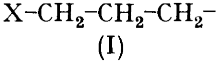
An Approach for Assessing the Relative Importance of Field and σ Inductive Contributions to Polar Substituent Effects based on the Non-proportionality of Field and σ Inductive Substituent Constants

By **William F. Reynolds**, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Evidence is presented showing that field effects and σ inductive effects are not proportional to one another and that field effects depend on the substituent group dipole moment while σ inductive effects depend upon group electronegativity. Correlations with σ_I and ι indicate that polar effects in a variety of systems are basically field effects. Problems associated with *a priori* calculations of field and σ inductive effects are discussed. In particular, it is suggested that the effective dielectric constant, D_E, should be evaluated empirically from gas-phase and solution acidities.

POLAR substituent effects in saturated organic systems can be divided into field effects (transmitted through space) and σ inductive effects (transmitted through the σ bond network).[1,2] After numerous attempts to separate these two effects, the consensus of opinion now seems to be that field effects are generally more important than σ inductive effects.[1-4] These investigations have relied on the synthesis of specific model compounds designed to test the predicted geometric dependence of field effects [5-7] and/or the predicted dependence of σ inductive effects on the number of σ bonding pathways.[1] The necessity for using model compounds appears to have arisen because most workers in this area have implicitly assumed that field and σ inductive effects of polar substituents are proportional to another. However, there have been at least four suggestions that this assumption is not valid.[8-11] Rather, while the field effect of a substituent group, X, should depend upon its dipole moment, μ_X,[5-7] its σ inductive effect should be determined by its group electronegativity, χ_X.[8] Evidence in support of this postulate and its use in separating field and σ inductive effects are examined below.

The field effect of a substituent is assumed to be transmitted through space.[5] The magnitude of the field effect can be predicted using the Bjerrum equation [5] or the Kirkwood–Westheimer modification of this equation,[6] both of which estimate the field effect in terms of the substituent dipole moment and its distance and orientation with respect to the acid proton. The field effect upon nuclear magnetic shielding also depends upon the substituent dipole moment, but with a different geometric term.[7,12] By contrast, the σ inductive effect is assumed to be transmitted through the σ bond system *via* successive bond polarization (I).[13] Factors in the range 0.2—0.7 have been suggested for the fall-off in polarization from bond to bond,[1] although some theoretical calculations suggest a much smaller fall-off factor.[14] The σ inductive effect should be proportional to χ_X [8] since polarization of the initial X–C bond (and subsequent polarization of successive bonds) depends upon the electronegativity difference between X and C.[15]



$$\mathrm{X{-}\overset{\delta+}{C}H_2{-}\overset{\delta\delta+}{C}H_2{-}\overset{\delta\delta\delta+}{C}H_2{-}}$$

(I)

χ_X and μ_X are not linearly related in the case of polyatomic substituents since the group dipole moment is often mainly determined by the polarity of bonds between pairs of atoms *within* the group [16] while the group electronegativity is primarily determined by the electronegativity of the atom which forms the point of attachment of the substituent to the rest of the molecule [8] (this point has long been recognized, *e.g.* see ref. 17). To give just one example, NH_2 and NO_2 have similar group electronegativities (χ_{NH_2} 3.35, χ_{NO_2} 3.40 [8]) but much different aliphatic group dipole moments (μ_{NH_2} 1.20 D, μ_{NO_2} 3.63 D[18]). χ_X and μ_X values for a typical set of polar substituents are compared in the Figure (using dipole moments for CH_3X derivatives [19] since only a limited number of aliphatic group moments are available [18]). Since μ_X and χ_X are clearly not proportional to one another, no linear relationship is expected between field and σ inductive effects of polar substituents.

Therefore it should, in principle, be possible to determine which of field effects and σ inductive effects are more important in a given system, provided that substituent parameter scales are available which characterize these two effects. One simply has to determine which substituent parameter scale gives the more precise correlation. In fact both field and σ inductive scales are available. Although Taft's polar substituent constant, σ_I, was originally labelled as an inductive parameter,[17] there is ample evidence in the literature that it is in fact a field parameter. For example several groups have reported a linear relationship between group dipole moment and σ_I of the general form (1) [20] where $f(\theta, r)$ is the geometric term from the Bjerrum [5] and Kirkwood–Westheimer [6] field effect equations. This is exactly what one would expect if σ_I is a field parameter. In addition, σ_I is directly

$$\mu_X f(\theta, r) = \rho_I \sigma_I(X) \qquad (1)$$

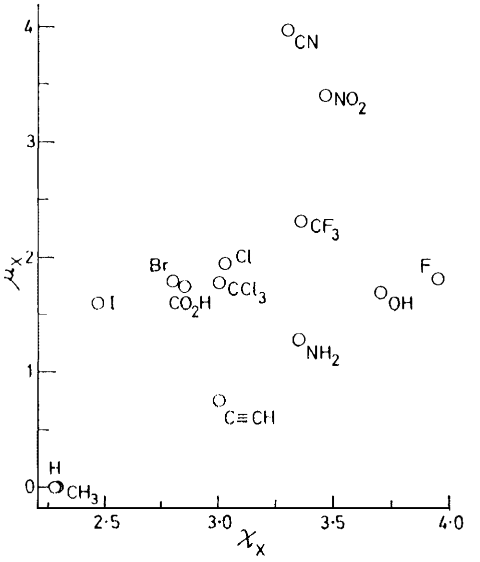
proportional to the theoretical through space field effect parameter, T_F, which has been derived from *ab initio* (STO-3G minimal basis set [21]) molecular orbital calculations on 4-substituted styrenes[10] and benzoic acids[22] [r 0.93 for a correlation of σ_I with T_F for 10 substituents but r 0.96 with NO_2 omitted (STO-3G calculations clearly overestimate the polar effect of this group[10,22,23])]. χ_X could be used as an inductive parameter.[8] Alternatively, Inamoto and Masuda have recently derived a new parameter, ι, which they claim is a pure inductive parameter.[24,25] In fact ι is linearly related to χ_X (r 0.985)[24] and also to the theoretical σ inductive parameter, Σq_σ, which measures the total σ electron withdrawal in aromatic systems[10] (r 0.91 for 10 substituents but r 0.97 with NO_2 omitted). Thus ι can be regarded as an inductive parameter, as claimed.[24,25] The main advantage of ι over χ_X is that values of ι have been derived for a large range of substituents.[24] As expected, there is only a weak relationship between ι and σ_I (see Figure 6 of ref. 24 and note the similarity to the Figure in this paper; r 0.35—0.65 for correlations of ι *versus* σ_I, depending upon the exact set of substituents used in the correlation, see Table 1).

