

## $\pi$ -Plus Contributions in $\Delta E$ and $\Delta C$ Dual-Parameter Correlations. Curved Hammett Plots and $^{19}\text{F}$ Shifts

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Structure-reactivity analysis with the dual-parameter  $\Delta E$  and  $\Delta C$  substituent constants illustrates deviations that can arise with conjugating substituents 4-X in a para position. Complications arise when the interaction of a 4-X substituent with the reaction site (rates or equilibria) or with a spectroscopic measurement (NMR shift) gives rise to additional  $\pi$ -contributions thereby leading to a deviation in a single-parameter Hammett linear free energy plot. The deviations for the 4-X groups are referred to in the  $\Delta E$  and  $\Delta C$  correlations as  $\pi$ -plus effects. Their presence in systems that give curved Hammett plots for rates, equilibria, and  $^{19}\text{F}$  chemical shifts is illustrated.

### Introduction

In a recent series of papers<sup>1</sup> an electrostatic-covalent, dual-parameter, set of substituent constants,  $\Delta E^X$  and  $\Delta C^X$ , has been reported to correlate chemical reactivity. The parameters are an extension of the  $E$  and  $C$  model, eq 1,

$$-\Delta H = E_A E_B + C_A C_B + W \quad (1)$$

which has been used<sup>2</sup> to correlate bond strengths of adducts measured in poorly solvating media. The electrostatic or charge-controlled component of the donor-acceptor interaction is given by  $E_A E_B$  where the subscript A indicates the acceptor's (electrophile's) tendencies to undergo electrostatic bonding and B is the tendency for the donor (nucleophile) to bond. The covalent or frontier-controlled component of the interaction is given by  $C_A C_B$ , where  $C_A$  and  $C_B$ , respectively, describe acceptor (LUMO) and donor (HOMO) tendencies to undergo covalent bonding. The  $E_B$  and  $C_B$  parameters that result can be used<sup>2</sup> as a dual-parameter scale to interpret the reactivity of a series of bases with a constant acceptor. Equation 2 is employed for constant acceptor correlations.

$$\Delta\chi = E_A^* E_B + C_A^* C_B + W \quad (2)$$

In eq 2,  $\Delta\chi$  is a measured physicochemical property accompanying a reaction,  $E_B$  and  $C_B$  are the tabulated literature donor parameters from the data fits to eq 1,  $C_A^*$  and  $E_A^*$  are covalent and electrostatic components of the physicochemical acceptor property  $\Delta\chi$ , and  $W$  is the value of  $\Delta\chi$  when  $E_B = C_B = 0$ , i.e., a non-zero intercept in two-parameter space. The asterisk superscript in eq 2 is placed on the reactant A or B held constant (in eq 2 this is A) in a series of reactions where the second component is varied.

Substituent constant analyses are carried out<sup>1</sup> with eq 3 where  $\Delta\chi^X$  is the measured property of the X-substituted compound and  $\Delta\chi^H$  is the measured property of the parent

$$\Delta\chi^X = d^E \Delta E^X + d^C \Delta C^X + \Delta\chi^H \quad (3)$$

hydrogen compound. The  $\Delta E^X$  and  $\Delta C^X$  are the dual-parameter electrostatic and covalent analogues of Hammett's  $\sigma$  values. These parameters relate to the relative ability of the different substituents to change the tendency of a member of the family to undergo covalent and electrostatic bonding. The  $\Delta E$  and  $\Delta C$  are in effect a factoring of  $\sigma$  into electrostatic and covalent components. The  $d^E$  and  $d^C$  parameters are the dual-parameter, electrostatic-covalent, analogues of  $\rho$  and take into account the fact that the relative importance of covalent and electrostatic contributions to different physicochemical properties will vary. Thus, the interpretation of the parameters is the same as  $\sigma$  and  $\rho$  with the covalent and electrostatic contributions treated independently. With the  $\Delta C/\Delta E$  ratio of most substituents being roughly 4, the product of  $(4d^C + d^E)$  is a quantity whose sign (not value) can be interpreted in a manner similar to that of  $\rho$ . For example, for rate and equilibrium data, a positive value for the quantity given by  $(4d^C + d^E)$  corresponds to a negative value for  $\rho$ . Hence, electron-donating groups will facilitate the process under investigation.

Two sets of substituent constants are reported. The 3-X substituents are employed on systems where the interaction between the substituent and the reactive center involves inductive interactions. The 4-X substituents are employed where conjugative (resonance) interactions dominate the mechanism for transmission of the substituent effect to the reactive or spectroscopic center.

The  $d$  parameters measure the demand made on the system by the constant attacking reagent,  $E^*$  and  $C^*$ , of eq 2, and the sensitivity,  $s$ , of the family to substituent change. For substituent changes made on a series of donors (nucleophiles) reacting with a given acceptor, eqs 4 and 5 describe the components of  $d$ .

$$d_A E = s_B^E E_A^* \quad (4)$$

$$d_A C = s_B^C C_A^* \quad (5)$$

Here,  $s$  is in effect a scaling factor related to the effectiveness of the substituent to influence the nucleophilicity of the family of reactants being varied. A value of 1 is assigned to  $s_B^E$  and  $s_B^C$  for the pyridine family of donors, and values of  $s$  for other systems give the family sensitivities relative to pyridine. Thus, unlike the Ham-

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mett<sup>3</sup> or Taft<sup>4</sup> or Swain–Lupton<sup>5</sup> treatments that are referenced to benzoic acids, the  $\Delta E$ – $\Delta C$  treatment takes the properties of pyridines as the reference series.

