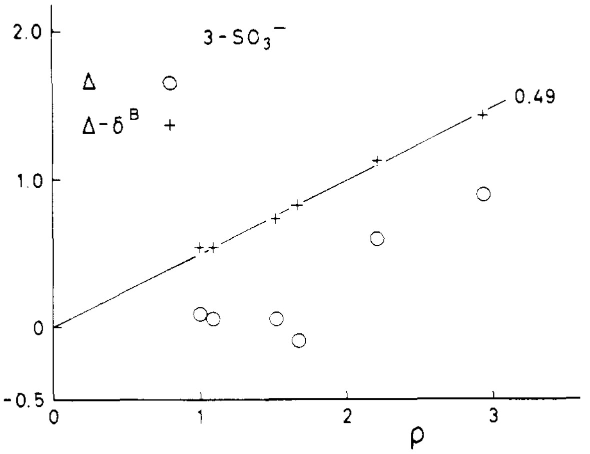


Figure 4. Δ and $\Delta - \delta^B$ of 3-SO_3^- vs. ρ for the series ArCOOH, ArOH, and $ArNH_3^+$. The line drawn has the slope of the average σ^L value, 0.49. The regression line through the origin for $\Delta - \delta^B$ has slope 0.49, $s = 0.03$, $R = 1.000$. Individual σ^L values range from 0.47 to 0.53, σ values from −0.06 to 0.30.

Table VI.[a] **Average (normal) σ^{Ln} Values from Equilibria and Rates with $\rho \geq 1$**

substituent	meta $\sigma^{Ln} \pm s$	meta n	para $\sigma^{Ln} \pm s$	para n
$CH_2NH_3^+$	0.18 ± 0.05[b]	6	0.18 ± 0.04[b]	8
$CH_2NMeH_2^+$			0.21 ± 0.01	4
$CH_2NMe_2H^+$			0.27 ± 0.05	4
$CH_2NMe_3^+$	0.30 ± 0.07	5	0.32 ± 0.04	6
$CH_2NEt_3^+$			0.28 ± 0.06	4
$CH_2NBu_3^+$			0.29 ± 0.06	4
$CH_2CH_2NH_3^+$			0.03 ± 0.02	4
$CH_2CH_2NMe_3^+$	0.07	1	0.03 ± 0.02	9
$(CH_2)_3NMe_3^+$	0.00	1	−0.06 ± 0.01	2
$(CH_2)_4NMe_3^+$			−0.08	1
NH_3^+	0.52	1	0.39	1
NMe_2H^+	0.60	1	0.56	1
NMe-*t*-BuH$^+$			0.47	1
NMe_3^+	0.59 ± 0.06[b]	10	0.53 ± 0.08[b,c]	14
NEt_2Me^+	0.54 ± 0.10	4		
N_2^+	1.11	1	1.32	1
SMe_2^+	0.76 ± 0.11	2	0.77	1
CH_2COO^-	0.01 ± 0.08	3	0.01 ± 0.05	3
$CH_2CH_2COO^-$	−0.06 ± 0.06	3	−0.04 ± 0.03	3
trans-CH=CHCOO$^-$			0.21 ± 0.02	2
$CMe_2CH_2COO^-$			−0.01	1
$CH_2SO_3^-$			0.13 ± 0.04	2
COO^-	0.24 ± 0.08	12	0.26 ± 0.09	8
O^-	−0.28[d]	1	−0.45[d]	1
PO_3H^-	0.24 ± 0.05	3	0.29	1
SO_3^-	0.49 ± 0.02	6	0.51 ± 0.05[b]	4
$CH_2CH(COO^-)_2$			0.06	1
$CH{=}C(COO^-)_2$			0.46	1
PO_3^{2-}	0.07	1	0.12	1

[a] The average (normal) σ^{Ln} values are given with their standard deviations s and the number of data, n. [b] Without restrictions as to ρ: 3-$CH_2NH_3^+$, $n = 14$, $\sigma^L = 0.31 \pm 0.17$; 4-$CH_2NH_3^+$, $n = 19$, $\sigma^L = 0.20 \pm 0.07$; 3-NMe_3^+, $n = 23$, $\sigma^L = 0.64 \pm 0.12$; 4-NMe_3^+, $n = 33$, $\sigma^L = 0.50 \pm 0.11$; 4-SO_3^-, $n = 15$, $\sigma^{Ln} = 0.54 \pm 0.08$. [c] Excluding $\sigma^L = 0.32$ from $ArCH_2COOEt$ (Table V): $n = 13$; $\sigma^L = 0.55 \pm 0.05$. [d] From the most recent, and probably most reliable, value in the ArOH series (footnote *u* of Table IV; $I = 0.1$; measurements under N_2). The values from the alkaline hydrolysis of ArOCOPh (Table V) are probably not reliable; 4-O^- is less negative than 3-O^- (as in the tosylates), which might be the result of instability of the products and incomplete ionization of substrates and products. All values: 3-O^-, $n = 3$, $\sigma^L = -0.28 \pm 0.07$; 4-$O^-$, $n = 5$, $\sigma^{Ln} = -0.45 \pm 0.13$.

have been derived from reactivity data which: (a) are free from through-resonance effects, (b) have $\rho \geq 1$. The first selection is obvious because eq 8 will fail, like the Hammett equation,[1] if through-resonance occurs (section 12). As to notation, we shall compromise between rigidity and simplicity, adding the superscript n only when for para substituents with a +M or −M effect σ^L might be ambiguous. The second selection, using a cutoff at an admittedly arbitrary level, intends to avoid undue weight being given to less reliable σ^L values. As to details in our selection procedure we mention that, if in one and the same solvent several data are specified, only one figure is used, either the one obtained by us, or, if only literature values are available, the average of these (e.g., 4-$NMe_3^+C_6H_4OH$). Again, the rate constants of the aryl tosylates have not been used because of uncertainty in mechanism (Table V), whereas a choice has been made for 3-O^- and 4-O^- (Table VI; section 12).

The σ^{Ln} values thus obtained are listed in Table VI; their standard deviations are not or hardly larger than those for σ^n values of dipole substituents.[1,4] Some additional statistical data are given in the legend of Table VI and the captions of the relevant figures.

The final test of eq 8 consists of a comparison of observed and calculated substituent effects. The column dev of Tables III–V gives the individual deviations. Figure 11 shows the adherence to eq 8 in six important systems in H_2O and 10, 50, and 75% ethanol, for nine substituents for which five or more data are available. For comparison Figure 12 shows a similar plot of Δ vs. $\rho\sigma$, where the σ "numbers" for the nine substituents are equated to Δ for ArCOOH in water. The regression lines for these two plots have, respectively: $\rho = 1.03 \pm 0.01$ and $\rho = 0.71 \pm 0.04$; $s = 0.10$ and 0.31; $R = 0.991$ and 0.910; intercepts 0.003 and 0.252. Hence, the improvement by using eq 8 is very satisfactory.

8. Equation 8; Detailed Discussion. In this section we shall consider a number of aspects of eq 8 which may not be immediately apparent from the above general discussion. Some of these are supported by additional experimental material.

(a) The Effect of Substituting 4-NMe_3^+ by 4-SO_3^-. The near equality of the σ^{Ln} values of 4-NMe_3^+ and 4-SO_3^-, 0.53 ± 0.08 and 0.51 ± 0.05, respectively, implies that

$$\Delta' = \log K(4\text{-}NMe_3^+) - \log K(4\text{-}SO_3^-)$$

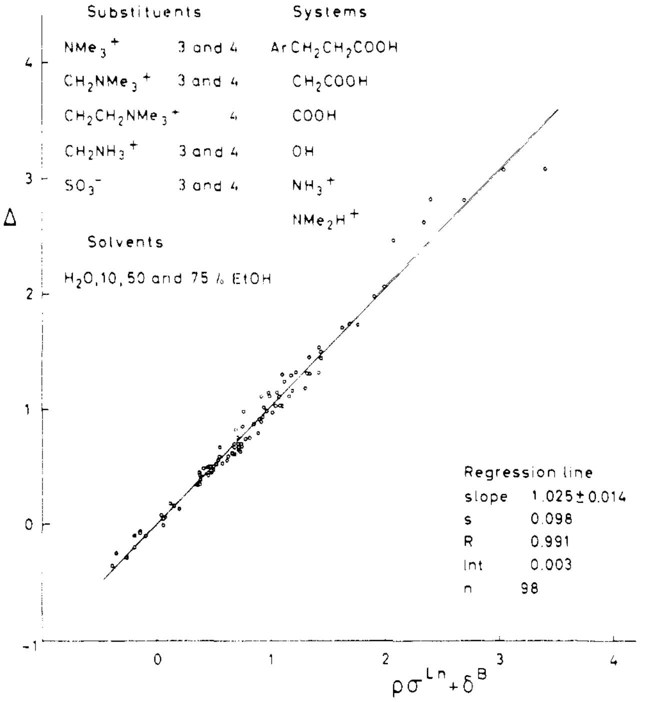


Figure 11. Showing the adherence to eq 8 (through-resonance absent).

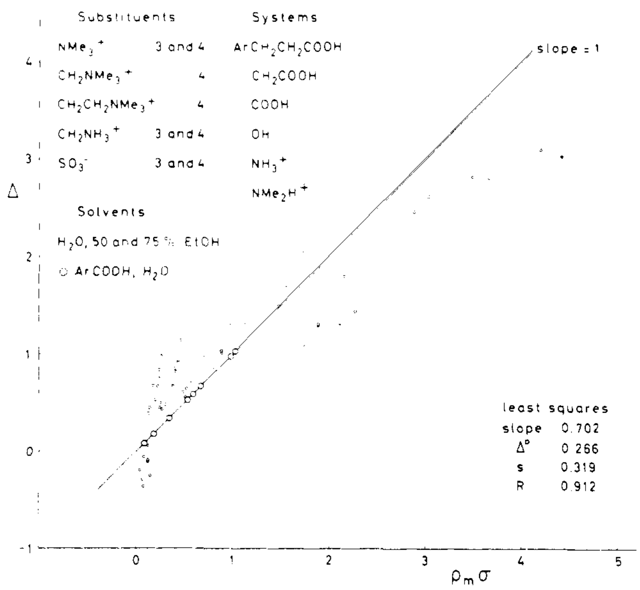


Figure 12. Relative failure of the Hammett equation $\Delta = \rho\sigma$ with charged substituents. The nine larger circles on the line through the origin with slope = 1 correspond with the data from the ArCOOH series in water used to define the σ "numbers".

is largely determined by the difference of the Bjerrum terms; the absolute value of Δ', $|\Delta'|$, is practically equal to $\Sigma|\delta^B|$, the sum of the absolute values of δ^B. Table VII gives the data for the acids of Table III. The aryl benzoates (Table V) also conform to this rule.

Such comparisons, which can be extended to other pairs with equal σ^L values, suggest in a direct way that δ^B is physically meaningful (cf. sections 8.g and 10). Also, they are attractive as a tool in judging mechanisms, in particular because neither ρ nor other reactivity data are required, and Δ' increases linearly with $1/D_S$. Specific applications are given in section 8.g.

Table VII.[a] **Illustrating that the pK_a* Difference between 4-NMe$_3^+$- and 4-SO$_3^-$-Substituted Acids is Approximately Equal to $\Sigma|\delta^B|$, the Sum of the Absolute Values of δ^B**

system	solvent	Δ'	$\Sigma\lvert\delta^B\rvert$	$100\,\Delta'/\Sigma\lvert\delta^B\rvert$
ArCOOH	H$_2$O	0.80	0.82	98
	10E	0.87	0.87	100
	50E	1.37	1.20	114
	75E	1.74	1.66	105
ArCH$_2$COOH	H$_2$O	0.67	0.82	82
	10E	0.70	0.86	81
	50E	1.07	1.19	90
	75E	1.43	1.65	87
trans-ArCH=CHCOOH	H$_2$O	0.61	0.63	97
	50E	0.92	0.92	100
	75E	1.23	1.27	97
ArCH$_2$CH$_2$COOH	H$_2$O	0.65	0.64	102
	10E	0.68	0.68	100
	50E	0.96	0.94	102
	75E	1.29	1.30	99

[a] $\Delta' = \log K(4\text{-NMe}_3^+) - \log K(4\text{-SO}_3^-)$. Solvents: water and aqueous ethanol as in Tables I and III.