TABLE 1

Correlations of polar substituent effects upon acid dissociation constants and ^{13}C and ^{19}F chemical shifts with σ_I and ι

System	Parameter	ρ_I [a]	r_I [b]	S.D.[c]	F [d]	ρ_ι [e]	r_ι [f]	S.D.	F	n [g]	$r_{(\sigma_I,\iota)}$ [h]
(II)	$\log(K_X/K_H)$ [i]	1.58 ± 0.04	0.998	0.04	1 918	0.89 ± 0.37	0.63	0.40	5.80	11	0.65
(III)	$\log(K_X/K_H)$ [j]	4.79 ± 0.15	0.993	0.14	1 073	2.11 ± 0.94	0.49	1.00	5.05	18	0.48
(IV)	δ_C(*para*) [k]	1.29 ± 0.10	0.969	0.08	168	0.31 ± 0.27	0.33	0.30	1.36	13	0.35
(V)	δ_F [l]	1.58 ± 0.10	0.977	0.08	233	0.47 ± 0.32	0.40	0.36	2.13	13	0.47
XCH_2CO_2H	$\log(K_X/K_H)$ [m]	4.10 ± 0.20	0.984	0.16	408	1.22 ± 0.59	0.50	0.80	4.32	15	0.53

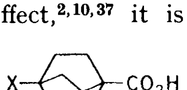
[a] Slope (± standard derivation of slope) for equation $\log(K_X/K_H) = \rho_I\sigma_I + C$ or $\delta_X - \delta_H = \rho_I\sigma_I + C$. σ_I Values from ref. 46. [b] Correlation coefficients for equations in footnote *a*. [c] Standard deviation of estimate. [d] F test of variance. A larger value indicates a more accurate correlation. [e] Slope (± standard deviation of slope) for $\log(K_X/K_H) = \rho_\iota\Delta\iota + C$ or $\delta_X - \delta_H = \rho_\iota\Delta\iota \times C$ ($\Delta\iota = \iota_X - \iota_H$). Values from ref. 24. [f] Correlation coefficients for equations in footnote *e*. [g] Number of data points. [h] Correlation coefficients for correlation of σ_I *versus* ι. [i] Data from refs. 26 and 27. [j] Data from ref. 29. [k] Data for C_6H_{12} solutions from ref. 30*b*. Other solvents give similar correlations. [l] Data for C_6H_6 solutions from ref. 30*b*. [m] Data from ref. 43.



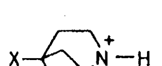
Plot of dipole moment, μ_X of CH_3X derivatives[19] *versus* substituent group electronegativity, χ_X[8]. For similar plots of σ_I *versus* ι and χ_X see refs. 24 and 8, respectively

Obviously the ideal systems for differentiating between field and σ inductive effects are those where only polar effects are present, avoiding the need to use multiparameter analysis to separate polar and resonance effects. The classic systems for this purpose are 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids (II) and quinuclidinium ions (III) where substituent effects on acidities have been determined.[26-29] In addition long range polar effects on substituent-induced chemical shifts (s.c.s.) in aryl groups can be assessed from recently reported ^{13}C and ^{19}F chemical shift data for (IV) and (V).[30,31] Results of correlations of acidities of (II) and (III) [expressed as log (K_X/K_H) where K = acid dissociation constant], *para* carbon chemical shifts in (IV), and ^{19}F chemical shifts for (V) *versus* σ_I and ι are summarized in Table 1. σ_I gives good to excellent correlations in all systems (Jaffé classifies Hammett correlations with $r > 0.95$ as good and $r > 0.99$ as excellent[32]) while ι gives totally unsatisfactory correlations in all cases.

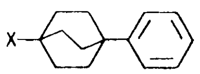
If one accepts the arguments presented above, then the data in Table 1 provide strong evidence that remote polar effects are almost exclusively field effects of one kind or another. The data for (V) are interesting since there has been considerable controversy concerning the origins of polar effects on ^{19}F chemical shifts in aryl fluorides.[33,34] However recent work on several model systems has clearly demonstrated that these polar effects are mainly due to field-induced polarization of the phenyl π electron system,[30,31,35,36] with possible minor contributions from direct field effects. While field-induced π polarization is usually classified as a π inductive effect,[2,10,37] it is a manifestation of the dipole moment of the substituent and is clearly proportional to σ_I.[10,30,31,35-37] Therefore, it can also be regarded as a form of field effect.[36] One solution to the semantic problem would be to classify both direct field effects and field-induced π polarization as polar effects while refer-



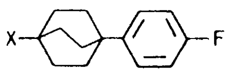
(II)



(III)



(IV)



(V)

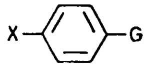
ring to σ inductive effects as electronegativity effects. This would pinpoint the origins of the different effects. However, the term polar effect has historically been applied to both field and σ inductive effects. While we have chosen to use the normal terminology, it should be noted that the procedure adopted effectively separates polar (including π polarization) effects from σ inductive effects.