The  $\Delta E^X$  and  $\Delta C^X$  values are linearly related to the  $E$  and  $C$  values of eq 1 for a family of donors by the eqs 6 and 7.

$$E_B^X = E_B^H + s_B^E \delta E^X \quad (6)$$

$$C_B^X = C_B^H + s_B^C \delta C^X \quad (7)$$

Similarly, when substituent changes are made on a family of acceptors (electrophiles) reacting with the same donor, the A and B subscripts on eqs 4 and 5 must be interchanged. In eqs 6 and 7, the B subscripts are changed to A. The sign of  $s_A$  will also differ from that of  $s_B$ . In this manner, the  $\Delta E$  and  $\Delta C$  parameters are tied to the very extensive solvation-minimized enthalpy data base of the  $E$ – $C$  model.<sup>2</sup>

When the reactivities of two different families of compounds, e.g., pyridine and aniline nucleophiles, toward the same reactant are compared, the value of  $d$  changes because  $s$  changes. When the same family of compounds is studied separately in different reactions with different constant reactants, the value of  $d$  changes because the  $E_A^*$  and  $C_A^*$  of the constant reactant change. These same factors would cause  $\rho$  to change in single substituent parameter approaches. In the  $\Delta E$ – $\Delta C$  model, this factoring of  $d$  to give  $s$  becomes possible when  $E_A^*$  and  $C_A^*$  are determined independently with eq 2.

In our earlier reports<sup>1</sup> it has been shown that data previously requiring  $\sigma_H$  (Hammett)<sup>3</sup>,  $\sigma_I$ ,  $\sigma_R$ ,  $\sigma^\circ$ ,  $\sigma^-$ , etc. (Taft)<sup>4</sup> and  $\sigma^+$  (Brown)<sup>6</sup> parameters could be fit with the one set of dual-substituent constants  $\Delta E$  and  $\Delta C$ . It has been shown<sup>7</sup> that the electrostatic-covalent eqs (2) and (3) can be converted to one-parameter equations by fixing the ratio of the covalent to electrostatic contributions. The single-parameter Hammett scale arises by fixing  $d^E$  of eq 3 at  $-2.10$  and  $d^C$  at  $-0.213$  with an intercept  $\Delta\chi^H$  at  $0.31$ . This corresponds to a  $d^C/d^E$  ratio of  $0.1$ . The different types of  $\sigma$  parameters all correspond to one-parameter scales with different ratios of the covalent and electrostatic contributions. They are appropriate for an analysis of physicochemical data only if the measured quantity has the same covalent/electrostatic ratio (i.e.,  $d^C/d^E$  ratio) as that implied in the scale employed. The new  $\Delta E$ – $\Delta C$  interpretation of most of this entire  $\sigma$  substituent data set is made on the basis of how the substituent influences the covalent (frontier controlled) and electrostatic (charge controlled) components of the equilibrium, transition state, or spectral change. This ratio is tacitly assumed to be constant in a one-parameter model.<sup>7</sup>

This treatment also differs from the dual substituent parameter methods of Taft<sup>4</sup> and of Swain–Lupton<sup>5</sup> where the dual substituent constants are used to model different

combinations of polar and resonance effects. This corresponds to a very different interpretation of the data fit. According to the Taft and Swain–Lupton interpretations, taking linear combinations of  $\sigma_I$  and  $\sigma_R$  corresponds to using linear combinations of 4-X and 3-X substituents. Polar effects (inductive through-bond and through-space effects) are given by the 3- $\Delta E^X$  and 3- $\Delta C^X$  parameters while the 4- $\Delta E^X$  and 4- $\Delta C^X$  parameters relate more to resonance effects. The  $\Delta E$ – $\Delta C$  model suggests that one possible interpretation of a data fit to a linear combination of  $\sigma_I$  and  $\sigma_R$  parameters is to provide scales in which the covalent contribution of the substituent can vary between the  $d^C/d^E$  ratios of  $\sigma_I$  and  $\sigma_R$ . The fact that covalent (frontier-controlled) and electrostatic (charge-controlled) properties of the family can vary with substituent and can vary even more in the reaction or spectroscopic properties being studied is the shortcoming of other dual-parameter approaches.

Our substituent sign convention generally is opposite to that found for the usual  $\sigma$  values in that our electron-withdrawing groups, EWG, have a negative sign while electron-donating groups, EDG, have a positive value. Consequently, our  $d$  values measuring the response of the system to substituent effects generally have a sign opposite to that of the more familiar Hammett  $\rho$  value. For arbitrary reasons,<sup>2</sup> the  $\Delta C^X$  parameters generally are considerably larger in value than the  $\Delta E^X$  constants. As a result, covalent and electrostatic contributions should be assessed by comparing the  $d^E \Delta E^X$  and  $d^C \Delta C^X$  terms of eq 3 and not by comparing  $d^E$  and  $d^C$ .

The purpose of this paper is to extend our analysis of chemical reactivity to a series of reactions of substituted phenyl derivatives that do not obey simple Hammett  $\sigma$  correlations. Systems of particular interest include those that are reported to give rise to curved Hammett plots. These systems have concerned chemists since the early 1950's.<sup>5</sup> Much of the early work has been reviewed by Young and Jencks<sup>8</sup> and some of the recent work by Richard.<sup>9</sup> Causes for the curvature are attributed to any one of several factors and have been summarized by Young and Jencks as the following:

1. A change in mechanism from  $S_N2$  to  $S_N1$  (or to an ion-pair mechanism) with change from an electron-withdrawing to an electron-releasing substituent.
2. A single mechanism with a different extent of bond formation and cleavage in the transition states. More complete bond breaking occurs in the transition state with electron-releasing substituents which stabilize positive charge development on the central carbon atom. This leads to a different  $\rho$ -value.
3. Different substituents act to stabilize the transition state with a different balance of polar and resonance effects.