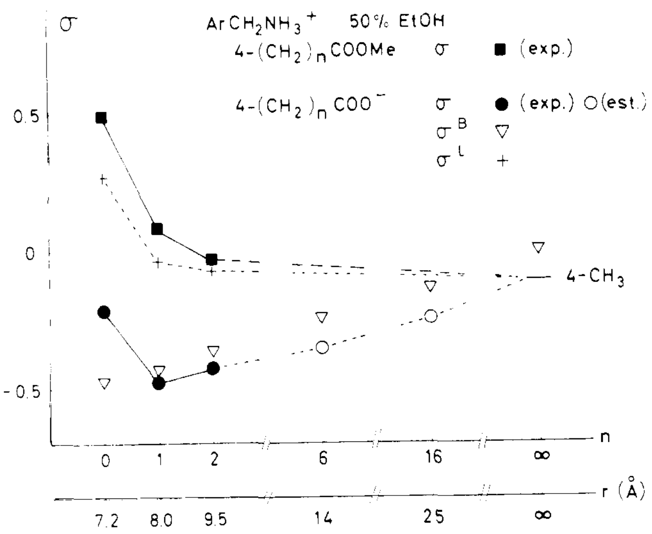


Figure 13. Showing regular attenuation of σ^L of 4-(CH$_2$)$_n$COO$^-$ as compared with irregular behavior of σ.

(b) The Substituent Series 4-(CH$_2$)$_n$COO$^-$. In Figure 13 the effects of these substituents on the dissociation of ArCH$_2$NH$_3^+$ in 50% ethanol are presented in terms of σ, σ^L, and $\sigma^B = \delta^B/\rho$; also indicated is the σ value observed for 4-Me as the value which should be approximated when n becomes very large. The most intriguing feature is that σ shows a minimum for $n = 1$, and this is also found in water, and for 3-(CH$_2$)$_n$COO$^-$ in water and 50% ethanol. This behavior can be understood as the result of the difference in the dependence of σ^L and σ^B upon n: σ^B becomes hardly less negative from $n = 0$ to $n = 1$, and σ^L changes more and in the opposite direction. The situation can be compared with the minimum in nonbonding potential functions as resulting from a combination of attractive and repulsive forces. Such a comparison emphasizes the phenomenological need of two factors.

Another important aspect of Figure 13 is that it shows that σ^L of 4-(CH$_2$)$_n$COO$^-$ and σ of 4-(CH$_2$)$_n$COOMe behave similarly, with σ^L somewhat lower. This supports the thesis that σ^L does represent the non-Bjerrum effects of the charged groups.

(c) The Substituent Series 4-(CH$_2$)$_n$NMe$_3^+$. In Figure 14 the effects are shown for the alkaline hydrolysis of ArCOOMe in water studied by Smith and Menger.[25] In this case σ^L and σ^B vary in the same direction, and, therefore, no minimum is observed. What is observed now is that σ approaches

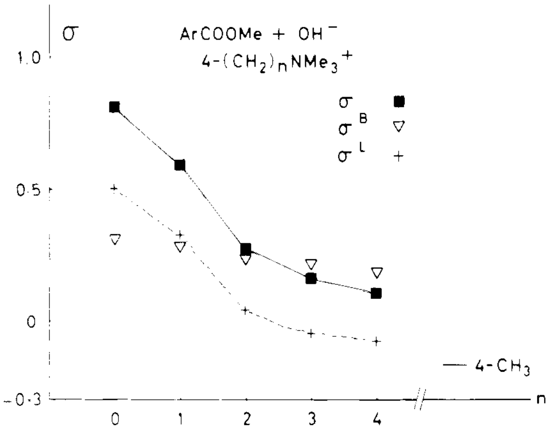


Figure 14. Showing that σ of 4-$(CH_2)_nNMe_3^+$ approaches σ of 4-alkyl only very slowly, whereas σ^L behaves more regularly. The "shoulder" at $n = 1$ is discussed in sections 8.c and 9.

σ(4-Me) very slowly mainly due to the slow decrease of σ^B with increasing n; eq 8 predicts that σ does not become zero before $n \simeq 10$.

Figure 14 shows a "shoulder" for σ^L and σ at $n = 1$, and this is also found with ArOH (n = 0–3) and ArCOOH (n = 0–2). There is reason to consider 4-$CH_2NMe_3^+$ as the exceptional member. The conformation of the $ArCH_2NMe_3^+$ moiety will be such that the plane through $C_{ar}CN$ is about perpendicular to that of the aromatic ring (cf. the homomorphous neopentylbenzene). Therefore, the charge is relatively close to the π electrons, and this may cause the π-inductive effect to be relatively large. We note that for $n = 2$ the conformation around the CH_2–CH_2 bond will be trans, implying that the charge is 1.5 Å farther away from the ring. In harmony with this interpretation the substituent series 3-$(CH_2)_nNMe_3^+$ does not show a shoulder in the ArOH system and follows normal attenuation with a factor of 0.5. Excepting $n = 1$, this same attenuation is followed for 4-$(CH_2)_nNMe_3^+$. Again, the corresponding low meta/para ratio for $n = 1$ we consider exceptional as explained in section 9.

(d) *cis*- and *trans*-Cinnamic Acids. These systems were studied because they have long chains of known and rather rigid conformations. The most important point is that in both systems σ(4-NMe_3^+) is large, showing that the very high σ values found for $ArCH_2CH_2COOH$ certainly cannot be blamed entirely to a cis or skew conformation around the CH_2–CH_2 bond (cf. section 8.e).

It is noteworthy that eq 8 predicts Δ of the *cis*-4-NMe_3^+ isomer within 10%. Since δ^B accounts for about 70% of the total effect this implies that D_s also serves well for this folded molecule. As to the more subtle comparison between the cis and the trans isomer, eq 8 predicts ΔpK_a^* values which are 0.12, 0.19, and 0.24 units higher for the cis isomer in water and 50 and 75% ethanol, respectively. The experimental values are 0.03, 0.16, and 0.15 pK_a units, and this is certainly not unsatisfactory. The situation is illustrated in Figure 15[24] in a direct comparison of Δ values in 50% ethanol; the point for 4-NMe_3^+ is away from the line determined by the dipole substituents (slope one) to the extent of the difference of the δ^B values.

(e) Conformational Aspects. In many of the compounds under discussion more than one conformation has to be considered for the calculation of δ^B. We shall give a few examples with different levels of complexity.

Little or no problem is believed to enter with functional groups like COOH, CH_2COOH, *cis*- and *trans*-CH=CHCOOH, OH, and NH_3^+ with substituents like 4-NMe_3^+, 4-COO^-, 4-SO_3^-, 4-$CH_2NMe_3^+$, 4-$CH_2CH_2NMe_3^+$; substituents in 3 position often present more uncertainty.

With 4-NMe_3^+-β-phenylpropionic acid there is reason to reckon with a larger contribution of the skew conformations than in the parent compound because of the interaction of the positive and the negative charge in the anion (in the 4-SO_3^- derivative the opposite holds). This may reduce r from 9.3 Å (trans) to 5.2 Å, increasing δ^B in water from 0.33 to 0.60, and corresponding with a variation of 0.9 σ units. However, δ^B = 0.60 is incompatible with the experimental Δ = 0.45. Again, the "symmetry" of Figure 1 with respect to NMe_3^+ and SO_3^- indicates that there is little difference in the conformational equilibria, and the precise adherence to eq 8 when using the maximum distance is in harmony with predominance of the trans conformation for either compound.

Even more complicated is 3-$CH_2NH_3^+$-β-phenylpropionic acid and for this compound the difference between calculated and observed Δ rises from 0.07 in water to 0.22 in 75% ethanol (cf. Figure 5[24]). It is not unreasonable to ascribe the differences and their increase with decreasing D_s to an increasing importance of skew conformations with the carboxylate anion and the positive pole on the same side of the benzene ring. Of course, the same zwitterion is involved with 3-$CH_2CH_2COO^-$ in the $ArCH_2NH_3^+$ series, and this might explain why in 50% ethanol the σ^L value, −0.13, is more negative than σ(3-Me) = −0.07. We note that this complication does not impair the main conclusions of section 8.b, since for the CH_2COO^- substituent the variation of δ^B corresponding with conformational variations is small.

For simplicity's sake we have used the maximum values of r throughout. Fortunately, in most cases this is quite acceptable either because this r is the only reasonable one, or because other conformations have very similar values of r. Finally, it should be realized that if D_s is applicable, the variation in the conformational equilibria is determined by the *difference* of the interactions in the several conformers, and even in the above cases this difference amounts to no more than a few tenths of a kilocalorie; accordingly, only small effects are to be expected.

(f) Bulk Effects. The alkylbenzoic acids listed in Table I show substituent effects which are somewhat irregular. It is embarrassing to find that with the 4-alkyl groups pK_a^* increases with the weight of this group in 50% ethanol, but decreases in 75% ethanol. Again, in 50% ethanol Δ is larger than in 75% ethanol: 3,5-di-Me, −0.26 and −0.23, respectively; 3,5-di-*t*-Bu, −0.46, −0.37; 3-neopentyl, −0.30, −0.20; 4-Me, −0.21, −0.21; 4-*t*-Bu, −0.21, −0.16; 4-neopentyl, −0.24, −0.15; 4-CEt_3, −0.28, −0.13. As far as can be ascertained, Δ(3-R) is half Δ(3,5-di-R). Previously, a similar behavior has been found in the series $ArCH_2COOH$[4] (3,5-di-*t*-Bu, −0.32, −0.26) and $ArCH_2CH_2COOH$[3] (3,5-di-*t*-Bu, −0.18, −0.08). Table VIII[24] lists all σ values.

A bulk (solvation) effect,[26] which we shall not try to specify, may be held responsible, since the methyl groups cause the less pronounced differences. Further, it would seem significant that the (all-) equatorial cyclohexanecarboxylic acids behave similarly[27] (Δ for 3,5-di-*t*-Bu, −0.22, −0.08, 4-*t*-Bu, −0.02, +0.07); apparently the presence of the aromatic ring is not essential. There is, however, no clear effect in the cinnamic acids.

We draw attention to these irregularities since they may be part of the total effect of poles, hidden by the large inductive and field effects. The procedure which suggests itself, then, is to compare NMe_3^+ not with H, but with the homomorphous *t*-Bu, and $CH_2NMe_3^+$ with the homomorphous CH_2-*t*-Bu, etc. Fortunately, such a procedure, as far as it can be pursued, does not change the general picture. Therefore, it would seem unwarranted to introduce this complication in our treatment. Quite generally, of course, irregularities as the above, with substituents as the above, should be another warning against overworking the Hammett equation, let alone eq 8.

(g) "Zero Cases" of Equation 8. It would seem useful to bring together the special cases in which one or more of the quantities of eq 8 are zero, or practically so; some of these provide new tests.

(1) $\delta^B = 0$ (Case 1); Substituent Effects at High Ionic Strengths. Recently, Palm et al.[28-30] have reported on the alkaline hydrolysis of ArOCOPh and ArOTs in aqueous solution containing additional electrolyte up to very high concentration. For compounds with charged substituents they found that at concentrations of 1-4 M of, e.g., NaCl, the substituent effects attain a constant value,[28] Δ^∞, as to be expected on the basis of the swamping electrolyte effect.[31] In addition they made the important observation[29] that the change in substituent effect from $I = 0$ to $I = 4$ is (approximately) equal to δ^B:

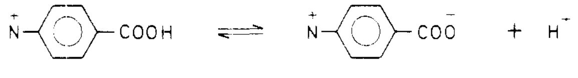
$$\Delta - \Delta^\infty = \pm\delta^B \qquad (11)$$

The explanation offered was that upon increasing the electrolyte concentration the charged substituents and the reagent or the transition state become gradually transformed into ion pairs[32] in which the pole-pole interactions cancel completely or largely.

Following up this approach we have measured dissociation constants at varying ionic strengths. Figure 16 shows our results for 4-NMe_3^+- and 4-SO_3^--β-phenylpropionic acid at several NaCl concentrations (the actual data are in Table IX[24]); Table X lists data in the ArCOOH series in 4 M NaCl for a number of substituents, in comparison with data at I = 0. Figure 16 shows what happens with the substituent effect when I is increased: the effect of 4-NMe_3^+ changes over 0.36 pK units, whereas $\delta^B = 0.33$; the effect of 4-SO_3^- changes over −0.29 pK units, whereas $\delta^B = -0.31$. For I = 2.5-4 the small effects of these groups are practically equal.