Closer range polar substituent effects are also well predicted by σ_I. For example, aqueous acidities of XCH_2CO_2H, XCH_2OH, and $XCH_2NH_3^+$ derivatives all give good correlations with σ_I [38-41] (*e.g.* r 0.975 for $XCH_2NH_3^+$ [41]). Gas-phase acidities and proton affinities are somewhat more difficult to interpret since these parameters appear to be affected by both substituent polarity and polarizability, particularly in the case of alkyl substituents.[42] However, Taft and his co-workers have developed methods for factoring out polarizability contributions.[41] When this is done, polar effects on gas-phase proton affinities and acidities of XCN_2OH and gas phase acidities for $XCH_2NH_3^+$ are accurately predicted by σ_I [41] (*e.g.* see Figure 1 of ref. 41).

Unfortunately it was not possible to carry out correlations with ι for many of the systems mentioned in the previous paragraph because ι values were unavailable for some of the substituents. However acid dissociation constants are available for many XCH_2CO_2H derivatives in aqueous solutions.[43] Correlation of the data for 15 derivatives with σ_I gives r 0.984 while no relationship is found with ι (Table 1). Thus even relatively short range polar substituent effects upon acid dissociation constants are basically field effects. The one case where σ inductive effects might be important is in systems where the substituent is directly attached to the acid function, *e.g.* HOX acidities. Unfortunately it is difficult to check this possibility. First, acid dissociation constants are not accurately known for certain key substituents (*e.g.* HOF, $HONO_2$). The second, and more important, problem is that many key ^-OX groups are significantly stabilized by resonance (*e.g.* ^-OCN, $^-ONO_2$, $^-OC_6H_5$, *etc.*). Since it is difficult to separate resonance contributions, it is not possible to determine whether the polar contributions are due to field or σ inductive field.

One parameter which does appear to be dominated by σ inductive effects is the α-carbon s.c.s. in XCH_3 and XCH_2CH_3 derivatives (r 0.94 for an s.c.s.–ι correlation for 18 substituents) [24]. σ inductive effects may also contribute to ^1H chemical shifts in these derivatives since the internal ^1H chemical shift difference, $\delta_{CH_3} - \delta_{CH_2}$, for CH_3CH_2X derivatives is reasonably well predicted by χ_X.[8] In fact, very recent theoretical calculations have suggested that field and σ inductive effects make comparable contributions to δ_{CH_3} in CH_3CH_2X derivatives.[44] While these observations might appear inconsistent with our conclusions that acid dissociation constants for XCH_2OH and $XCH_2NH_3^+$ derivatives are dominated by direct field effects, this is probably not the case. We have previously shown that polar effects on acid dissociation constants in aromatic derivatives (*e.g.* benzoic acid derivatives) are dominated by the direct electrostatic interaction between the substituent and the charged CO_2^- group (field effect) with only minor contributions from polarization of the intervening phenyl π electron system (π inductive effect).[22] However, in the case of polar effects on neutral probes such as ^{19}F chemical shifts in aryl fluorides, polarization of the intervening π electron system is more important than direct field effects.[30,31,35] By analogy, it is reasonable to expect that charged and neutral probe groups should show different relative sensitivities to field and σ inductive effects in alkyl derivatives, *i.e.* that acid dissociation constants will be dominated by field effects while through-bond polarization (σ inductive effect) makes a significant contribution to ^1H chemical shifts at short range. However, the latter effect must drop off very rapidly with distance since calculations for bicyclooctane derivatives indicate minimal inductive effects for γ carbons.[9]

In cases where polar groups are directly attached to an aromatic group, identification of polar effects is again complicated by the presence of significant resonance interactions.[2] However, in this case, dual substituent parameter correlations can be used to separate polar and resonance contributions to substituent effects.[2] For example, Inamoto and Masuda [24,25] have reported 33 correlations of ^{13}C s.c.s. for derivatives of the type (VI)



(VI)

where G is a probe group containing one or more carbon atoms with ι plux Exner's σ_R resonance parameter [45] [equations (2)]. However, many of these correlations are

$$\text{s.c.s.} = a(\iota + b\sigma_R) \qquad (2)$$

of low precision (particularly for dual substituent parameter correlations) with only 10 of 33 correlations having $r > 0.95$ (and none with $r > 0.99$). By contrast s.c.s. in closely related systems often give very precise correlations with Taft's σ_I and $\sigma_R{}^\circ$ scales [46] (*e.g.* see refs. 47 and 48) [equation (3)]. For example, correlation co-

$$\text{s.c.s.} = \rho_I\sigma_I + \rho_R\sigma_R \qquad (3)$$

efficients are shown in Table 2 for ten cases where correlations have been reported for the same data set, using both ι, σ_R, and $\sigma_I,\sigma_R{}^\circ$.[47,49-52] While r is not a particularly useful parameter for judging goodness of fit in a multiparameter correlation, there is sufficient difference in r in each case to be confident that the $\sigma_I,\sigma_R{}^\circ$ correlations are distinctly superior.