Young and Jencks successfully correlated curved Hammett plots using a modified Yukawa–Tsuno approach, eq 8. Points deviating from the line defined by the usual  $\sigma\rho^n$

$$\log(k/k_0) = \rho\sigma^n + \rho^r(\sigma^+ - \sigma^n) \quad (8)$$

terms are constrained to fit the line by the correcting term  $\rho^r(\sigma^+ - \sigma^n)$ . Separate polar and resonance parameters are given by the  $\rho$  and  $\rho^r$  terms, respectively. These authors<sup>8</sup>

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Table 1. Substitution Reactions of Benzyl Halides and Benzyl Tosylate<sup>a</sup>

X	$\Delta E^X$	$\Delta C^X$	RCH <sub>2</sub> Cl, Me <sub>3</sub> N		RCH <sub>2</sub> Br, Py		RCH <sub>2</sub> Tos, H <sub>2</sub> O		<sup>35</sup> Cl NQR (MHz)	
			expl	calcd <sup>b</sup>	expl	calcd <sup>c</sup>	expl	calcd <sup>d</sup>	expl	calcd <sup>e</sup>
4-OCH <sub>3</sub>	0.048	0.285	-0.78	(-1.27)						
3-CH <sub>3</sub>	0.034	0.128			0.07	0.03	-3.33	-3.33		
4-CH <sub>3</sub>	0.050	0.192	-1.11	(-1.29)	0.22	(0.04)	-2.13	(-3.18)		
H	0	0	-1.27	-1.30	0	0.02	-3.63	-3.63	33.630	33.519
3-F	-0.115	-0.429			-0.10	-0.04	-4.63	-4.63		
4-F	-0.036	-0.168			0.08	(-0.01)	-3.22	(-4.0)	33.511	33.626
3-Cl	-0.120	-0.461			-0.05	-0.04	-4.71	-4.71	33.891	33.881
4-Cl	-0.090	-0.323			0.02	(-0.03)	-3.91	(-4.39)	33.574	33.789
3-Br	-0.118	-0.456	-1.36	-1.32	-0.05	-0.04	-4.69	-4.69		
4-Br	-0.074	-0.380	-1.20	(-1.33)	0.03	(-0.04)	-4.00	(-4.49)		
3-I	-0.107	-0.405			-0.02	-0.04	-4.58	-4.58		
4-I	-0.082	-0.219			0.08	(-0.01)	-3.94	(-4.17)		
3-NO <sub>2</sub>	-0.213	-0.968			-0.09	-0.11			34.215	34.160
4-NO <sub>2</sub>	-0.254	-0.640	-1.27	-1.28	-0.04	-0.05	-5.23	-5.23	34.284	34.283
3,5-NO <sub>2</sub>	-0.427	-1.97	-1.42	-1.43						

<sup>a</sup> The systems in parentheses were not used in the data fit but are calculated using reported  $\Delta E$  and  $\Delta C$  values with the best fit  $d^E$ ,  $d^C$ ,  $\Delta\chi^H$  values. <sup>b</sup> Log  $k$  (M<sup>-1</sup> min<sup>-1</sup>) reaction of XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl with trimethylamine in benzene at 100 °C, ref 5.  $d^E = -0.55$ ,  $d^C = 0.18$ ,  $\Delta\chi^H = -1.30$ ,  $\bar{x} = 0.021$ , % fit = 14. <sup>c</sup> Log  $k/k_H$  reaction of XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br with pyridine in acetone at 20 °C, ref 10.  $d^E = -0.151$ ,  $d^C = 0.167$ ,  $\Delta\chi^H = 0.016$ ,  $\bar{x} = 0.02$ , % fit = 13. <sup>d</sup> Log  $k$  hydrolysis of substituted benzyl tosylates in 55.6% aqueous acetone at 25 °C, ref 11.  $d^E = 1.23$ ,  $d^C = 2.01$ ,  $\Delta\chi^H = -3.63$ ,  $\bar{x} = 0.00$ . <sup>e</sup> <sup>35</sup>Cl NQR frequencies for substituted benzyl chlorides, ref 14.  $d^E = -3.02$ ,  $d^C = 0.00$ ,  $\Delta\chi^H = 33.52$ ,  $\bar{x} = 0.08$ , % fit = 11.

favor item 3 as the reason for the deviations from the simple Hammett treatment.

Curved or U-shaped Hammett plots show that both EDG and EWG increase reactivity at benzylic carbon. Moreover, the hallmark of much of these data is that the range in reactivity from the most to the least reactive substrate is less than 1000-fold, often of the order of only 10-fold. We have selected several diverse examples of classical curved Hammett plots for examination by the  $\Delta E$ - $\Delta C$  approach. They include kinetic investigations involving authentic bimolecular reactions as well as a solvolysis study. We also have included an equilibrium case. Tables of experimental and calculated values (logarithmic scale for rates and equilibria) are given so that the quality of the correlation may be judged on a point-by-point basis. Furthermore, we will show that the same interpretation used on these systems is applicable to the interpretation of the solvolysis of cumyl chlorides (the basis of the  $\sigma^+$  scale) and to the interpretation of <sup>19</sup>F chemical shifts in substituted benzenes. These new interpretations of this diverse set of data illustrate the point that the  $\Delta E$  and  $\Delta C$  approach is more than simply a scale that fits data better.