The data in Table X show good adherence to eq 11. For the positive poles Δ^∞ and $\Delta - \delta^B$ are practically identical; for the SO_3^- groups Δ^∞ is somewhat smaller than $\Delta - \delta^B$. For either type Δ^∞ is slightly below the average σ^{Ln}. As to the dipoles 3-Cl and 3-NO_2, $\Delta - \Delta^\infty$ is of the right sign, in the right order, and of the right magnitude.[33] Similar behavior has been found in the series $ArCH_2COOH$, $ArNH_3^+$, and ArOH.[27]

As noted by Palm,[7a] the possibility of sifting out δ^B by measurements at high I suggests that the Bjerrum term can be allotted a physical meaning, and this is strongly supported by other evidence in the present paper. Accordingly, in our weakness, we shall temporarily yield to Hammett's temptation[34] and take a closer look at the "mechanism" of eq 11 and the dichotomy of eq 8. The first and most general point to be made is that in an equilibrium like eq I, the building up of the ionic atmosphere mimicks the effect of an increase of the dielectric constant,[35] decreasing δ^B. Secondly, using the Bjerrum model and assuming ion pair formation, it can be argued that almost all the work gained when the proton goes to infinity has to be supplied again when the sodium ion comes in to form the ion pair (eq II). If the N^+ group also forms an ion pair (eq III), either work term becomes smaller so that more complete cancellation occurs.



(I)

(II)

(III)

When considering the ion pairing in more detail, the model with unchanged nuclear distance used for the acids by Eucken[18] and Smallwood[18] (section 5) seems naive, although it accounts for eq 11. Assuming solvent-separated ion pairs with nuclear distances of 5–6 Å[36] would cause serious disagreement with eq 11 and other observations in this paper. The intimate ion pair with a nuclear distance of 2.5–3 Å[36,37] would seem most reasonable; the imperfect cancellation of the work terms when the charges in question are aligned is possibly absorbed in σ^L.

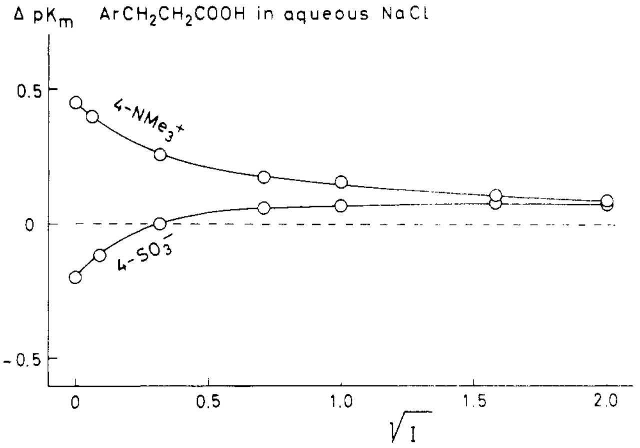


Figure 16. Dependence of ΔpK_m upon ionic strength for 4-NMe_3^+- and 4-SO_3^--β-phenylpropionic acid.

Table X.[a] Substituent Effects, ΔpK_m, in ArCOOH in 4 M NaCl, at 25 °C, as Compared with Values at Zero Ionic Strength

	$I = 4$	$I = 0$		
	ΔpK_m	$\Delta - \delta^B$ (H_2O)	σ^{Ln} (Table VI)	Δ (H_2O)
3-Cl	0.34	0.35		0.37
3-NO_2	0.66	0.66		0.71
4-OH	−0.36			−0.37
3-$CH_2NH_3^+$	0.13	0.14	0.18 ± 0.05	0.59
3-$CH_2NMe_3^+$	0.21	0.23	0.30 ± 0.07	0.68
3-NMe_3^+	0.50	0.54	0.59 ± 0.06	1.03
4-$CH_2NH_3^+$	0.10	0.13	0.18 ± 0.04	0.53
4-$CH_2NMe_3^+$	0.28	0.27	0.32 ± 0.04	0.67
4-$CH_2CH_2NMe_3^+$	−0.02	0.01	0.03 ± 0.02	0.34
4-NMe_3^+	0.53	0.55	0.53 ± 0.08	0.98
3-SO_3^-	0.41	0.53	0.49 ± 0.02	0.08
4-SO_3^-	0.39	0.57	0.51 ± 0.05	0.18

[a] For pK_m see Experimental Section; I, ionic strength.

The adherence to eq 8 and eq 11, then, is in conformity with the following dissection of the dissociation process: (1) the OH covalency stretches, disrupting the quantum mechanical bonding, to form a pair of ions, possibly an (intimate) ion pair; (2) the proton goes to infinity, completing the dissociation.

The energetics of the first stage is determined by factors of chemical structure, of which σ^L is a property of the substituent and ρ is governed by the structure of initial and final state and the intervening system (cf. section 11). In support of various arguments in the literature,[38] this suggests that the dependence of ρ upon solvent will not be primarily determined by D_s, but rather by specific local interactions with the solvent molecules. On the other hand, the energetics of the second stage of the dissociation is linearly related to $1/D_s$ (eq 2–5) and depends on structure only as far as this determines r. Of course, for a bimolecular reaction the formation of the transition state can be similarly dissected. The relation of this model to that of Kirkwood and Westheimer will be discussed in section 10.

The above experimental results can be expressed as:

$$\Delta^{\infty} = \rho^{\infty}\sigma^{\infty} \simeq \rho^{\infty}\sigma^{L} \simeq \rho^{L}\sigma^{L} \simeq \rho\sigma^{L} \qquad (12)$$

Ironically, a simple ρ–σ relation is applicable to ionic reactions for pole and dipole substituents provided the measurements are made at high salt concentrations. Considering the fact that the preparative organic chemist preferentially and usually applies concentrations of, say, 0.1–1 M, it follows that in everyday chemistry the set of simple equations 12 may be a better guide than eq 8. Here we may also discern one of the reasons why the large variations of σ of poles have escaped proper notice so long. Experimental work which should have sounded the alarm, like the alkaline ester hydrolysis of ethyl 4-NMe_3^+-β-phenylpropionate, was carried out at fairly high concentrations so that the derived nonthermodynamic σ value, 0.8, came close to the σ values from thermodynamic dissociation constants in systems like ArCOOH and $ArNH_3^+$.

Equation 12 can be used to derive σ^L values. Such a procedure is especially attractive and advantageous in that it avoids the calculation of r, δ^B, and ionic strength corrections. However, the complications met with in concentrated salt solutions should not be underestimated[39] and are, for instance, evident in some of the experimental results of the Tartu group.[30] Apparently, the two approaches to σ^L do not always give concurrent results.

Some further data obtained at high ionic strengths will be discussed in sections 8.g.5 and 12.

(2) δ^B = 0 (Case 2); Reactions with Neutral Reagents—the DDM Reaction. Up till now this paper has dealt with processes in which charged particles go out to infinity or come in from infinity (pK_a, alkaline ester hydrolysis). In such reactions typical values for δ^B are 0.05 with dipole substituents and 0.5 with pole substituents. When considering processes in which neutral particles go out or come in, typical δ^B values are smaller by an order of magnitude, i.e., 0.05 for pole substituents and practically zero for dipole substituents. Hence, for such reactions, the expression:

$$\Delta = \rho^{L}\sigma^{L} \qquad (13)$$

should hold, at least approximately. The reaction of carboxylic acids with diphenyldiazomethane (DDM) can serve as an example. The work by Roberts et al.[40] on the ArCOOH series in ethanol, with ρ = 0.98,[1] gives for 4-NMe_3^+ σ = 0.69;[1] this value is reasonably close to σ^L = 0.53 ± 0.08, and it is far from σ = 2.0 to be expected from eq 8 if removal of the proton to infinity were decisive (σ = 0.53 + 1.41/0.98 = 2.0). From our own work in 75% ethanol,[27] ensuring the presence of nonpaired ions, we mention one example. In the $ArCH_2CH_2COOH$ series we find for 4-NMe_3^+ σ = 0.2, a surprisingly low value but much closer to σ^L = 0.53 than to σ = 2.1 derived from the experimental pK_a* in the same solvent. It is not clear whether these (and other) imperfections are due to kinetic complications or indicative of the limitations of eq 8 and 13. Attention may also be drawn to the required (re)orientation of the dipolar reagent when the transition state is formed. Further work is needed, but there is no reason to doubt that the Bjerrum terms are small.

Another important aspect of the data on the DDM reaction is that the ρ values are much higher than can be accounted for by simple electrostatic calculations. Thus, the substituent effects observed for 4-nitrobenzoic acid in ethanol (Δ = 0.70[41]) and 75% ethanol (Δ = 0.68) correspond with an effective dielectric constant far below unity: ${}^{e}D_E$ = 0.2. This value is based on a model in which the dipoles of the NO_2 group (μ = 4 D) and the DDM molecule (μ = 1.4 D;[42] 1 Å beyond the proton) are aligned, and is, therefore, a maximum value. Similar impossibly low values of ${}^{e}D_E$ are obtained from the substituent effects found in aliphatic compounds like 4-bromobicyclooctanecarboxylic acid,[43] chloroacetic acid,[44] and β-chloropropionic acid.[44] These observations present further evidence that the field effect is not the only factor of importance.

(3) δ^B = 0 (Case 3); S_N1 Reactions. Although in an S_N1 reaction the leaving group goes to infinity as a charged group, δ^B should be practically zero, since in the transition state the leaving group is still nearby. Hence, eq 13 should be applicable.

An interesting example is provided by the σ^+ values of 3- and 4-NMe_3^+, ~0.4, derived by Okamoto and Brown[45] for their standard solvolysis of *tert*-cumyl chlorides in 90% acetone at 25 °C. These values were not in line with other known values and have been either disregarded or given ad hoc explanations; in part 1 of this series[1] they were deleted for averaging purposes as highly improbable on statistical grounds. However, being not far from σ^L values, they conform to the pattern of the present paper.

In fact, the adherence to eq 13 is even better than suggested by the original data which were obtained using ~0.05 M initial concentration. Measurements at lower concentrations on the solvolysis of the parent compound and its 3-NMe_3Cl derivative show the substituent effect to increase with decreasing concentration (see Experimental Section). Correction to I = 0 yields σ = 0.50 for 3-NMe_3^+, comformable to σ^L = 0.59 ± 0.06.

It might be argued that σ^L applies because of ion pairing in 90% acetone (cf. section 8.g.1). We believe this not to be the case on the basis of the substituent effect observed for 4-$CH_2CH_2NMe_3I$-benzoic acid in this solvent. At I = 0.01 we find ΔpK_m = 0.5, whereas δ^B = 1.03. Anticipating section 8.g.4 this indicates that at this concentration the free ion is present to a considerable extent. When accepting that this result is also applicable to the solvolysis of the *tert*-cumyl chloride in question, it follows that the value at I = 0 relates to the effect of NMe_3^+.

(4) σ^L = 0. In this case eq 8 reduces to

$$\Delta = \delta^{B} \qquad (14)$$

implying adherence to the Bjerrum expressions 2 and 3 due to cancellation of the non-Bjerrum effects in the substituent-phenyl moiety. Our best documented example is 4-$CH_2CH_2NMe_3^+$, for which Δ approximates δ^B to a degree illustrated in Figure 17. Negative poles with $\sigma^L \simeq 0$ are 3- and 4-CH_2COO^-, and, interestingly, 3-PO_3^{2-}. Conversely, such substituents can be used to estimate either δ^B by comparison with the parent compound (see section 8.g.5), or $\Sigma|\delta^B|$ as in section 8.a. An application was given in section 8.g.3.