The data in Table 2 suggest that field effects are more important than σ inductive effects on aromatic systems. In fact, in view of the data in Table 1, it appears probable that polar effects in these systems are not predicted at all by ι and that fair correlations are obtained with equation (2) only because the resonance contributions are reasonably well predicted by σ_R. This emphasizes the necessity of carrying out a careful analysis of the validity of any multi-parameter correlation, testing the statistical significance of each parameter in the correlation. A useful program for this purpose is the stepwise multiple regression program STPRG [53] which tests the relative significance of each variable. This has been used to analyse substituent effects from two different aromatic systems with two different types of probe groups: *para*-carbon s.c.s. in C_6H_5X derivatives (in CCl_4 at infinite dilution) [54] and acid dissociation constants for 4-substituted pyridinium ions.[55] Results of the analyses are summarized in Table 3.

TABLE 2

Comparison of correlation coefficients for correlations of sidechain ^{13}C chemical shifts in XC_6H_4Y [a] derivatives with $\sigma_I,\sigma_R{}^\circ$ and ι,σ_R

Y [b]	$r_{(\sigma_I,\sigma_R{}^\circ)}$ [c]	Reference	$r_{(\iota,\sigma_R)}$ [d]	Reference
$-Si(\overset{*}{C}H_3)_3$	0.991	49	0.923	25
$-CH_2\overset{*}{C}H_3$	0.986	50	0.870	24
$-\overset{\overset{\displaystyle O}{\|}}{C}-Ph$ [e]	0.996	51	0.984	24
$-O\overset{*}{C}H{=}CH_2$	0.991	47	0.958	25
$-OCH{=}CH_2{}^*$	0.997	47	0.944	25
$-S\overset{*}{C}H{=}CH_2$	0.997	47	0.954	25
$-SCH{=}CH_2{}^*$	0.997	47	0.948	25
$-Se\overset{*}{C}H{=}CH_2$	0.997	47	0.957	25
$-SeH{=}CH_2{}^*$	0.995	47	0.944	25
$-C(CH_3){=}CH_2{}^*$	0.998	52	0.844	24

[a] *para*-Substituted derivatives with a variable substituent X and a fixed substituent Y containing one or more carbons. [b] Correlation for asterisked carbon. [c] Correlation coefficient for correlation with equation (3). [d] Correlation coefficient for correlation with equation (2). [e] Correlation for *ipso*-carbon.

TABLE 3

Multiple parameter correlations of substituent effects on acidities and chemical shifts

System	Parameter	Correlation [a]	ρ_ι [b]	p_I [b]	ρ_R [b]	r [c]	F [d,e]	S.D. [f]	T_ι [e,g]	T_I [e,g]	T_R [e,g]	n [h]	Ref.
$4-XC_5H_5N^+$	$\log(K_X/K_H)$	$\sigma_R(BA)$			3.20 ± 0.51	0.850	39.0	1.19			6.2	17	55
		$\iota,\sigma_R(BA)$	3.92 ± 0.99		4.05 ± 0.42	0.928	46.0	0.93	4.0		9.6		
		$\sigma_I,\sigma_R(BA)$		5.14 ± 0.16	2.69 ± 0.06	0.998	1 949	0.14		32.8	43.3		
		$\iota,\sigma_I,\sigma_R(BA)$	0.28 ± 0.23	4.95 ± 0.22	2.77 ± 0.09	0.998	1 345	0.15	1.2	22.7	31.2		
XC_6H_5	$\delta_C(para)$	$\sigma_R{}^\circ$			21.2 ± 1.2	0.981	309	1.15			17.6	14	54
		$\iota,\sigma_R{}^\circ$	2.29 ± 1.12		22.2 ± 1.2	0.985	197	1.06	2.0		18.7		
		$\sigma_I,\sigma_R{}^\circ$		4.85 ± 0.74	20.0 ± 0.6	0.996	720	0.56		6.6	35.5		
		$\iota,\sigma_I,\sigma_R{}^\circ$	-1.11 ± 0.83	5.86 ± 1.03	19.2 ± 0.8	0.996	516	0.57	1.3	4.7	23.7		
XCH_2CO_2H	$\log(K_X/K_H)$	ι	1.22 ± 0.59			0.50	4.3	0.80	2.1			15	43
		σ_I		4.10 ± 0.20		0.984	408	0.16		20.2			
		ι,σ_I	-0.07 ± 0.14	4.16 ± 0.25		0.984	192	0.17	0.5	16.9			

[a] Terms include in general correlation: parameter = $\rho_\iota\Delta\iota + \rho_I\sigma_I + \rho_R\sigma_R\cdot\sigma_R{}^\circ$ and $\sigma_R(BA)$ are different resonance scales.[46] [b] Regression coefficient for individual terms ± standard deviation of regression coefficient. [c] Multiple correlation coefficient (adjusted for numbers of degrees of freedom in correlation). [d] F Test of variance. [e] Larger value of F or T means a better overall correlation (F) or a greater significance of an individual regression coefficient (T). [f] Standard deviation of estimated parameter (adjusted for numbers of degrees of freedom). [g] ρ/standard deviation in ρ. [h] No. of data points in correlation.

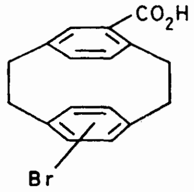
The program gives several parameters which can be used to judge goodness of fit. Regardless of whichever parameter is chosen for this purpose, it is apparent that σ_I fits the data much better than ι. Furthermore, when all three of σ_I, ι, and σ_R are included in a correlation, there is no statistically significant improvement due to the addition of ι (*e.g.* note that the F test of the variance decreases relative to the σ_I–σ_R correlation). The program was also used to correlate the acidity of XCH_2CO_2H derivatives with $\sigma_I + \iota$. Again there is negligible improvement due to the addition of ι. Thus, there is no reason to regard the polar effects in these systems as a mixture of field and σ inductive effects; only the former is important. Finally, it is interesting to note that while ι, $\sigma_R{}^\circ$ give a reasonable ^{13}C chemical shift correlation (r 0.985), this is entirely due to the $\sigma_R{}^\circ$ term (r 0.981 for a correlation with $\sigma_R{}^\circ$ alone). This illustrates the point made above that even good multi-parameter correlations cannot be taken as evidence of the validity of a particular substituent parameter unless a proper statistical analysis is carried out.