## Results and Discussion

**Benzyl Chloride, Bromide, and Tosylate (1).** The first set of data<sup>5</sup> fit in Table 1 correspond to nucleophilic attack of trimethylamine on phenyl-substituted benzyl chlorides in benzene at 100 °C. The reported correlation with Hammett parameters produced two different curved lines. The H, 3-Br, and 3,5-(NO<sub>2</sub>)<sub>2</sub> substituents gave one line. The 4-CH<sub>3</sub>O, 4-CH<sub>3</sub>, 4-Br, and 4-NO<sub>2</sub> substituents gave a second line. The data are fit with eq 3 using reported  $\Delta E$  and  $\Delta C$  values.<sup>1b</sup> Four of the seven substituents are well behaved while 4-CH<sub>3</sub>O, 4-CH<sub>3</sub>, and 4-Br give an observed reactivity greater than that calculated. The best fit parameters are  $d^E = -0.55$ ,  $d^C = 0.18$ , and  $\Delta\chi^H = -1.30$ . These parameters are tentative for they are based on only four data points. Any of the three explanations offered in the introduction could be the cause of the deviations observed. As more systems are analyzed by  $\Delta E$ - $\Delta C$  in this paper, another explanation for the deviation of this system will be presented. If the tentative  $d^C/d^E$  ratio of -0.3 is established by study of more 3-X substituents, the

Hammett substituent constants, with a  $d^C/d^E$  ratio of 0.10, would be inappropriate for a one-parameter analysis of these data.

The fit for nucleophilic attack of pyridine on phenyl-substituted benzyl bromides in acetone at 25 °C, the pioneering work of Baker and Nathan,<sup>10</sup> is also listed in Table 1. Similar results are obtained as with the reaction of trimethylamine with benzyl chloride. The 4-CH<sub>3</sub> and 4-F substituents give an observed rate constant that clearly deviates in the direction of being faster than predicted. The 4-CH<sub>3</sub> was the most electron-releasing substituent studied, and it is anticipated that an EDG such as 4-OCH<sub>3</sub> would also deviate.

The next system analyzed is the solvolysis of substituted benzyl tosylates in 55.6% aqueous acetone.<sup>11</sup> We now know that such a series having 4-methyl as the most EDG does not react by an S<sub>N</sub>1 pathway with an intermediate benzylic carbocation but rather by an S<sub>N</sub>2 mechanism with solvent acting as the nucleophile.<sup>9,12,13</sup> The 4-CH<sub>3</sub> and those substituents with lone pairs that can undergo conjugative interactions with the ring must be omitted to obtain a good data fit. In all cases, the omitted substituents lead to an increased rate above that predicted by 4- $\Delta E$  and 4- $\Delta C$  for normal conjugative interactions. The  $d^E$  and  $d^C$  values for the well-behaved substituents are both significant, giving a ratio of 1.6. Though there is appreciable error in the  $d^E$  and  $d^C$  values, it can be concluded that again this ratio is much too covalent for a Hammett correlation.

A pattern is developing in the substituents that deviate from the  $\Delta E$ - $\Delta C$  data fit. The deviant substituents are either 4-CH<sub>3</sub> or a 4-X group containing a lone pair of electrons. Furthermore, the magnitudes of the deviations of the halogen lone pair conjugative substituents from predicted values parallel the expected effectiveness of

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halogen lone pair overlap with the  $\pi^*$  orbital, *i.e.*,  $4\text{-F} > 4\text{-Cl} \sim 4\text{-Br} > 4\text{-I}$ . The deviation for the  $4\text{-CH}_3$  substituent is attributed to nonorthogonality of the C-H bonds, *i.e.*, hyperconjugation.

This attempted data fit emphasizes an important limitation of the application of the conjugative substituent parameters to complex reactions. The normal influence of the conjugative substituent is to change the electron density in the  $\pi$  and  $\sigma$  orbitals of the para atom in the ring. This electron density is transmitted to the reactive group by  $\pi$  and  $\sigma$  mechanisms. When the  $\pi$ - and  $\sigma$ -mechanisms are proportioned to the total electron density on the ring atom to which the reactive group is attached, a normal conjugative effect is observed and the 4-X substituents are relevant. When the change in electron density on this ring carbon influences the ground state or transition state and final product proportionally and in the same direction, the 4-X substituents are also relevant. However, conjugative substituents can give rise to other changes in the molecule that involve the  $\pi$ -system and cause deviations from the values predicted with the 4-X substituents. When additional  $\pi$ -contributions are operative<sup>13</sup> for a measurement involving conjugative substituents, the phenomenon henceforth will be referred to as a  $\pi$ -plus effect. The lone pair and hyperconjugative substituents will be referred to as LPC (lone pair conjugative) substituents.

In the above systems, a  $\pi$ -plus effect can arise from the nonorthogonality of the hydrogens of the  $\text{CH}_2\text{Cl}$  group with the  $\pi$  orbitals. This interaction can be viewed as arising from the mixing of the C-H electrons with  $\pi^*$  lowering the energy and stabilizing the C-H bond, *i.e.*, a  $\sigma, \pi^*$  interaction. In the transition state the benzylic hydrogens are orthogonal to the  $\pi$ -system and the stabilization from benzylic hydrogen- $\pi^*$  interactions in the ground state (hyperconjugation) is lost in going to the transition state. With lone pair conjugative substituents (LPC), this  $\pi^*$  interaction is less important in the ground state because of a higher energy  $\pi^*$  orbital, less energy will be lost in going to the transition state, activation energies will be less, and the rates will be faster. In this case, the  $\pi$ -plus refers to an extra  $\pi$ -mechanism involving a change in the interaction of the reactive group and the  $\pi$ -system in the ground and transition state.