(5) ρ = 0; Acidic Hydrolysis of Alkyl Benzoates. The mechanism accepted for the hydrolysis of alkyl benzoates in dilute acid involves fast reversible protonation followed by rate-limiting attack of water.[46] If for either step eq 8 applies it follows[47] that

$$\Delta = \rho_1\sigma^{Ln} + \delta_1{}^{B} + \rho_2\sigma^{Ln} + \delta_2{}^{B} = (\rho_1 + \rho_2)\sigma^{Ln} + \delta_1{}^{B} + \delta_2{}^{B} \qquad (15)$$

where ρ_1 and $\delta_1{}^B$ refer to the protonation and ρ_2 and $\delta_2{}^B$ to the attack by water. Since for this hydrolysis ρ = 0[46] (i.e., $\rho_1 = -\rho_2$[47]) and $\delta_2{}^B$ is small as a consequence of the lack of charge of the reagent, eq 15 reduces to

$$\Delta = \delta_1{}^{B} \qquad (16)$$

Again, at high ionic strengths, $\delta_1{}^B$ should also vanish for poles, so that Δ^∞ = 0.

Table XI gives our data for methyl benzoates in 20% methanol–water and water and shows good agreement with the above. We consider these data as the simplest, most direct evidence in favor of the applicability of D_s. The strength of the argument as compared with other ones in this paper stems from the absence of appreciable effects for dipoles at I = 0.

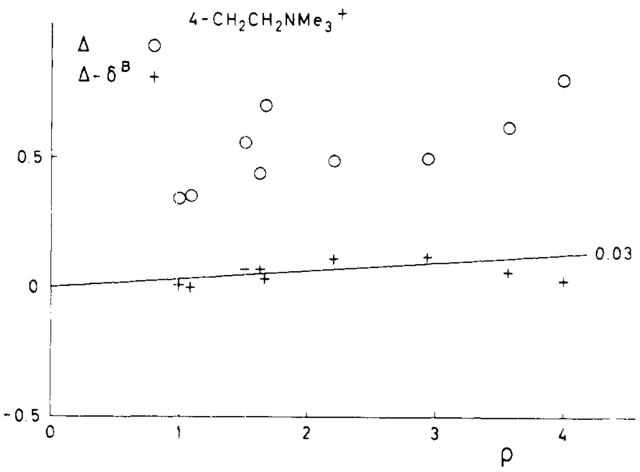


Figure 17. Δ and Δ − δ^B of 4-$CH_2CH_2NMe_3^+$ vs. ρ. The line drawn has the slope of the average σ^L value, 0.03. The regression line through the origin has slope 0.02, s = 0.04. Individual σ^L values range from 0.00 to 0.05, σ values from 0.17 to 0.42.

From this point of view the smallness of the effects at $I = 1$ appear as supporting the formation of (dipolar) ion pairs at high ionic strength discussed in section 8.g.1. The data at $I = 0$ can, alternatively, be taken to provide an experimental determination of the effective dielectric constant; this yields ${}^eD_E = 1.1D_s$ as an average, i.e. ${}^eD_E = D_s$ within the combined errors.

Three more points may be made. First, the zero effect of 4-$CH_2CH_2NMe_3^+$ at $I = 1$ is very special in that it is due to ρ, σ^L, and δ^B all being zero. Secondly, the differences between 4-NMe_3^+ and 4-SO_3^- at $I = 0$ extend those of section 8.a. Thirdly, and most elementary, the formal calculation of σ for the poles at $I = 0$ yields values of uncertain sign somewhere between five and infinity, and thus provides a nice illustration of the failure of the Hammett equation with charged substituents.

9. The Meta/Para Ratio of the Inductive Effect. On several previous occasions we have presented evidence "that as a rule the influence of the negative inductive effect from the meta and from the para position differs little, with some tendency toward predomination of this effect from the meta position".[48] Examples included: poles without a resonance effect, NMe_3^+ and NH_3^+; a dipole without a resonance effect, NMe_2O ($\Delta_m/\Delta_p = 1.16$); and NO_2 in compounds where the nitrobenzene resonance is effectively damped by the presence of one or two alkyl groups in ortho position. The last case may be illustrated here by the following substituent effects on dissociation constants in 50% ethanol, in pK_a units (Table I): 4-NO_2 in benzoic acid, 1.19; in 3-methylbenzoic acid, 1.13; in 3,5-dimethylbenzoic acid, 1.05; in 3,5-di-*tert*-butylbenzoic acid, 1.05; 3-NO_2 in benzoic acid, 1.07; in 4-methylbenzoic acid, 1.07; and in 4-*tert*-butylbenzoic acid, 1.06. Removal of the nitrobenzene resonance raises the meta/para ratio of the substituent effect of the NO_2 group from 1.07/1.19 = 0.88 to 1. Similar cases can be found in the series $ArCH_2COOH$[4] and $ArCH_2CH_2COOH$.[3]

The present data provide an extensive confirmation of the above thesis for charged substituents. Thus, our best example as regards number and magnitude of effects, NMe_3^+, yields $\Delta_m/\Delta_p = 1.13 \pm 0.07$ for 23 pairs; for reactions with $\rho \geq 1$, $\Delta_m/\Delta_p = 1.09 \pm 0.06$ for 10 pairs. Of course, eq 8 calls for a reevaluation for poles in that not Δ but Δ − δ^B or σ^L should be considered. However, the consequences are small, since $\delta_m{}^B \simeq \delta_p{}^B$. The above ten pairs yield 1.09 ± 0.12 for the Δ − δ^B ratio.

Special consideration deserve the $CH_2NH_3^+$ and $CH_2NMe_3^+$ groups. For $CH_2NH_3^+$ meta < para for Δ − δ^B in the $ArNH_3^+$ series and for $CH_2NMe_3^+$ the same holds in the ArOH series, whereas meta ≃ para in ArCOOH. We regard

Table XI.[a] **Acid Hydrolysis of ArCOOMe in Dilute $HClO_4$ at Low and High Ionic Strengths, at 122 °C**

substituent	registry no.	$\sqrt{I}$	10^5k	5 + log $k°$	Δ	δ^B
Solvent: 20% Methanol						
H	93-58-3	0.10	137	2.137	0	
		0.22	143	2.155	0	
3-Cl	2905-65-9	0.10	125	2.097	−0.04	
3-NO_2	618-95-1	0.10	116	2.064	−0.07	
		0.22	108	2.033	−0.12	
4-NO_2	619-50-1	0.10	144	2.158	0.02	
		0.22	130	2.114	−0.04	
4-$CH_2CH_2NMe_3^+$	67689-01-4	0.143	90	1.77	−0.41	−0.44
		0.315	104	1.70		
4-NMe_3^+	67689-02-5	0.140	76	1.70	−0.46	−0.58
		0.323	98	1.67		
3-SO_3^-	17625-03-5	0.141	311	2.67	0.53	0.60
		0.319	230	2.68		
4-SO_3^-	5399-63-3	0.144	275	2.62	0.48	0.52
		0.318	209	2.64		
Solvent: 20% Methanol, 1 M $NaClO_4$						
H		1.02	167		0[b]	
4-NO_2		1.02	155		−0.03[b]	
4-NMe_3^+		1.05	166		0.00[b]	
4-$CH_2CH_2NMe_3^+$		1.05	156		−0.03[b]	
3-SO_3^-		1.05	171		0.01[b]	
4-SO_3^-		1.05	179		0.03[b]	
Solvent: Water						
H		0.23	195	2.29	0	
4-NMe_3^+		0.142*	103	1.85	−0.44	−0.53
		0.317*	134	1.85		
		0.317	133	1.84		
4-SO_3^-		0.142	365	2.72	0.44	0.48
		0.318	283	2.73		

[a] k in L. mol^{-1} s^{-1} at ionic strength I; $k°$ calculated for $I = 0$ (equated to k for the dipole-substituted compounds); 3-SO_3^- sodium salt; 4-SO_3^- potassium salt; ammonio salts were perchlorates except those with an asterisk, which were chlorides. [b] Substituent effects in the presence of 1 M $NaClO_4$.

this as evidence of an extra interaction which can be described as a hyperconjugative, or a π-inductive effect,[49] which should be most effective in the para-substituted phenols and anilines. We may note here that this interaction should and does turn up also in the pK_a values in the series $ArCH_2NH_3^+$, leading to negative shifts of σ_p with respect to σ^n for +M substituents.[4,27] In section 8.c the same effect was related to the shoulder in Figure 14, showing the abnormal attenuation of σ^L of 4-$(CH_2)_nNMe_3^+$.

In several papers Exner et al.[50] have put forward that the meta/para ratio of the inductive effect is uniformly 1/1.14 = 0.88 in several solvents. Our data do not support this; a meta/para ratio above 1 would seem the rule, and this ratio is not invariable with regard to solvent and reaction series. Some comment would seem in order.

The analysis by Exner et al. is based on: (a) a comparison in several solvents of Δ_m and Δ_p of benzoic acids with substituents which were believed to have no resonance effects, including groups like CF_3, SO_2CH_3, and also NO_2, and (b) a similar comparison of differences denoted here as $\Delta_m{}^{Me}$ and $\Delta_p{}^{Me}$, being the differences between the pK_a values of compounds substituted by CH_3 and CH_2Y. Comparison a is unsatisfactory from our point of view, since we regard Δ_p to contain a resonance or hyperconjugative component as demonstrated above for nitrobenzoic acid. Comparison b would seem to suffer from the fact that in 4-methylbenzoic acid the σ value is somewhat exalted[1,4] and that the responsible (hyperconjugative) interaction will be affected by Y. In our above discussion we had to regard the Δ_m/Δ_p ratio of $CH_2NH_3^+$ and $CH_2NMe_3^+$ as somewhat exceptional and the reasons adduced hold generally for CH_2Y. Apart from that, the $\Delta_m{}^{Me}$ and $\Delta_p{}^{Me}$ values are rather small, and the pK_a values used by Exner et al. might, therefore, not be accurate enough for the purpose.[51] The latter uncertainties may be illustrated here for the group with the largest effect, CH_2CN. In 50% ethanol Exner et al. find $\Delta_m/\Delta_p = 0.23/0.26 = 0.88$ and $\Delta_m{}^{Me}/\Delta_p{}^{Me} = 0.41/0.50 = 0.82$; we find $\Delta_m/\Delta_p = 0.34/0.27 = 1.26$, and $\Delta_m{}^{Me}/\Delta_p{}^{Me}$ in 10, 50, and 75% ethanol as 0.91, 0.96, and 1.02, respectively. Even in the last example, with the largest effects, the ratio $\Delta_m{}^{Me}/\Delta_p{}^{Me}$ (0.55/0.54) ranges from 0.88 to 1.18 when allowing errors of 0.02 in the four pK_a values involved.[51] Thus, the conclusions by Exner et al. would appear doubtful, both due to the method of comparison and the smallness of the effects concerned.

Summarizing, we think that the combined data are in harmony with the thesis that in most cases the inductive effect of a substituent is transmitted slightly more effectively from the meta than from the para position, but there is little doubt that the reverse also occurs. Perhaps the most sensible way of looking at this statement is the conclusion that "additional effects" affecting the meta/para ratio are usually small. Section 11 contains related material.

10. The Kirkwood–Westheimer (K–W) Model. There are two principal reasons for comment on the cavity model of substituent effects developed by Kirkwood and Westheimer[20] and discussed and modified by many others.[52] The first is that the present treatment with its emphasis on D_s would seem to be entirely incompatible with the K–W model and its calculated ${}^tD_E$ values which, especially with dipole substituents, are very much lower than D_s. The second reason is that, although many of the present data can be fitted into the framework of the K–W model, some others cannot, even approximately. These discrepancies will now be exemplified; their interpretation leads to a reevaluation of the K–W model, which removes its incompatibility with the present treatment.

(1.a). As noted before, the 3-SO_3^- group often shows positive σ values, contrary to what the negative charge predicts. Again, in the ArOH series the effects of 3-SO_3^- and 3-PO_3^{2-}, $\Delta = +0.59$ and -0.88, are especially intriguing since the cavities should be virtually identical. Observations like these have been explained for COO^- [52f] and SO_3^- [53] by invoking the dipole component of the charged substituent. Such a procedure, although in its dichotomy conjuring up a relation with eq 8, is hardly attractive, since it requires further parametrization of inaccessible quantities. Also, it is not in harmony with the analysis given below.

(1.b). The "vertical" set of data points at $\delta^B = 0.50–0.52$ in Figure 2 demonstrates a failure not only of the Bjerrum equation, but also of the K–W model. Once more the cavities are almost the same, but now the observed effects include both pole and dipole components of one and the same substituent.