To summarize the discussion up to this point, correlations of the substituent parameters σ_I and ι with both acidities and s.c.s. in aliphatic and aromatic derivatives clearly indicate that field effects are far more important than σ inductive effects in determining acidities and that σ inductive effects contribute to s.c.s. only at very close range. These conclusions are based on the assumption that σ_I is a field parameter while ι is a σ inductive (electronegativity) parameter.

The main advantage of this approach is that it relies on empirical substituent parameter correlations and thus is not subject to any errors in existing models for prediction of field and σ inductive effects. In fact, there are very serious problems with *a priori* prediction of either type of substituent effect upon acidities in particular. For example, fall-off factors from 0.2 to 0.7 have been suggested for σ inductive effects.[2] For XCH_2CO_2H derivatives (substituent four bonds from the acid proton), the predicted σ inductive effect can vary over a range of 150, depending upon the fall-off factor chosen, while for 4-substituted benzoic acids (substituent seven bonds from proton), the predicted fall-off factor can vary by 6 500! In the case of field effects, the main difficulty concerns estimation of the effective dielectric constant, $D_{\rm E}$, which appears in the denominator of the equation for calculating field effects by the cavity model.[6] For example, Wepster and his co-workers have recently concluded that it is necessary to assume $D_{\rm E} = D_{\rm S}$, the dielectric constant of the solvent, in order to calculate field effects accurately.[56] This leads to very small estimates of dipolar field effects, particularly in aqueous media (*e.g.* $\Delta pK_{\rm A}$ 0.05 for the field effect of the nitro group and $\Delta pK_{\rm A}$ 0.02 for the chloro group in 4-substituted benzoic acid derivatives). However, most other workers have assumed smaller values of $D_{\rm E}$.[7,57-60] The real problem, as has been pointed out by several groups,[7,56,57,59] is that it is possible to calculate values of $D_{\rm E}$ from 1 up to greater than $D_{\rm S}$, depending upon the choice of parameters (in fact, Hermann's calculations suggest that $D_{\rm E}$ can be less than 1 [61]). These observations suggest that it would be better to treat $D_{\rm E}$ as an empirical parameter to be evaluated from the slope of a plot of gas-phase *versus* solution acidities or basicities.

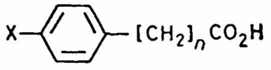
Comparisons of this type indicate that substituent effects on acidities of substituted methyl alcohols,[41] acetic acids,[62] pyridinium ions,[63] phenols,[64] and benzoic acids [64,65] are respectively reduced by factors of 3, 4, 4, 7, and 10 * on going from the gas phase to aqueous solution while other data suggest that the substituent effects of charged substituents (*e.g.* NH_3^+) are reduced relative to dipolar substituents by a factor of 4—6 on going from the gas-phase to aqueous media.[66] These suggest empirical $D_{\rm E}$ values of *ca.* 3—10 or more for polar substituents in aqueous media and *ca.* 15—60 or greater for charged substituents with the larger values likely associated with larger molecules. These estimates are surprisingly close to the original values suggested by Kirkwood and Westheimer [6] for polar and charged substituents and also to those estimated by Tanford [57] and also parallel the estimated of Kirkwood and Westheimer in suggesting larger values of $D_{\rm E}$ for larger cavities.[6] They differ from the model of Wepster *et al.*[56] in predicting different values of $D_{\rm E}$ for polar and charged substituents.

While these data basically support the cavity model, the agreement may be at least partly fortuitous. Recent investigations suggest that solvent effects on acidities and basicities mainly reflect specific solvation, particularly of the ionic form of the acidic or basic function.[41,67,68] Similar solvation effects of charged substituents would be expected, thus accounting for the additional attenuation of substituent effects for these groups. However, regardless of the actual origins of the solvation effects, the empirical $D_{\rm E}$ values should still be valid. Smaller values of $D_{\rm E}$ would be expected for less polar solvents in the case of either specific or general solvation.



(VII)

While there are serious problems in *a priori* evaluation of $D_{\rm E}$, it does appear to be possible to predict, using simple electrostatic calculations, the observed angular and distance dependence of polar substituent effects in model systems.[4,58,60,69] The data of Acevedo and Bowden for bromo-substituted carboxy[2.2]paracyclophanes (VII) [4] are particularly impressive in this regard. They find excellent agreement between calculated field effects and observed polar effects for four different isomers, including the observation of reversed dipolar substituent effects in two isomers.[4] Although not stated, it appears that the calculations assumed $D_{\rm E}$ *ca.* 4 (*i.e.* $D_{\rm E}$ *ca.* 0.1$D_{\rm S}$). Certainly the observed effects are much smaller than would be predicted assuming $D_{\rm E} = D_{\rm S}$ (*e.g.* $\Delta pK_{\rm A}$ 0.35 for the pseudo *para*-isomer compared to a calculated field effect of 0.03 pK units assuming $D_{\rm E} = D_{\rm S}$: polar effects for other isomers are similarly underestimated). In cases like this where large residual effects are noted after subtraction of field effects, Wepster *et al.* attribute the residual effects to through-bond effects.[56] However, observed polar effects differ in both sign and magnitude for pairs of isomers where the substituent is the same number of bonds from the acid proton, *e.g.* $\Delta pK_{\rm A}$ −0.40 for the pseudo-*gem*-isomer but +0.31 for the pseudo-*meta*-isomer, both with nine bonds between the substituent and the proton. Since it is highly improbable that two through-bond effects could differ so grossly at such long range, it must be concluded that the data of Acevedo and Bowden are incompatible with the model of Wepster *et al.* while they can be wholly explained in terms of field effects, assuming $D_{\rm E}$ *ca.* 4.