The mixing of the leaving group atomic orbitals and the  $\pi$  orbitals of the ring also could give rise to a  $\pi$ -plus contribution. The halide is not orthogonal to the  $\pi$  system of the phenyl group in the ground-state geometry, and its bond strength could be influenced by mixing the chlorine and the ring  $\pi$  orbitals. The NQR spectra of benzyl chlorides have been interpreted<sup>14</sup> to imply a large hyperconjugative interaction between the ring and C-Cl bond, *i.e.*, a  $\pi, \sigma^*$  interaction. As seen in Table 1, these data lead to an excellent fit to  $\Delta E$  and  $\Delta C$ . The limited data set suggests that there is no  $\pi$ -plus contribution involving chlorine.

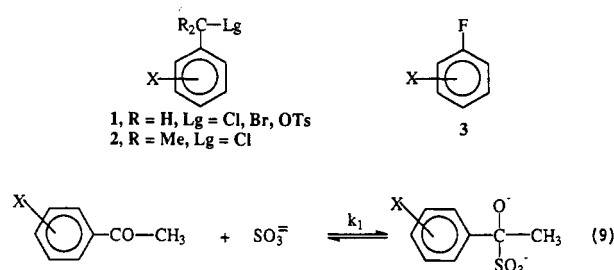
The final extra contribution from LPC substituents involves the extra stabilization from a conjugative interaction involving the developing carbocation in the transition state. This delocalization energy lowers the transition-state energy and speeds the rate. In this case, the  $\pi$ -plus refers to a  $\pi$ -contribution that is more important than expected from the electron density on the ring carbon that is para to X because of the extra stabilization from delocalization energy in the transition state.

Table 2. Rate and Equilibrium Data for the Reaction of Substituted Acetophenones with Bisulfite

substituent	$\log K_{\text{add}}$		$\log k_1$ ( $\text{M}^{-1} \text{s}^{-1}$ )		$\log k_{\text{OH}}$	
	expl	calcd <sup>a,d</sup>	expl	calcd <sup>b,d</sup>	expl	calcd <sup>c,d</sup>
H	0.74	0.68	1.89	1.90	-7.46	-7.38
4-CH <sub>3</sub>	0.48	0.49	1.66	1.63	-7.42	-7.47
4-OCH <sub>3</sub>	0	(0.50)	1.36	(1.63)	-7.24	(-7.48)
4-Cl	0.90	1.01	2.28	2.39	-7.21	-7.23
4-NO <sub>2</sub>	1.64	1.63	3.28	3.26	-6.96	-6.97
3-Br	1.20	1.12	2.58	2.55	-7.21	-7.18
4-Br	0.95	0.96	2.36	2.32	-7.20	-7.24

<sup>a</sup> The log of the equilibrium constant for formation of ketone bisulfite, ref 8. Calculated with  $d^E = -3.77$ ,  $d^C = 0.01$ ,  $\Delta\chi_{\text{H}} = 0.68$ ,  $\bar{x} = 0.05$ , % fit = 4. <sup>b</sup>  $\log_{10}$  of the second-order rate constant for the attack of  $\text{SO}_3^{2-}$  on the carbonyl compounds, ref 8. Calculated with  $d^E = -5.11$ ,  $d^C = -0.10$ ,  $\Delta\chi_{\text{H}} = 1.90$ ,  $\bar{x} = 0.03$ , % fit = 2. <sup>c</sup>  $\log_{10}$  of the second order rate constants for the specific base catalyzed breakdown of the ketone bisulfites, ref 8. Calculated with  $d^E = -1.34$ ,  $d^C = -0.11$ ,  $\Delta\chi_{\text{H}} = -7.38$ ,  $\bar{x} = 0.04$ , % fit = 8. <sup>d</sup> The values in parentheses were not used in the data fit but calculated from the 4-OCH<sub>3</sub> substituent constant parameters. With only six well-behaved substituents, the  $d^E$  and  $d^C$  parameters are tentative.

**Substituted Acetophenones.** Table 2 contains an analysis of rate and equilibrium constants for the reaction of substituted acetophenones with bisulfite,<sup>8</sup> eq 9. Young



and Jencks obtained a good linear Hammett plot for the rate constant ( $k_1$ ) expressing the addition of bisulfite ion to the carbonyl group, but the associated equilibrium constant ( $K_{\text{add}}$ ) for this step showed that the 4-MeO and 4-Me points deviated from the correlation in the sense that the observed values of  $K_{\text{add}}$  were smaller than those predicted when using the normal  $\sigma$  value. A better fit resulted on using  $\sigma^+$ , and it was concluded that an enhanced contribution by resonance for a conjugating EDG is required. The rate constant  $k_{\text{OH}}$  for the hydroxide ion catalyzed breakdown of the sulfite adduct gave a curved Hammett plot with  $\sigma$  but was described well by eq 8.