(2.a). The substituents 4-$CH_2NMe_3^+$, 4-$CH_2NEt_3^+$, and 4-$CH_2NBu_3^+$ show almost the same effects in the ArCOOH series in each of the solvents. The K–W model predicts an increase of Δ along with the increase in bulk of the substituent, since this should increase the (average) depth d of the charge. Quantitatively, the observed pK_a difference between 4-$CH_2NMe_3^+$- and 4-methylbenzoic acid,[1] 0.84 pK_a units, can be accounted for with a spherical cavity with the charges on a diameter at a distance of 8 Å, $D_i = 2$, $D_s = 78$, depth of the hydrogen of COOH 1 Å, and depth of the positive charge 1.5 Å. Increasing d of the charge to 2.0, 2.5, and 3.0 Å, while keeping COOH at d = 1 Å, gives calculated Δ values of 1.07, 1.32, and 1.65 pK_a units, respectively.[54] The actual increase of d can be approximated by the radii of $NAlk_4^+$ ions; the difference between NMe_4^+ and NBu_4^+ is given as 2.7[55] (from mobilities), 1.5,[55] and 1.3 Å[56] (from molecular volumes). Thus, this K–W model predicts the effect of 4-$CH_2NBu_3^+$ to be about twice that of 4-$CH_2NMe_3^+$.

(2.b). Inserting material with low dielectric constant between functional group and substituent should also influence the substituent effect; quantitative estimates are not possible, however. Such an influence is not observed: in 4-chloroaniline and 4-chloro-3,5-di-*tert*-butylaniline[57] the effects of Cl are almost equal (in 50% ethanol, 0.83 and 0.78[27]), and the same holds for 4-NMe_3^+ in 4-NMe_3^+-aniline and 4-NMe_3^+-2,6-di-*tert*-butylaniline (in water, 2.46 and 2.40[27]). Of course, this lack of influence is also indicated by the fact that inhibition of resonance by large alkyl groups usually gives sensible results. Following the same line of thought it may be noted that the value of $\rho = 2.46$ for the methanolysis of ArCOO(*l*-menthyl) is close to $\rho = 2.54$ for the alkaline hydrolysis of ArCOOEt in 85% ethanol; enlarging the bulk in the side chain at the site of reaction apparently does not have a strong influence either.

(3). In section 8.g.2 we calculated ${}^eD_E = 0.2$ for the reaction of 4-nitrobenzoic acid with the dipole reagent DDM in 75% ethanol, an "impossible" value for the Bjerrum approach and also beyond the K–W model. A further test of the cavity model is provided by the DDM reaction in solvents with $D_s \simeq D_i \simeq 2$, formally implying ${}^tD_E \simeq 2$. Available data[58] in toluene (D_s = 2.4) and dioxane (D_s = 2.2) may not be free from kinetic problems;[58] the ρ values of 2.7 and 2.0, respectively, are hardly in doubt and yield ${}^eD_E = 0.1$.

Before attempting an interpretation of these and other data it is necessary to take a closer look at the K–W model. Figure 18 gives an illustration of the variation of the calculated dielectric constant, ${}^tD_E$, with the position of two charges, one of which is inside the spherical cavity with radius 4 Å, internal dielectric constant $D_i = 1$, and $D_s = 78.5$; Table XII[24] gives the actual figures, also for some other radii and values of D_i. Concentrating first on the interaction of the inside charge with the other charge at the edge of the cavity it appears that ${}^tD_E$ is close to D_s. Thus, ${}^tD_E = 100$ with depth of the substituent charge d = 2 Å. As even more important than its precise value (see below) we regard that ${}^tD_E$ is: (a) almost independent of

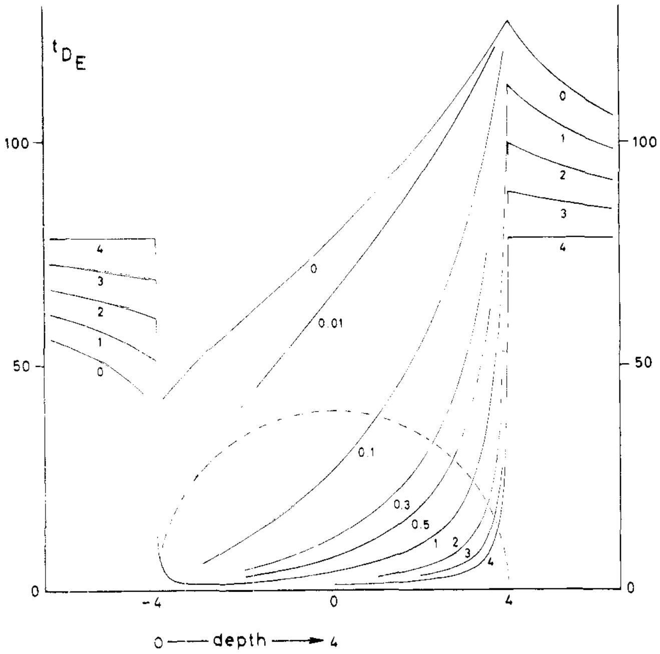


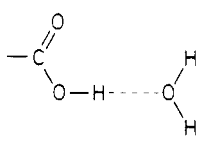
Figure 18. Effective dielectric constants, $^{t}D_E$, for the interaction of two charges, A and B, on a diameter of a spherical cavity of radius 4 Å; D_s = 78.5 (outside), D_i = 1 (inside). Charge A goes from the edge of the cavity (−4) to the center (0), increasing its depth from 0 to 4 Å. Charge B goes from +6 to −6. The numbering of the curves corresponds with the depth of the inside charge A (the substituent); the curve for depth 1 Å has been drawn fully. The $^{t}D_E$ values for depths 4–8 Å are obtained by mirroring with respect to the center. The actual values are given in Table XII,[24] together with some values for radii 3 and 5 Å, for D_i = 2 and 4, and for "D_s" = 1; they were obtained using computer programs written by Dr. C. F. Wilcox.

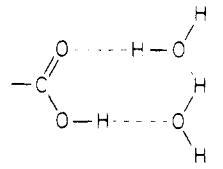
D_i ($^{t}D_E$ = 98 for D_i = 4); (b) slightly dependent on the radius ($^{t}D_E$ = 92, 100, and 105 for radii of 3, 4, and 5 Å); (c) not strongly dependent on the depth of the substituent (with radius 4 Å and d = 1, 2, and 3 Å, $^{t}D_E$ = 112, 100, and 89). Hence, the contribution to Δ by the outside-the-cavity part of the dissociation is given by δ^B in a good first approximation. Specifically, a corresponds with a lack of influence on δ^B by structural factors within the cavity, b with applicability of δ^B to long and (not too) short molecules, and c with very small values of δ^B for dipole substituents. We emphasize that c provides a physical background for the failure of poles in the Hammett equation; the outside-the-cavity term for poles is considerable, almost structure independent, and an order of magnitude greater than that for dipoles, which is almost negligible. Of course, these generalizations are in conformity with the success of using D_s in the Debye–Hückel theory. In particular, the considerable δ^B for poles corresponds with the considerable effect of ionic strength on the activity coefficients of ions, and the small δ^B for dipoles corresponds with the small effect of ionic strength on the activity coefficients of dipole molecules and zwitterions. In fact, from the point of view of the Debye–Hückel theory, *the failure of poles in a relation which holds for dipoles is almost trivial.*

The above results would seem to indicate that the $\rho^L\sigma^L$ term of eq 8 represents the inside-the-cavity part of the electrostatic interactions. Indeed, with both charges inside, the K–W model is well suited to generate a broad spectrum of $^{t}D_E$ values, and, hence, to rationalize a large variety of data. In Figure 18 this flexibility finds its expression in the steepness of the curves inside the cavity near the surface, as a consequence of which "almost any desired value of . . . [$^{t}D_E$] . . . can be obtained . . . by adjusting the depth below the surface" (Tanford[52a]); most results can be explained by a "considerate choice of adjustable parameters" (Siegel and Komarmy[52d]). For instance, with radius 4 Å, D_i = 2, D_s = 78.5, and d = 1 Å, the outside term accounts for 0.31 pK_a units, the first 0.5 Å inside the cavity for 0.39 units, the second 0.5 Å for 0.49 units, the next 1 Å for 1.50 units.

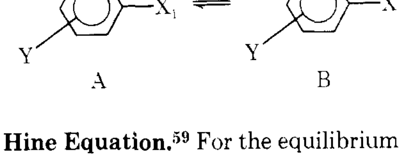
Even so, the flexibility of the K–W model is not sufficient to account for the observations mentioned earlier in this section, or, e.g., those in sections 8.b, 8.g.2, and 8.g.5. We interpret this as meaning that it is mistaken to assume that the electrostatic interactions in question are responsible for the full substituent effect. Quantifying this statement, the very low values of $^{e}D_E$ = 0.1–0.2 for the dipole–dipole interactions in the DDM reaction imply that the electrostatic effects do not exceed 10% of the observed effects; the absence of a clear difference in the $CH_2NAlk_3^+$ series of substituents leads to a similar estimate for the inside part of pole–pole interactions. Generalizing these conclusions, δ^B appears to be a good measure of the electrostatic effects for the entire dissociation process.

The question now arises whether the applicability of D_s can be reconciled with the K–W model. In the spirit of the above quotations this means asking whether it is possible to adjust the parameters so that $^{t}D_E \simeq D_s$. The answer is affirmative. In this connection we first note that with radius 4 Å, D_i = 1, and D_s = 78.5, this holds for two charges each at a depth of 0.4 Å. With D_i = 4 these depths increase to 0.7 Å, with D_i = 8 to 1 Å. As to the credibility of such "effective depths" we find it difficult to see why these would be less "reasonable" than d = 1.5 Å required to obtain the experimental Δ for 4-$CH_2NBu_3^+$-benzoic acid when the radius estimated for NBu_4^+ is 4.1–4.9 Å.[55,56] Furthermore, when depicting the solvated COOH group as in IV or V, any a priori definition of the depth of the proton appears as illusory. The same arguments apply to COO^- or NH_3^+ as substituent or reaction center. Also, it would seem likely that the change of the dielectric constant in the neighborhood of the cavity surface is less abrupt than the model assumes; flattening out the discontinuity will increase the depths for which $^{t}D_E \simeq D_s$ holds.


IV


V

Summarizing, we conclude that the cavity model supports the Bjerrum term to be the factor discriminating between poles and dipoles in the Hammett equation. In our further analysis the K–W model is reduced to the Bjerrum model. Retaining the cavity concept, this means that when the proton or reagent comes in from infinity to its position in the acid or transition state, it never reaches the region where $^{t}D_E$ drops considerably below D_s. It may not go unnoticed that this model and the ion pair model of section 8.g.1 are compatible and complementary. We refrain here from an attempt at specifying the differences, since they are of little consequence to eq 8 and discussion would probably imply overworking either model.



11. The Hine Equation.[59] For the equilibrium A ⇌ B Hine derived an equivalent of the Hammett equation:

$$\Delta = \tau[\sigma(X_1) - \sigma(X_2)]\sigma(Y) \qquad (17)$$

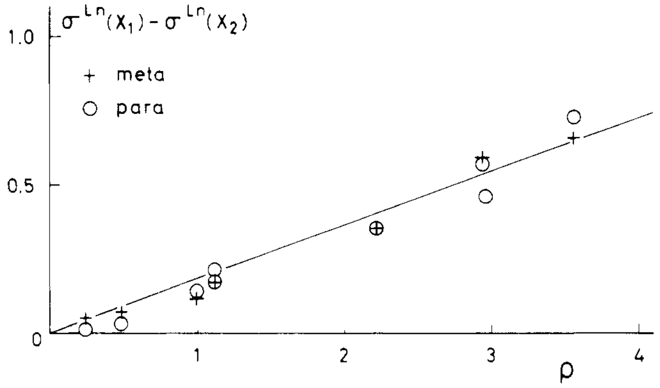


Figure 19. Testing the revised Hine equation (eq 18) in water. For each acid–base pair $\sigma^{Ln}(X_1) - \sigma^{Ln}(X_2)$ is plotted vs. ρ; e.g., $\sigma^L(3\text{-}NH_3^+) - \sigma^L(3\text{-}NH_2) = 0.52 - (-0.07) = 0.59$ vs. ρ of $ArNH_3^+$, 2.941.[1] The regression line through the origin for $\rho \geqslant 1$ has slope 0.181, $s = 0.05$, $R = 0.993$, $n = 12$, and gives $\tau^L = 5.5$. The standard deviation for ρ is 0.29.

identifying ρ as $\tau[\sigma(X_1) - \sigma(X_2)]$, where τ is the dimensionless, solvent- and temperature-dependent transmission factor for the "polar interaction" between Y and X.