(VIII)

It is tempting to reject the approach of Wepster *et al.* on the grounds that it cannot account for the data of Acevedo and Bowden [4] as well as other systems where a pronounced angular dependence of field effects has been noted [1,2,4,58,60,69] (see also ref. 4 for earlier work by

---

* Ideally one should correlate acidities for the last three sets of data with σ_I and σ_R and use the ratio $\rho_I(g)/\rho_I(aq)$ to determine the attenuation of polar effects. In practice, this makes little difference, *e.g.* $\rho_I(g)/\rho_I(aq) = 10.4$ for benzoic acid.[22]

Bowden). However since Wepster's approach does give significantly improved Hammett correlations for charged substituents, it is clearly worthy of more detailed consideration. The main problem which they consider is the effect of polar and charged substituents on acidities (and reactivities) in systems such as (VIII). While a series of dipolar substituents give good Hammett plots, it is impossible to obtain a consistent σ parameter for a given charged substituent. Typically the magnitude of σ for a substituent such as $N(CH_3)_3^+$ increases significantly with increasing n. They conclude that this deviation is due to the field (Bjerrum) term of the charged substituent and divide the total effect upon $\Delta(\equiv \log K_X/K_H)$ into Bjerrum, δ_B, and through-bond (Lewis), δ_L, contributions [equation (4)]. σ_B is calculated by an

$$\Delta = \delta_B + \delta_L \qquad (4)$$

electrostatic calculation, assuming $D_E = D_S$. Then this contribution is subtracted and a new Hammett correlation is carried out [equation (5) where $\rho_L \gtrsim \rho$, the

$$\Delta - \delta_B = \rho_L\sigma_L \qquad (5)$$

slope for dipolar substituents]. When this is done, much more consistent σ_L values are obtained for charged substituents. It is noteworthy that this method predicts very small field effects for dipolar substituents in solution.

However, it is important to realize that the apparent increase in σ values for charged substituents would be expected, even if there were significant field effects due to dipolar substituents. The field effects due to monopolar (charged), δ_M, and dipolar substituents, δ_D, respectively, show the angular and distance dependence given in equations (6) and (7). However $\cos\theta \gtrsim 1$ for *para* derivatives of (VIII). Hence equation (8), where σ_M

$$\delta_M \propto r^{-1} \qquad (6)$$

$$\delta_D \propto \cos\theta r^{-2} \qquad (7)$$

$$\delta_M/\delta_D = \sigma_M/\sigma_D \propto r \qquad (8)$$

and σ_D are σ constants estimated from a Hammett plot for dipolar substituents. Consequently, the estimated σ constant for a monopolar substituent in (VIII) should increase with increasing n and r.

This raises the possibility that the calculations of Wepster and his co-workers do not remove the entire field effect due to charged substituents, as intended,[56] but rather remove a fraction of the total field effect sufficient to make the charged substituent behave in a manner approximately equal to that of a dipolar substituent. If true, the estimated δ_L values for both polar and charged substituents[56] should include significant contributions due to field effects. At least four arguments can be advanced to support this viewpoint.

(1) Intimate ion pairing, which is observed to reduce Δ_M to *ca.* δ_L,[56] is equivalent to converting a monopolar substituent to a dipolar one and should not remove the total field effect.

(2) The observed polar effects of $N(CH_3)_3^+$ poles can be totally accounted for by electrostatic calculations with values of D_E consistent with those estimated above for charged substituents (see Table 4: D_E tends to increase with increasing size, as noted above).

TABLE 4

Estimated values of the effective dielectric constant, D_E, from acidities of $3\text{-}N(CH_3)_3^+$ and $4\text{-}N(CH_3)_3^+$-substituted derivatives of $C_6H_5[CH_2]_nCO_2H$

n	Isomer [a]	$\log(K_X/K_H)$ [b]	r [c]	D_E [d]	$\langle D_E\rangle$ [e]
0	3	1.03	6.3	39	37
	4	0.98	7.2	35	
1	3	0.65	7.5	50	52
	4	0.61	7.3	54	
2	3	0.50	8.7	56	57
	4	0.45	9.3	58	

[a] 3- or 4-substituted derivatives. [b] Acidity data from ref. 56. [c] Distance (in Å) from substituent to acid proton. Data from ref. 56. [d] Effective dielectric constant [$D_E = (243/r)\log(K_X/K_H)$].[56] [e] Average value of D_E for the pair of isomers.

(3) After correction for δ_B, the residual δ_L for charged substituents is often proportional to σ_I,[56] suggesting that the residual term in these cases is still a field term (possibly including contributions from field-induced π polarization). In other cases (including $[CH_2]_nNH_3^+$ and SO_2^- substituents) δ_L is not proportional to σ_I,[56] indicating that it is likely to be a composite of field and through-bond (including resonance) effects. In particular this may account for some of the cases where δ_L *ca.* 0 (*e.g.* opposed field and resonance effects for $[CH_2]_nNH_3^+$ should yield a small δ_L).