A satisfactory fit of the equilibrium and rate data for six of the seven substituents is obtained by our treatment. When the 4-OCH<sub>3</sub> substituent is omitted (see Experimental Section) the fits given in Table 2 result. The 4-OCH<sub>3</sub> substituent gives rise to smaller observed equilibrium values ( $K_{\text{add}}$ ) and smaller rate constants for addition ( $k_1$ ) than are calculated. The 4-OCH<sub>3</sub> substituent has to be eliminated from both kinetic and equilibrium measurements. The deviation may be due to a  $\pi$ -plus effect, but the possible reactivity of the donor OCH<sub>3</sub> group with the solvent is a potential complication. Data for the 3-CH<sub>3</sub>, 3-F, and 4-F substituents would help clarify the interpretation. The  $d^E$  and  $d^C$  values for this system are tentative because a limited number of substituents are used in the fit. On the basis of the limited data available, we conclude that the observed curvature in the Hammett plot is not due to an enhanced resonance contribution but to an inappropriate covalent contribution in the  $\sigma$  parameters.

Table 3. Solvolysis of Cumyl Chloride

substituent	log $k^X/k^H$		substituent	log $k^X/k^H$	
	expl <sup>a</sup>	calcd <sup>b</sup>		expl <sup>a</sup>	calcd <sup>b</sup>
H	0	-0.14			
3-OCH <sub>3</sub>	-0.215	-0.47	4-OCH <sub>3</sub>	3.53	(0.61)
3-CH <sub>3</sub>	0.30	0.32	4-CH <sub>3</sub>	1.41	(0.53)
3-C <sub>2</sub> H <sub>5</sub>	0.29	0.40	4-C <sub>2</sub> H <sub>5</sub>	1.34	(0.31)
3-CH(CH <sub>3</sub> ) <sub>2</sub>	0.27	0.55	4-CH(CH <sub>3</sub> ) <sub>2</sub>	1.27	(0.53)
3-C(CH <sub>3</sub> ) <sub>3</sub>	0.27	0.35	4-C(CH <sub>3</sub> ) <sub>3</sub>	1.16	(0.65)
3-F	-1.60	-1.69	4-F	0.33	(-0.66)
3-Cl	-1.81	-1.78	4-Cl	-0.52	(-1.3)
3-Br	-1.84	-1.75	4-Br	-0.68	(-1.2)
3-I	-1.63	-1.59	4-I	-0.61	(-1.2)
3-NO <sub>2</sub>	-3.06	-3.19	4-C <sub>6</sub> H <sub>5</sub>	0.81	(-0.25)
4-NO <sub>2</sub>	-3.59	-3.27			
4-CF <sub>3</sub>	-2.78	-2.4			
4-CN	-2.99	-3.22			
4-SiMe <sub>3</sub>	-0.09	-0.02			

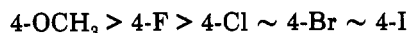
<sup>a</sup> Data from ref 6. <sup>b</sup> Calculated with  $d^E = 9.87$ ,  $d^C = 0.98$ , and  $\Delta\chi^H = -0.14$ .  $\bar{x} = 0.13$ , % fit = 4.

In all of the physicochemical properties in Tables 1 and 2, the 4-NO<sub>2</sub> conjugative substituent which does not contain lone pairs on the atom attached to the ring is well behaved. In some instances this could be due to the limited data set. It is also important to note that all of the  $\pi$ -plus mechanisms have overlaps of atoms with  $\pi$ -orbitals that differ in the ground state and products or transition state. Lone pair 4-X substituents will always  $\pi$ -bond to the phenyl ring and transmit electron density to the para reactive group.

**Cumyl Chloride Solvolysis (2).** The solvolysis of substituted phenyldimethylcarbinyl chlorides (cumyl chlorides) (2) in 90% acetone at 25 °C provides the basis for the  $\sigma^+$  system.<sup>6</sup> The nonorthogonality of the methyl groups to the ring  $\pi$ -system as well as the extra delocalization energy in the transition state suggests the possible existence of a  $\pi$ -plus contribution in this system. The data was analyzed earlier<sup>1a</sup> in a master fit as a normal 4-X conjugative system, and the data fit was less than satisfactory ( $\bar{x} = 0.3$  and % fit = 7). The treatment of the data as a  $\pi$ -plus system in which the LPC substituents are omitted from the fit is given in Table 3.

A good fit results with  $\bar{x} = 0.13$  and a % fit of 4. The parameters from this fit are again tentative with a  $d^C/d^E$  ratio of 0.10. This ratio is similar to the value of 0.10 for the fit of the Hammett parameters to  $d^E$  and  $d^C$ . A slightly improved fit with a ratio of 0.4 results if the 4-NO<sub>2</sub> and 4-CN substituents are omitted from the fit. The main factor that led to a separate  $\sigma^+$  scale for these data is the  $\pi$ -plus contribution.

The pattern in the magnitude of the deviations of the LPC substituents is consistent with their ability to  $\pi$ -bond to the phenyl ring:



The hyperconjugative deviations are in the expected order:



The 4-C<sub>6</sub>H<sub>5</sub> group gives a  $\pi$ -plus contribution comparable to that of 4-CH<sub>3</sub> or 4-F. It is of interest to note that the 4-CF<sub>3</sub> and 4-Si(CH<sub>3</sub>)<sub>3</sub> substituents do not give rise to a  $\pi$ -plus contribution, but behave as typical 4-X conjugative substituents.