The present work suggests that σ should be replaced by σ^{Ln} and that δ^B should be added. In the absence of through-resonance this gives:

$$\Delta = \tau^L[\sigma^{Ln}(X_1) - \sigma^{Ln}(X_2)]\sigma^{Ln}(Y) + \delta^B \qquad (18)$$

As long as Y and X are neutral σ^n can be used for σ^{Ln}; in a case like the third dissociation constant of 4-carboxybenzenephosphonic acid the equilibrium involves $PO_3H^- \rightleftharpoons PO_3^{2-}$ as influenced by 4-COO^-, and all three σ values are σ^{Ln} values.

Figure 19 shows the adherence to eq 18 for aqueous solution (the relevant values are in Table XIII[24]). The data give no reason to discern between $\tau_m{}^L$ and $\tau_p{}^L$ (cf. section 9), and, using values of $\rho \geq 1$, the regression line through the origin yields $\tau^L = 5.5$.

A more complete evaluation will not be attempted here because of a lack of data in other solvents and at other temperatures, and because of the general uncertainty in each of the σ^L values involved and the smallness of their differences even in favorable cases. We give only one application.

In a previous paper[5] we noted that ρ is considerably larger for $ArNMe_2$ than for benzoquinuclidines, and this was related to the absence of "aniline resonance" in the latter system. This difference in ρ is accounted for by eq 18 as the result of the positive σ shift of an amino group when the amino group is twisted 90° around the $C_{ar}N$ bond. For 4-NMe_2 this shift is from $\sigma^n = -0.25$[4] to $\sigma_{90°} = 0.0$.[60] Taking $\sigma^L(4\text{-}NH^+)$ as 0.60 in either system, the ratio of the ρ values is calculated as $(0.60 + 0.25)/(0.60 - 0.0) = 1.42$; the ratio observed in 50% ethanol[5] is $4.29/2.87 = 1.49$. Apparently, the Hine equation also copes with the effects of the resonance components of σ^{Ln}.

12. Resonance and Through-Resonance Effects. Table VI shows that for groups with a –M effect $\sigma_p{}^{Ln} \geq \sigma_m{}^{Ln}$. We regard this to be the result of small resonance contributions superimposed upon the inductive effect as discussed in section 9. It is probably typical that even for N_2^+, which is such a strong π acceptor (see below), the difference between $\sigma_p{}^{Ln}$ and $\sigma_m{}^{Ln}$ is no more than 0.2 units in ArCOOH.

The reliability of some of the σ^{Ln} values for the π donor O^- is in doubt. In the alkaline hydrolysis of aryl benzoates the meta value is more negative than the para value. The values in the alkaline hydrolysis of aryl tosylates, while showing the same unlikely order, are 0.2–0.3 units more negative. Perhaps experimental and kinetic problems play a part here. The most recent values from the second dissociation constants of 1,3- and 1,4-dihydroxybenzene, carefully determined in a nitrogen atmosphere at not too high I, conform to expectation, should be free from resonance saturation effects,[5] and are considered as reliable (Table VI). We take occasion to mention that the σ^n and $\sigma_R{}^n$ values for 4-O^-, given "with hesitation" in a previous paper,[4] should be withdrawn without hesitation: neither the ionic strength nor δ^B was taken into account (the derivation of the $\Delta\sigma_R{}^+$ value,[2] −1.8, is hardly affected by these factors). Further work is required, also with respect to $\sigma_I{}^L$.

Exalted σ^L values are found when through-resonance occurs; thus, all values for 4-COO^- are higher than σ^{Ln} (Figure 20[24]). The relevant Yukawa–Tsuno and Hine equations as discussed in a previous paper[2] may be rewritten by replacing σ^n by σ^{Ln}, $\Delta\sigma_R{}^{\pm}$ by $\Delta\sigma_R{}^{L\pm}$, and adding δ^B. This gives:

$$\Delta = \rho\sigma^{Ln} + \rho r^{\pm}\Delta\sigma_R{}^{L\pm} + \delta^B \qquad (19)$$

and

$$\Delta = \tau^L[\sigma^{Ln}(X_1) - \sigma^{Ln}(X_2)]\sigma^{Ln}(Y) + \omega_p\Delta\sigma_R{}^{L\pm}(Y)\Delta\Delta\sigma_R{}^{L\mp}(X_1,X_2) + \delta^B \qquad (20)$$

respectively, with $\tau^L = 5.5$ as derived in section 11, and $\omega_p = 2.4$ as derived before.[2]

The required $\Delta\sigma_R{}^{L+}$ and $\Delta\sigma_R{}^{L-}$ values can be obtained in the usual way. From the $ArNH_3^+$ series in water ($r^- \equiv 1$) follow $\Delta\sigma_R{}^{L-}$ for 4-COO^- = 0.14, and 4-SO_3^- = 0.12. The ArOH series ($r \simeq 1$) gives $\Delta\sigma_R{}^{L-}$ for 4-SMe_2^+ = 0.25, 4-COO^- = 0.23, 4-SO_3^- = 0.12, and 4-PO_3^{2-} = 0.03. These values cannot be very accurate in view of the several uncertainties, but they do not seem unreasonable when compared with, e.g., those for 4-COOMe and 4-SO_2Me, 0.28 and 0.32, respectively. Remarkably low is $\sigma^L(4\text{-}COO^-) = 0.14$ in 3,5-dimethyl-4-COO^--phenol. The (partial) steric inhibition of the through-resonance does predict a negative shift as compared with $\sigma^L(4\text{-}COO^-) = 0.49$, but the shift is larger than $\Delta\sigma_R{}^{L-}$ and σ^L should not be lower than $\sigma^L(3\text{-}COO^-) = 0.24$. Special attention should be given to the 4-N_2^+ group with the very large $\Delta\sigma_R{}^{L-} = 1.7$; we note that this value is little affected by the inclusion of δ^B, since the through-resonance term in the aniline is as large as 5 kcal mol^{-1}.

The negative pole with a +M effect, O^-, has $\sigma_p{}^L = -0.85$ in the alkaline hydrolysis of ethyl benzoates in 60% acetone. The exaltation, −0.40 σ^L units, when combined with $\Delta\sigma_R{}^{L-} = -1.8$[2,4] (in water), yields a Yukawa–Tsuno r value of 0.22, in reasonable agreement with $r = 0.28$ obtained from data on dipole substituted esters.

In 4 M NaCl solution the through-resonance is not perceptibly impaired. This has been illustrated in Table X for 4-OH in ArCOOH; from the ArOH series we mention σ^{∞} (4-COO^-) = 0.44[27] and σ^{∞} (4-NO_2) = 1.21.[27] In harmony with this, the UV spectra in 4 M NaCl of the particles involved hardly differ from those in water (see Experimental Section). Such observations suggest that the (through-)resonance is also fully developed in the ion pair type transition states of S_N1 reactions (cf. section 8.g.3) and help in understanding why the interaction energies are practically the same in S_N1 reactions and carbonium ion equilibria.[1] It is interesting to apply the appropriate Hine equations and derive σ^{Ln} and $\Delta\sigma_R{}^{L-}$ of the functional group of the standard σ^+ reaction *in its transition state.* Taking $\rho = -4.48$,[1] $\sigma(4\text{-}CMe_2Cl) = \sigma(4\text{-}CH_2Br) = 0.17$, τ^L and ω_p as found for water, and the through-resonance energy for 4-OMe as 4.2 kcal mol^{-1},[1] we obtain $\sigma^{Ln}(4\text{-}C\cdots Cl) = 1.0$ and $\Delta\sigma_R{}^{L-}(4\text{-}C\cdots Cl) = 1.8$. These calculations show that the electronic properties of this functional group in the transition state in question are similar to those of 4-N_2^+ with $\sigma^{Ln} = 1.3$ and $\Delta\sigma_R{}^{L-} = 1.7$.

13. Naphthalene Derivatives. Figure 21 gives a comparison of the substituent effects of NO_2 and SO_3^- in naphthylamines based on Bryson's data[61] (Table XIV[24]). The corre-

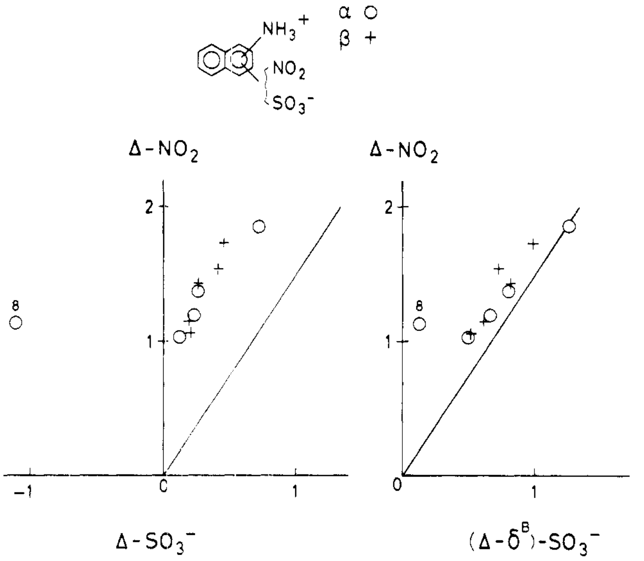


Figure 21. Δ for NO_2 vs. Δ and vs. $\Delta - \delta^B$ for SO_3^- in 1- and 2-aminonapthalenes (excepting 1,2, 1,4, and 2,1 substitution). The slope of the line drawn, 1.5, corresponds with the ratios of meta and para σ^{Ln} values.

lation of the Δ values is poor; $\Delta(NO_2)/\Delta(SO_3^-)$ varies strongly from 2.6 to 8.6 (and −1 for the peri compounds). The correlation is much improved by taking δ^B into account; $\Delta(NO_2)/(\Delta - \delta^B)(SO_3^-)$ varies only from 1.5 to 2.1 with an average of 1.8 (and 9 for the peri compounds), and this ratio is reasonably close to $\sigma(3\text{-}NO_2)/\sigma^L(3\text{-}SO_3^-) = 1.45$ and $\sigma^n(4\text{-}NO_2)/\sigma^{Ln}(4\text{-}SO_3^-) = 1.53$.

14. Poles in the Ortho Position. We wish to draw attention here only to the results for 2-$CH_2CH_2NMe_3^+$-phenol. This should be a simple case because σ_0^L may be assumed to be very small so that ρ_{ortho} is not important, and because the ortho effect is small. Accordingly, it is satisfactory that $\Delta = 0.55$ equals the sum of $\delta^B = 0.69$ (with the plane of $C_2C_\alpha C_\beta N$ perpendicular to the plane of the benzene ring) and the steric factor, −0.14 ± 0.10, as estimated by de Ligny et al.[62] for 2-methylphenol.