(4) Calculated δ_B values for (VII) are very small (see above). Consequently, $\Delta \gtrsim \delta_L$. However, since Δ values for the various isomers of (VII) show a pattern entirely consistent with field effects, it follows logically that δ_L contains significant contributions due to dipolar field effects. These effects should be even more important for closer range substituent effects, *e.g.*, acidities of benzoic acid derivatives.

While not all points can be considered in detail, one specific point made by Wepster and his co-workers must be commented upon. This concerns the reaction of diazodiphenylmethane with carboxylic acids. It is argued that the data for these reactions are inconsistent with a field effect model since this would require $D_E \gtrsim 0.2$.[56] This conclusion assumes that the reaction involves neutral reagents and, therefore, that the substituent effect is a dipole–dipole interaction. However, the mechanism of this reaction involves proton transfer to form charged intermediates[70] and substituent effects similar to the corresponding substituent effects on acid dissociation would be expected and are observed.[70] Thus D_E values for this reaction are similar to those estimated above for acid dissociation. In fact, data for these reactions are entirely consistent with a field model and show excellent correlations with σ_I in the case of substituted acetic acids.[70] In another system, reversed dipolar substitutent effects are noted for this reaction, again suggesting a field effect.[71] Thus, rather than representing evidence against a field effect model, the diazodiphenylmethane reaction provides further evidence in support of this model.

In summary, it is argued that field effects and σ inductive effects are not parallel polar phenomena but rather that the field effect depends upon the substituent group dipole moment while the extent of σ electron withdrawal is determined by the group electronegativity. This allows the use of distinct substituent parameter scales to characterize field (polar) effects (σ_I[46]) and σ inductive (electronegativity) effects (ι[24] or χ_X[8]). Comparisons of correlations of substituent effects in a number of aromatic and aliphatic derivatives indicates that field effects are more important than σ inductive effects except possibly for neutral probe groups (*e.g.* ^{13}C or ^{1}H chemical shifts) at very close range.

The main advantage of this approach is that it relies on empirical substituent parameter correlations rather than *a priori* calculations of field and σ inductive effects. Predictions based on the latter calculations are strongly dependent on the exact parameters used, *e.g.* the value of D_E for field effect calculations and the fall-off factor for σ inductive calculations. Detailed consideration of previous results suggests that it is best to treat D_E as an empirical parameter to be evaluated from comparisons of gas-phase and solution acidities. When this is done, the results are generally consistent with the dominance of field (polar) effects over σ inductive effects.

These conclusions have considerable pedagogical significance. Many widely used introductory organic chemistry texts stress σ inductive effects when discussing substituent effects (*e.g.* see ref. 72). This might not matter if the two effects differed only in the predicted angular dependence of the field effect. However, if one accepts that these are two independent phenomena, then the continued emphasis on σ inductive effects is most unfortunate, particularly since field effects appear to be far more important in most cases.

Financial support from the Natural Science and Engineering Research Council of Canada is gratefully acknowledged.

[9/1167 *Received*, 23*rd July*, 1979]

REFERENCES

[1] L. M. Stock, *J. Chem. Educ.*, 1972, **49**, 400.

[2] R. D. Topsom, *Progr. Phys. Org. Chem.*, 1976, **12**, 1.

[3] J. M. Rees, J. H. Ridd, and A. Ricci, *J.C.S. Perkin II*, 1976, 224.

[4] S. Acevedo and K. Bowden, *J.C.S. Chem. Comm.*, 1977, 608.

[5] (*a*) N. Bjerrum, *Z. Phys. Chem.*, 1923, **106**, 219; (*b*) A. Eucken, *Angew. Chem.*, 1932, **45**, 203.

[6] (*a*) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 1938, **6**, 506; (*b*) F. H. Westheimer and J. G. Kirkwood, *ibid.*, p. 513.

[7] A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.

[8] P. R. Wells, *Progr. Phys. Org. Chem.*, 1968, **6**, 111.

[9] R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, 1970, **92**, 7007.

[10] W. F. Reynolds, P. G. Mezey, and G. K. Hamer, *Canad. J. Chem.*, 1977, **55**, 522.

[11] B. G. Ramsay, *J. Organometallic Chem.*, 1977, **135**, 307.

[12] J. G. Batchelor, J. Feeney, and G. C. K. Roberts, *J. Magnetic Resonance*, 1975, **20**, 19.

[13] G. E. K. Branch and M. Calvin, 'The Theory of Organic Chemistry,' Prentice–Hall, New York, 1941.

[14] J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, 'Valence Theory,' Wiley, New York, 1965.

[15] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1960, 3rd edn.

[16] W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 2191.

[17] R. W. Taft in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956.

[18] C. W. N. Cumper, *Tetrahedron*, 1969, **25**, 3131.

[19] A. L. McClellan, 'Tables of Experimental Dipole Moments,' Freeman, San Francisco, 1963.

[20] B. L. Poh, *Austral. J. Chem.*, 1979, **32**, 427 and references therein.

[21] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657.

[22] P. G. Mezey and W. F. Reynolds, *Canad. J. Chem.*, 1977, **55**, 1567.

[23] M. Taagepera, W. J. Hehre, R. D. Topsom, and R. W. Taft, *J. Amer. Chem. Soc.*, 1976, **98**, 7438.

[24] N. Inamota and S. Masuda, *Tetrahedron Letters*, 1977, 3287.

[25] N. Inamoto and S. Masuda, *Chem. Letters*, 1978, 177.

[26] J. D. Roberts and W. T. Moreland, *J. Amer. Chem. Soc.*, 1953, **75**, 2167.

[27] H. D. Holtz and L. S. Stock, *J. Amer. Chem. Soc.*, 1964, **86**, 5188.

[28] C. F. Wilcox and J. S. McIntyre, *J. Org. Chem.*, 1965, **30**, 777.