**<sup>19</sup>F Nuclear Magnetic Shielding in Some Benzene Derivatives (3).** Table 4 presents the change in chemical

Table 4. Changes in <sup>19</sup>F Chemical Shifts due to Substituents in Fluorobenzenes

substituent X	$\delta^F$ (I)		substituent X	$\delta^F$ (I)	
	expl	calcd <sup>a</sup>		expl	calcd <sup>a</sup>
3-C(CH <sub>3</sub> ) <sub>3</sub>	0.50	0.60	3-CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub>	1.1	1.1
3-C <sub>2</sub> H <sub>5</sub>	0.75	0.90	3-SCH <sub>3</sub>	-0.30	-0.25
3-CH <sub>3</sub>	1.20	0.80	3-CH <sub>2</sub> Cl	-0.53	-0.25
3-F	-3.0	(-2.2) <sup>b</sup>	3-CH <sub>2</sub> Br	-0.50	-0.42
3-Cl	-2.0	-2.2	3-CH <sub>2</sub> I	-0.73	-0.50
3-Br	-2.4	-2.2	3-CH <sub>2</sub> CN	-1.2	-1.0
3-I	-2.3	-2.0	3-C <sub>6</sub> H <sub>5</sub> CO	-0.94	-1.0
3-NO <sub>2</sub>	-3.5	-3.5	4-N(CH <sub>3</sub> ) <sub>2</sub>	15.9	(1.5) <sup>c</sup>
3-CN	-2.8	-3.1	4-OCH <sub>3</sub>	11.6	(0.7) <sup>c</sup>
3-CF <sub>3</sub>	-2.2	-2.0	4-F	6.7	(0.4) <sup>c</sup>
3-OH	-1.2	-1.3	4-Cl	3.1	(-1.7) <sup>c</sup>
3-OCH <sub>3</sub>	-1.1	-1.1	4-Br	2.5	(-0.8) <sup>c</sup>
3-CH <sub>2</sub> CF <sub>3</sub>	-0.43	-0.64	4-I	1.6	(-1.9) <sup>c</sup>
3-NH <sub>2</sub>	0.4	(-0.3) <sup>b</sup>	4-CH <sub>3</sub>	5.4	(1.1) <sup>c</sup>
3-N(CH <sub>3</sub> ) <sub>2</sub>	-0.1	(-1.3) <sup>b</sup>	4-CH <sub>3</sub> C(O)	-6.1	(-5.9) <sup>c</sup>
3-C <sub>6</sub> H <sub>5</sub>	0.15	0.23	4-OH	11.4	(1.9) <sup>c</sup>
3-CH <sub>3</sub> OCO	-1.3	-1.5	4-NH <sub>2</sub>	14.4	(4.6) <sup>c</sup>
3-OC <sub>6</sub> H <sub>5</sub>	-1.9	-1.9	4-C <sub>6</sub> H <sub>5</sub>	3.0	(-1.3) <sup>c</sup>
3-C <sub>2</sub> H <sub>5</sub>	0.63	0.39	4-CN	-8.8	(-6.4) <sup>c</sup>
3-CH <sub>2</sub> OCH <sub>3</sub>	0.53	0.47	4-NO <sub>2</sub>	-9.0	(-6.3) <sup>c</sup>
3-CH <sub>3</sub> SO <sub>2</sub>	-3.3	-3.3	4-CF <sub>3</sub>	-5.1	(-3.0) <sup>c</sup>

<sup>a</sup> <sup>19</sup>F Chemical shift in ppm relative to fluorobenzene, ref 16c. Calculated with  $d^E = 34.55$ ,  $d^C = -3.86$ ,  $\Delta\chi^H = 0.133$ ,  $\bar{x} = 0.19$ , % fit = 4. <sup>b</sup> Omitted from the fit, cause unknown. 3-CH<sub>3</sub>CO and 3-CH<sub>3</sub>C(O)NH were also omitted. These systems are calculated with the parameters in a. <sup>c</sup> Omitted from fit because of  $\pi$ -plus contributions.

shifts of the fluorine atom in fluorinated aromatics (3) caused by substituents on the ring relative to the shift for fluorobenzene.<sup>15,16</sup> An increase in electron density on fluorine results in an increase in <sup>19</sup>F magnetic shielding (upfield shift) giving a positive sign for the shift difference.<sup>16c</sup> In general, the <sup>19</sup>F chemical shifts of substituted fluorobenzenes are expected to depend upon the ground-state electron population of the p-orbitals on the fluorine. The chemical shift is also dependent on the energy difference between the ground and average energy of all the excited states. The effectiveness of the interaction between the fluorine lone pairs and the ring  $\pi^*$  orbital also depends on the energy of  $\pi^*$ . All the above changes will be shown to parallel the 3-X substituent constants. With 4-X substituents, the average energy and the fluorine p-ring  $\pi^*$  overlaps are potential  $\pi$ -plus contributions. This is the delocalization mechanism discussed earlier. Though the delocalization effect exists in the ground and spectral excited states, the interaction will influence trends in spectral measurements and is considered a  $\pi$ -plus effect.

In the early literature<sup>15</sup> analysis of the <sup>19</sup>F chemical shifts of fluorobenzenes was interpreted with Hammett parameters by employing a different correlation for the meta and para substituents. Different effects were proposed to be operative at the meta and para positions. Subsequently,<sup>16</sup> the meta and para substituents were correlated separately with  $\sigma_I$  and  $\sigma_R^0$  parameters, respectively, using a dual-substituent constant parameter equation. Substituents in which the resonance effects are electron

(15) (a) Meyer, L. H.; Gutowsky, H. S. *J. Phys. Chem.* **1953**, *57*, 481. (b) Gutowsky, H. S.; McCall, D. W.; McGarvey, B. R.; Meyer, L. H. *J. Am. Chem. Soc.* **1952**, *74*, 4809. The chemical shift convention used in this work differs from the most recent convention.