15. Saturated Systems. In view of the peculiarities of polar effects in aromatic systems it may be pointed out that also in saturated systems $\Delta - \delta^B$ shows a simpler relation with structural factors than Δ. The following illustrations extend and corroborate the relevant work by Palm and his associates[63] while emphasizing other aspects; the data used are in Table XV.[24]

Figure 22 compares substituent effects in the series $NH_3^+(CH_2)_nCOOH$ and $CN(CH_2)_nCOOH$. The values for Δ define a reasonably straight line which, however, misses the origin by 0.5 pK_a units. When plotting $\Delta - \delta^B$ of the former series vs. Δ (or $\Delta - \delta^B$) of the latter a straight line through the origin is approximated. Similar behavior of Δ vs. Δ and of $\Delta - \delta^B$ vs. $\Delta - \delta^B$ is shown in Figure 23 for $SO_3^-(CH_2)_nCOOH$ vs. $NH_3^+(CH_2)_nCOOH$, and in Figure 24[24] for $PO_3^{2-}(CH_2)_nNH_3^+$ vs. $SO_3^-(CH_2)_nNH_3^+$. The correspondence with the aromatic systems is apparent from, e.g., changes in sign of Δ (but not of $\Delta - \delta^B$), and the deviation from a 2:1 ratio of the effects of PO_3^{2-} and SO_3^-.[64]

The above implies that the Taft equation[65]

$$\Delta = \rho_I\sigma_I \qquad (21)$$

fails with charged substituents and may be rewritten as

$$\Delta = \rho_I^L\sigma^L + \delta^B \qquad (22)$$

where $\rho_I^L \simeq \rho_I$ and for dipoles $\sigma_I^L \simeq \sigma_I$ (cf. section 6). We have derived σ_I^L values for some pole substituents from correlations

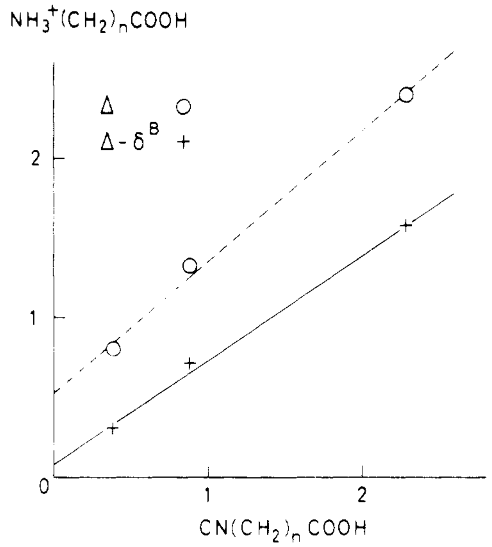


Figure 22. Δ and $\Delta - \delta^B$ for $NH_3^+(CH_2)_nCOOH$ vs. Δ for $CN(CH_2)_nCOOH$. The regression line drawn for Δ has slope 0.83, intercept 0.52; for $\Delta - \delta^B$ slope = 0.66 ± 0.05, s = 0.07, R = 0.997, intercept 0.08.

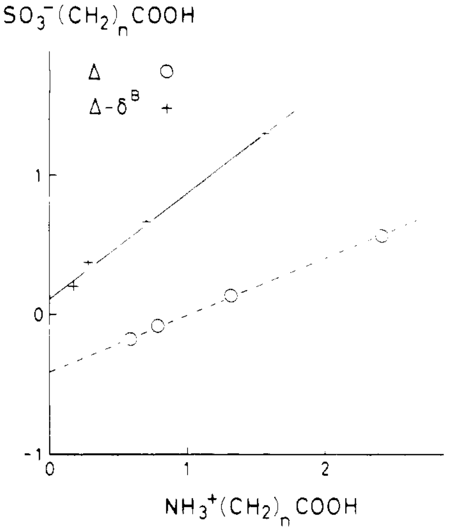


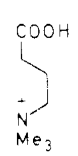
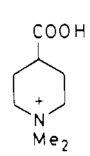
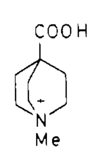
Figure 23. Δ vs. Δ and $\Delta - \delta^B$ vs. $\Delta - \delta^B$ for the carboxylic acid dissociation of $SO_3^-(CH_2)_nCOOH$ and $NH_3^+(CH_2)_nCOOH$. The regression line drawn for Δ has slope 0.40, intercept −0.41; for $\Delta - \delta^B$ slope = 0.76 ± 0.04, s = 0.04, R = 0.997, intercept = 0.11.

as in Figures 22–24, taking the slope of the least-squares line through the origin as the ratio of the σ_I or σ_I^L values. Contrary to common practice, the data points for n = 1 were not used in order to evade the complications due to hydrogen bonding and/or steric effects[66] (and accepting possible conformational complications with $n > 1$; cf. section 8.e). Again, scaling with current σ_I values[65] was sought by choosing $\sigma_I(CN) = 0.56$[65] as a basis. The acids $Y(CH_2)_nCOOH$ vs. $CN(CH_2)_nCOOH$ give the σ_I^L values (meta σ^L values in parentheses): NH_3^+, 0.45 (0.52); NMe_3^+, 0.61 (0.59); SO_3^-, 0.44 (0.49). The acids $Y(CH_2)_nNH_3^+$ vs. $SO_3^-(CH_2)_nNH_3^+$ then give the σ_I^L values: COO^-, 0.24 (0.24); PO_3^{2-}, 0.14 (0.07). The agreement of σ_I^L and meta σ^L values is not unsatisfactory considering the uncertainties involved in their derivation.

The observation by Grob et al.[67] that the pK_a of $NMe_3^+(CH_2)_nCOOH$ (and related systems) is approximately linearly related with $1/r$ for n = 1–3 needs special comment. Referring to the $1/r$ dependence of the field effect the authors conclude that "the strength of these acids is determined by the field effect of the (trimethyl)ammonio group only."

However, this conclusion presupposes ${}^{e}D_E$ to be constant and this is not the case. Qualitatively this follows from the fact that extrapolation of Δ to $1/r = 0$ ($n = \infty$) misses the origin by 1-2 pK_a units. Quantitatively, direct calculation from the substituent effects in water (section 4; eq 2, replacing D_s by ${}^{e}D_E$ and δ^B by Δ) yields ${}^{e}D_E = 22$, 30, and 46 for $n = 1$, 2, and 3, respectively.[68] Similar variations are found from the other data in water and 50% ethanol, with and without corrections for steric and ionic strength effects. In terms of eq 22 the linearity appears as a consequence of the attenuation factor 2 for ρ_I per CH_2 group, in combination with the geometries leading to $(1/r_{n=1} - 1/r_{n=2}) \simeq 2(1/r_{n=2} - 1/r_{n=3})$, and the $1/r$ dependence of δ^B. Figure 25[24] shows the linearity for $n = 1$-3, the deviation from linearity for $n > 3$, and the adherence to eq 22 for the series $NH_3^+(CH_2)_nCOOH$.

Cyclic and bicyclic compounds also conform to eq 22. We mention the pK_a values of bicyclooctane carboxylic acids[52h,i] (NH_3^+, NMe_3^+, COO^-) and quinuclidines[69] (COO^-). The pK_a values found by Grob et al.[67] for the compounds VI–VIII are

	VI	VII	VIII
Δ	0.90	1.28	1.76
δ^B	0.50	0.55	0.57
$\Delta - \delta^B$	0.40	0.73	1.19

of interest in that the $\Delta - \delta^B$ values are in the ratio 1:2:3, in harmony with what the number of paths and the Lewis mechanism predicts.

16. Concluding Remarks. We see no reason why the present approach would be limited to the substituents and reactions discussed above. Indeed, electrostatic effects of poles have been invoked in various fields, for instance in coordination chemistry by Quagliano and Vallarino et al.,[70] in comparisons of anion radicals with their parent compounds by Neta et al.,[71] and in Epstein's studies of the "charge effect"[72] which are closely related to parts of the present paper. In these and in many other cases[73] it is or may be useful to consider the Bjerrum term as a separate part of the total effect.

An important extension is the application to ionic gas-phase equilibria and reactions. Since, now, "D_s" = 1, the Bjerrum term[74] is already large for dipole substituents. In 3-nitrobenzoic acid, for example, the substituent effect has been found as 9.6 kcal mol^{-1},[75] with the Bjerrum term at 5.5 kcal mol^{-1}. This implies that $\rho^L \simeq 0.5\rho$, and that about half the attenuation of substituent effects when going from the gas phase to aqueous solution[76] is due to the nonstructural Bjerrum effects. It is interesting to note that in 4-fluoroaniline the substituent effect in the gas phase, 2.0 kcal mol^{-1},[76] is practically equal to the Bjerrum term; this leaves little space for a structural effect, in line with the small effect observed in water.[1,5] For singly charged substituents and reagents typical Bjerrum terms in benzene derivatives amount to 50 kcal mol^{-1},[77] exceeding by far the total effect of dipoles. Hence, it may be expected that in the gas phase the substituent effect of a pole is dominated by the Bjerrum term.

Limitations of eq 8 have been indicated on several occasions in this paper. In addition, we draw attention here to the fact that δ^B does not take care of any electron reorganization occurring during the reaction. Good examples are the aromatic nitration of $PhNMe_3^+$ and related reactions, in the transition state of which the positive charge of the reagent is spread over the carbon atoms of the ring; in fact, several electrostatic calculations have been based on such a model.[78] Two notes are pertinent. First, the conditions of these aromatic substitutions are invariably such as to ensure extensive ion pairing (e.g., 5 M H_2SO_4). This has been pointed out and experimentally supported by Modro and Ridd,[78] and means that both δ^B and the extra electrostatic interactions are greatly reduced (cf. section 8.g.1). Secondly, and more general, the extra interactions appear in the $\rho\sigma^L$ term, since they cause an increase in ρ (cf. ref 5 and section 11). With this in mind it is satisfactory that our $\sigma^L(3\text{-}NMe_3^+) = 0.59$ and $\sigma^L(4\text{-}NMe_3^+) = 0.53$ in eq 13 serve well for aromatic substitutions at high ionic strengths.[79] The absorption of the extra electrostatic interactions in $\rho\sigma^L$ also implies that eq 8 cannot serve to assess the degree of electron reorganization; in conjunction with eq 8, δ^B is the quantity to be used (cf. Table V, note *i*). Of course, the present paper suggests that the extra electrostatic interactions with poles will not follow the same relationship as those with dipoles; the general success of eq 8 can then be taken to indicate that the errors involved are not large, possibly because the factors in question are not predominant.

As to the practical application of eq 8 we add two remarks. The first one is obvious: we recommend the inclusion of compounds with substituents like NMe_3^+, SO_3^-, and $CH_2CH_2NMe_3^+$ in reactivity studies whenever feasible. Our second point is almost apologetic. New symbols had to be introduced to avoid confusion with existing ones; we are aware that this may lead to further confusion. As a token of amendment we state that when accepting eq 8, which is at the heart of the present paper, it is perfectly reasonable to write

$$\Delta = \rho\sigma + \delta^B \qquad (23)$$

emphasizing that only δ^B, the Bjerrum term, has been added to the original Hammett equation. Its application is simple: (1) ρ is derived with a standard set of σ values of meta-dipole substituents (Table II, footnote *a*); (2) σ is a "normal" σ value, for dipole substituents σ^n or σ^o (ref 1 and 4) and for pole substituents σ^{Ln} of Table VI; (3) δ^B for poles is obtained from eq 3 or 2, δ^B for dipoles (eq 4 and 5) is usually negligible, with gas-phase data as notable exceptions. Again, further simplification occurs in many reactions (e.g., sections 8.g.3 and 8.g.5) or under special reaction conditions (section 8.g.1). Through-resonance will cause deviations from eq 8 or 23; in such cases further terms can be added as in section 12, and their notation simplified if desired.

Finally, it may be instructive to show graphically how previous[1] and present work relates "abnormal behavior" to the same reference. In Figure 26 the line with slope 1.5 represents the correlation of substituent effects in ArOH and ArCOOH (in 50% ethanol) for meta-dipoles, i.e., it represents the "normal behavior" for meta substitution and for para substitution in the absence of through-resonance[1,4] or resonance saturation[5] as expressed in $\Delta = \rho\sigma^n$. The data point for 4-NH_2 deviates from the line as a result of the difference in through-resonance between 4-aminobenzoic acid and 4-aminobenzoate anion, the horizontal arrow being a measure of this difference.[1] Similarly, 4-NO_2 is off because of the difference in the through-resonance in the phenol equilibrium, the vertical arrow measures this difference.[1] The data points for the poles lie off the line because of the Bjerrum terms in both phenols and benzoic acids. Subtraction of the several δ^B values brings each positive pole close to the reference line; 4-SO_3^- needs a further correction, the vertical arrow measuring the through-resonance effect in the phenol equilibrium.