[29] E. Ceppi, W. Eckhardt, and C. A. Brob, *Tetrahedron Letters*, 1973, 3627.

[30] W. Adcock and T. C. Khor, (*a*) *Tetrahedron Letters*, 1976, 3063; (*b*) *J. Amer. Chem. Soc.*, 1978, **100**, 7799.

[31] (*a*) D. F. Ewing, S. Sotheeswaran, and K. J. Toyne, *Tetrahedron Letters*, 1977, 2041; (*b*) D. F. Ewing and K. J. Toyne, *J.C.S. Perkin II*, 1979, 243.

[32] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[33] J. Fukunaga and R. W. Taft, *J. Amer. Chem. Soc.*, 1975, **97**, 1612 and references therein.

[34] W. Adcock and D. B. Gupta, *J. Amer. Chem. Soc.*, 1975, **97**, 6871 and references therein.

[35] W. F. Reynolds and G. K. Hamer, *J. Amer. Chem. Soc.*, 1976, **98**, 7296.

[36] W. Kitching, M. Bullpitt, D. Gartshore, W. Adcock, T. C. Khor, D. Dodrell, and I. D. Rae, *J. Org. Chem.*, 1977, **42**, 2411.

[37] W. F. Reynolds, I. R. Peat, M. H. Freedman, and J. R. Lyerla, *Canad. J. Chem.*, 1973, **51**, 1857.

[38] H. K. Hall, *J. Amer. Chem. Soc.*, 1957, **79**, 5441.

[39] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, 1960, **82**, 795.

[40] M. Charton, *J. Org. Chem.*, 1964, **29**, 1222.

[41] R. W. Taft, M. Taagepera, J. L. M. Abboud, J. F. Wolf, D. J. Defrees, W. J. Hehre, J. E. Bartmess, and R. T. McIver, *J. Amer. Chem. Soc.*, 1978, **100**, 7765.

[42] J. I. Brauman and J. K. Blair, *J. Amer. Chem. Soc.*, 1968, **90**, 5636, 6501.

[43] G. Kortüm, W. Vogel, and K. Aldrussow, *Pure Appl. Chem.*, 1960, **1**, 189.

[44] A. A. Cheremisin and P. V. Schastnev, *Z. Strukt. Khim.*, 1979, **20**, 221.

[45] O. Exner, in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, New York, 1972.

[46] S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1973, **10**, 1.

[47] R. A. McClellan and W. F. Reynolds, *Canad. J. Chem.*, 1977, **55**, 536.

[48] D. F. Ewing in 'Correlation Analysis in Chemistry,' eds. N. B. Chapman and J. Shorter, Plenum Press, New York, 1978.

[49] C. D. Schaeffer, J. J. Zuckerman, and C. H. Yoder, *J. Organometallic Chem.*, 1974, **80**, 29.

[50] R. H. Kohler, M.Sc. Thesis, University of Toronto, Toronto, 1975.

[51] M. J. Shapiro, *Tetrahedron*, 1977, **33**, 1091.

[52] I. R. Peat, Ph.D. Thesis, University of Toronto, Toronto, 1973.

[53] STPRG, IBM System 360 Scientific Subroutine package III.

[54] R. W. Taft, personal communication.

[55] R. W. Taft and C. A. Grob, *J. Amer. Chem. Soc.*, 1974, **96**, 1236.

[56] A. J. Hoefnagel, M. A. Hoefnagel, and B. M. Wepster, *J. Org. Chem.*, 1978, **43**, 4720.

[57] C. Tanford, *J. Amer. Chem. Soc.*, 1957, **79**, 5348.

[58] C. L. Liotta, W. F. Fisher, E. L. Slightom, and C. L. Harris, *J. Amer. Chem. Soc.*, 1971, **94**, 2121.

[59] S. Ehrenson, *J. Amer. Chem. Soc.*, 1976, **98**, 7510.

[60] C. T. Want and E. T. Grubbs, *J. Org. Chem.*, 1977, **42**, 534.

[61] R. B. Hermann, *J. Amer. Chem. Soc.*, 1969, **91**, 3152.

[62] K. Hiraoka, R. Yamdagni, and P. Kebarle, *J. Amer. Chem. Soc.*, 1973, **95**, 6833.

[63] M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 1369.

[64] R. B. McMahon and P. Kebarle, *J. Amer. Chem. Soc.*, 1977, **99**, 2222.

[65] R. Yamdagni, T. B. McMahon, and P. Kebarle, *J. Amer. Chem. Soc.*, 1974, **96**, 4035.

[66] W. F. Reynolds, T. A. Modro, and P. G. Mezey, *J.C.S. Perkin II*, 1977, 1066.

[67] R. W. Taft, J. F. Wolf, J. L. Beauchamp, G. Scorrano, and E. M. Arnett, *J. Amer. Chem. Soc.*, 1978, **100**, 1240.

[68] R. W. Taft in ' Kinetics in Ion-Molecule Reactions,' NATO Advanced Study Institute Series (B–Physics), ed. P. Ausloos, Plenum Press, New York, 1979, vol. 40, p. 271.

[69] R. Golden and L. M. Stock, *J. Amer. Chem. Soc.*, 1972, **94**, 3080.

[70] K. Bowden, M. Hardy, and D. C. Parkin, *Canad. J. Chem.*, 1968, **46**, 2929.

[71] K. Bowden and D. C. Parkin, *Canad. J. Chem.*, 1969, **47**, 185.

[72] R. T. Morrison and R. N. Boyd, ' Organic Chemistry,' Allyn and Bacon, Boston, 1973, 3rd edn.