Experimental Section

Some data on the preparation and the physical data of the carboxylic acids of Tables I and III, a number of compounds of Table IV and the methyl benzoates of Table XI, and also a chart regarding

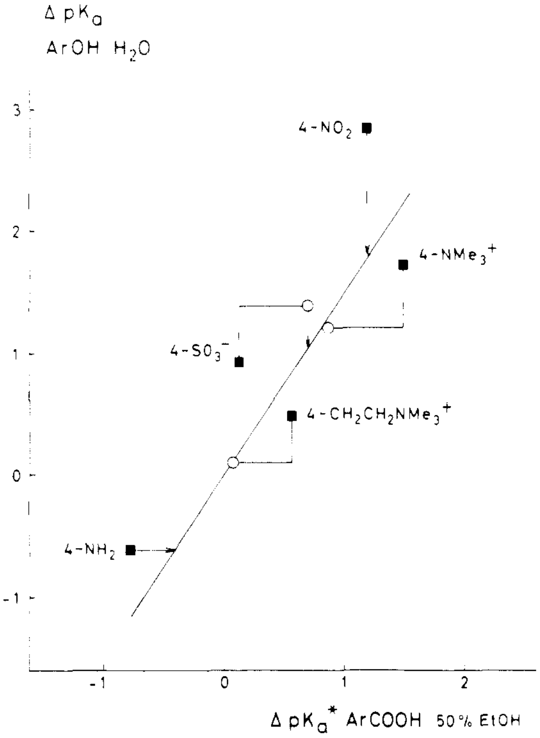


Figure 26. Substituent effects in ArOH and ArCOOH, demonstrating deviations from the Hammett correlation due to through-resonance and field effects (see text). The line with slope 1.5 is drawn through the origin and the data point for 3-NO_2 (3-nitrophenol $\Delta = 1.60$) and represents normal Hammett behavior: $\Delta = \rho\sigma^n$ (see ref 1 and 4). The squares are experimental points, the circles are obtained by subtracting δ^B. The pK_a^* of 4-aminobenzoic acid in 50% ethanol is not complicated by the presence of zwitterions.

geometrical details used in the calculation of distances are given in the Supplementary Material.[24]

Dissociation Constants. The thermodynamic pK_a^* values were determined as previously described[3,4,80] and exemplified.[3] The molar acitivity coefficients y^* were calculated from

$$-\log y^* = Az^2I^{0.5}/(1 + 5BI^{0.5})$$

where z is the charge number of the species involved, and A, B, and I also have their usual meaning.[81] We note that in the paper describing the method[80] a simpler equation was given; in fact, the above equation was used there and elsewhere.[3,4,5]

The nonthermodynamic pK_m values (Tables IX[24] and X) in 0.1–4 M NaCl are defined by

$$pK_m = R + \log \{[RCOOH] - [H^+]\}/\{[RCOO^-] + [H^+]\}$$

where R is the reading of the pH meter calibrated with aqueous buffers 4.008 and 6.865 at 25 °C; $[H^+]$ is obtained via the readings for known concentrations of HCl in the appropriate NaCl solution.[82] Our readings for 0.00210 M HCl were: 2.72, 2.70, 2.62, 2.34, and 2.00, in 0.10, 0.50, 0.98, 2.50, and 4.00 M NaCl, respectively. For $PhCH_2CH_2COOH$ pK_m ranges from 4.65 to 4.23 ($I = 0.004$–4); for PhCOOH $pK_m = 3.63$ at $I = 4$.

In section 8.g.3 some measurements in 90% acetone were mentioned. This solvent is a mixture of 90 vol of acetone and 10 vol of water; $D_s = 25.3$.[83] The "pH" reading with 0.00210 M HCl was 1.40. For PhCOOH $pK_m = 7.55$ at $I = 0.01$; for 4-$CH_2CH_2NMe_3I$-benzoic acid $pK_m = 7.09$ at $I = 0.003$–0.004.

Electronic Spectra (section 12). Solutions of 4-hydroxybenzoic acid in water and in 4 M NaCl at pH values of 1–2, 6–7, and 12 gave the spectra of the molecule, its monoanion (COO^-), and its dianion, respectively. The data of the relevant maxima in nanometers and their molecular extinction coefficients are as follows (water first): pH 1–2—255.0 (15 200), 255.0 (15 400); pH 6–7—246.0 (13 100), 246.0 (13 400); pH 12—280.0 (18 800), 280.0 (18 500).

For 4-nitrophenol the data for the acid and the anion are as follows: pH 3—315.5 (9900), 317.5 (10 300); pH 12—399.0 (18 600), 401.0 (19 800).

Solvolysis of $ArCMe_2Cl$ in 90% Acetone (section 8.g.3). Adopting the procedures of Brown and Okamoto[84] measurements were made at 25 °C on $PhCMe_2Cl$ (I) and its 3-NMe_3Cl derivative (II) varying initial concentrations from 0.07 to 0.001 M. For I the overall rate constants show a tendency to increase with 0.07 M initial concentration, but they are practically constant and almost the same at 0.01, 0.002, and 0.001 M. Accordingly, the average of these latter values may be taken as the rate constant at $I = 0$: $k = 12.1 \pm 0.1\ s^{-1}$ (ref 84: $k = 12.4\ s^{-1}$). For II the overall rate constants show an increase of about 20% with initial concentration 0.062 M; this increase becomes smaller the lower the concentration. Again, the rate coefficient is rather strongly dependent on initial concentration; the average values of $10^5 k$ (in s^{-1}) are: 0.49 (0.062 M), 0.21 (0.012 M), 0.14 (0.002 M), and 0.12 (0.001 M). It was found that when applying a correction $2 \log y^*$ to each data point (using the average I) the rate coefficients in each run become constant and practically the same for each initial concentration. Accordingly, the average of the rate constants thus obtained, $k = 0.071 \pm 0.003\ s^{-1}$, may be taken as holding for $I = 0$. Using $\rho = -4.479$[1] this yields $\sigma = 0.50$ for 3-NMe_3^+.

Acidic Hydrolysis (section 8.g.5, Table XI). The methods described by Timm and Hinshelwood[46] were adopted. The initial concentrations after mixing were: 0.01 M ester and 0.01 M $HClO_4$; 0.05 M ester and 0.05 M $HClO_4$; and 0.05 M ester, 0.05 M $HClO_4$, and 1 M $NaClO_4$. The solvent "20% methanol" was made by filling up 800 g of water with methanol to 1 L at 25 °C (17.7% methanol by weight, $d = 0.967$). This solvent compromises with respect to solubility and position of the equilibrium (67 ± 3% at $I = 0.02$ and $I = 0.10$; 60 ± 1% at $I = 1$). The catalyst does not react with 20% methanol. Halide ions lead to the formation of methyl halides, so that ammonio halide esters had to be converted to perchlorates (except in water, see Table XI). An average of five data points was obtained for each run, varying between 20 and 80% of the final equilibrium. The individual rate coefficients are considered to be accurate to ±5%; they have not been corrected for solvent expansion (for water about 6%). The dielectric constants at 122 °C of 20% methanol (44) and of water (48) were obtained by extrapolation.[83]

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Registry No.—3,5-Dimethylbenzeneacetic acid, 42288-46-0; 3-methylbenzeneacetic acid, 621-36-3; 3-fluorobenzeneacetic acid, 331-25-9; 3-bromobenzeneacetic acid, 1878-67-7; *trans*-3(3-fluorophenyl)-2-propenoic acid, 20595-30-6.

Supplementary Material Available: preparation and properties of compounds; geometrical details; Tables VIII, IX, XII–XV; Figures 5–10, 15, 20, 24, and 25 (25 pages). Ordering information is given on any current masthead page.

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Absolute Configurations and Absolute Rotations of C_2-Bishomocubane, *ditwist*-Brendane, and Twistane

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(+)-*endo*-Dicyclopentadiene-1,8-dione 8-ethylene ketal (**13**), a common synthetic intermediate for both (−)-C_2-bishomocubane (**5**) and (−)-*ditwist*-brendane (**3**), was degraded to (+)-(1*R*,2*S*,4*R*)-methyl 3-(*endo*-2-norbornyl)propionate (**23**), indicating the (1*S*,2*S*,3*S*,4*S*,5*R*,7*S*,8*S*,9*R*) and (1*R*,2*R*,4*R*,6*R*,7*R*,8*R*) absolute configurations to (−)-**5** and (−)-**3**, respectively. Enantiomer differential shifts observed in NMR spectra of (−)-*exo*-*ditwist*-brendan-3-ol acetate (**32**) and (−)-twistan-2-ol acetate (**43**) have assigned absolute rotations $[\alpha]_D$ −304°, $[\alpha]_D$ −44°, and $[\alpha]_D$ −440° to (−)-*ditwist*-brendane (**3**), (−)-C_2-bishomocubane (**5**), and (−)-twistane (**2**), respectively.

Preceding papers from our laboratory have reported syntheses and absolute configuration determinations of various gyrochiral[1] cage-shaped hydrocarbons, among which the representatives are (−)-*twist*-brendane (C_2 symmetry) (**1**),[2] (−)-twistane (D_2 symmetry) (**2**),[3] (−)-*ditwist*-brendane (C_2 symmetry) (**3**),[4] (−)-C_2-bishomocubane (C_2 symmetry) (**5**),[5] and (−)-D_3-trishomocubane (D_3 symmetry) (**7**)[4,6] (Chart I). Inspection of their molecular models reveals that all these levorotatory species bear as a common structural unit the bicyclo[2.2.2]octane moiety (**9**) held in the D_3 conformation with *M* helicity (**10**)[7] (Chart II). Although symmetrical C(3)–C(6), C(5)–C(7), and C(2)–C(8) diagonal bridgings with three methylene groups retain the original D_3 symmetry of bicyclo[2.2.2]octane affording chiral D_3-trishomocubane molecule (**7**), direct diagonal bridgings with three single bonds yield cubane (**12**), an achiral molecule with O_h symmetry. Characteristically, this cubane molecule (**12**) can be regarded to be composed of two enantiomeric D_3-bicyclo[2.2.2]octane moieties (**10** and **11**), and which enantiomeric component element is to be expanded determines the chiralities of resulting C_2-bishomocubane (**5**) and D_3-trishomocubane (**7**). Beside the tricyclic members **1** and **2**, whose absolute configurations have been correlated to their synthetic intermediates with known absolute configurations, the absolute configuration determination of the tetracyclic (**3**) and the pentacyclic cage-shaped compounds (**5** and **7**) have been carried out by means of circular dichroism (CD) spectral analyses of the intermediate ketones (−)-**4**, (−)-**6**, and (−)-**8**. Reliability of this CD analysis has been supported by ample examples among which we can cite a recent X-ray crystallographic determination of the absolute configuration of (−)-D_3-trishomocubane (**7**)[8] which eventually verified our result obtained by means of the CD spectral analysis.[4] Nevertheless, attempts have been made in our laboratory to secure another direct and unambiguous experimental evidence to establish the absolute configurations of *ditwist*-brendane (**3**) and C_2-bishomocubane (**5**). In this paper, we report conversion of the (+)-ketone **13**, their common synthetic intermediate, into (+)-(1*R*,2*S*,4*R*)-methyl 3-(*endo*-2-norbornyl)propionate (**23**) to confirm our previous assignments[4,5] of their absolute configurations.

Chart I

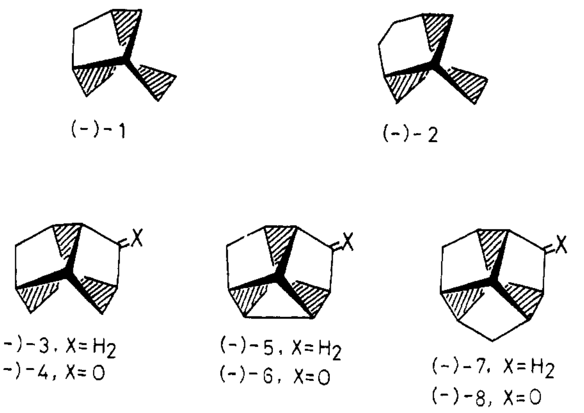
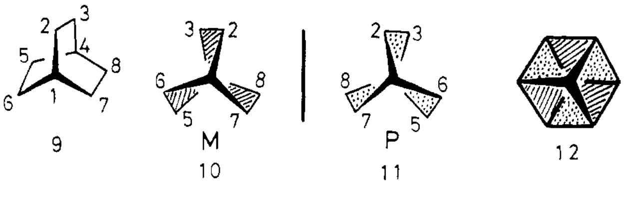


Chart II



Results and Discussion

Degradation of (+)-*endo*-Dicyclopentadiene-1,8-dione 8-Ethylene Ketal (13) into (+)-(1*R*,2*S*,4*R*)-Methyl 3-(*endo*-2-Norbornyl)propionate (23) (Scheme I).[9] Photocyclization of the (+)-unsaturated ketone **13** to give (−)-

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