(16) (a) Taft, R. W., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 1045. (b) Wells, P. R.; Ehrenson, S.; Taft, R. W. *Prog. In Phys. Org. Chem.* **1968**, *6*, 147. (c) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. (d) Taft, R. W.; Price, E.; Fox, I. R.; Lewis, I. C.; Andersen, K. K.; Davis, G. T. *J. Am. Chem. Soc.* **1963**, *85*, 709. (e) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159.

releasing (lone pairs) and electron withdrawing (4-NO<sub>2</sub>) were grouped together in the dual-parameter correlation.

The  $\Delta E$ - $\Delta C$  analysis provides a similar interpretation. In our fit of the data all the 3-X substituents are treated with 3- $\Delta E^X$  and 3- $\Delta C^X$  parameters leading to the results in Table 4. The average deviation is 0.19 and the percent fit an excellent 4. The effect of 3-substituents is primarily an inductive effect and correlates with the electronic charge in the  $\pi$  and  $\sigma$  p-orbitals of fluorine. An EWG leads to a downfield chemical shift ( $-\delta$ ) while an EDG provides an upfield shift ( $+\delta$ ). The good correlation suggests that the average energy of all the excited states and fluorine conjugation with the ring parallels the changes predicted by  $\Delta E^X$  and  $\Delta C^X$ . The substituents 3-F, 3-NH<sub>2</sub>, and 3-N(CH<sub>3</sub>)<sub>2</sub> are omitted. The cause of their deviation is unknown. The nitrogen substituents are the strongest donor groups studied, and charge transfer complexes may exist with the solvent.

The  $d^E$  and  $d^C$  parameters from this data fit then are used to calculate the shifts for the 4-substituents, and the results are given in parentheses under the column labelled  $\delta^F_{\text{cal}}$ . Large deviations between experimental and calculated values are observed for 4-substituents. It is significant that each of the 4-substituents with lone pairs calculates a value that is downfield from the predicted value and the magnitudes of the deviations parallel the ability of the substituent to  $\pi$ -bond to the ring: 4-N(CH<sub>3</sub>)<sub>2</sub> > 4-NH<sub>2</sub> ~ 4-OCH<sub>3</sub> ~ 4-OH > 4-F > 4-Cl > 4-Br ~ 4-I. This trend supports the proposal that lone pair conjugation to the ring gives rise to a  $\pi$ -plus effect that decreases the paramagnetic contributions to the shift. When the atom directly bonded to the ring in the para position has a lone pair of electrons, the conjugative interaction by this atom raises the energy of  $\pi^*$  appreciably. This interaction increases the average energy difference between the excited and ground states and also decreases the ring-fluorine  $\pi$ -bonding. Both effects cause the observed <sup>19</sup>F resonance to occur at much higher field than predicted with 4- $\Delta E^X$  and 4- $\Delta C^X$ . A decrease in the effectiveness of the conjugative interaction of the fluorine to the ring results because of a poor energy match of the  $\pi^*$ -orbital and the fluorine lone pair. The evaluation of the average energy term is difficult, and its contribution is uncertain. The average electronic excitation energy contribution is reported<sup>17</sup> not to be important for the interpretation of electronic substituent effects on the <sup>15</sup>N shifts in *N*-arylmethylidene derivatives. Molecular orbital calculations<sup>16e</sup> indicate that the <sup>19</sup>F shifts for the 4-X substituents correlate with the fluorine  $\pi$ -orbital population. Thus, the  $\pi$ -plus conjugative interaction of X has a direct influence on the fluorine  $p$ - $\pi$  orbital population that is not reflected in a proportional manner in the  $\sigma$  bond from carbon to fluorine. The calculated values for all of the 4-X substituents with lone pairs deviate in the same direction from the experimental value, and the deviations are attributed to  $\pi$ -plus contributions. The  $\pi$ -perturbation from lone pair conjugative substituents influences the chemical shift by a mechanism other than its normal conjugative influence, *i.e.*, it is enhanced.

In contrast to the LPC substituents, the 4-X substituents that decrease the energy of  $\pi^*$  (4-NO<sub>2</sub> and 4-CN) by a conjugative interaction have deviations in the opposite direction. This is the expected trend for either the average energy or conjugative fluorine  $\pi$ -plus explanations.

Table 5. Observed and Predicted <sup>19</sup>F Shift Changes for Multiply Substituted Fluorobenzenes<sup>a</sup>

substituents	$\delta^F_{\text{expl}}$	$\delta^F_{\text{calcd}}$
3-NO <sub>2</sub> , 4-NH <sub>2</sub> ; -0.033; -0.488	14.3	1.04
3,5-F; -0.230 -0.858	-5.5	-4.5
3-F, 5-I; -0.222; -0.8315	-4.5	-4.4
3-F, 4-NH <sub>2</sub> ; 0.0656; 0.0506	11.5	2.3
3-NO <sub>2</sub> , 4-F; -0.2489; -1.136	2.0	-4.0
3-F, 4-NO <sub>2</sub> ; -0.3685; -1.069	-14.9	-8.7
3,4-F <sub>2</sub> ; -0.1504; -0.5973	2.4	-2.8
3-Cl, 4-F; -0.1558; -0.6294	3.9	-2.8
3-Br, 4-F; -0.1537; -0.6241	4.0	-2.8
3-I, 4-F; -0.1426; -0.5735	4.55	-2.6
3,4-F <sub>2</sub> , 5-CF <sub>3</sub> ; -0.287; -1.267	-0.7	-4.8

<sup>a</sup> Data from ref 15. Calculated using the same parameters as in Table 4.

The  $d^C/d^E$  ratio of the <sup>19</sup>F fit is -0.11. The negative  $d^C$  indicates that those substituent properties that increase covalency in the C-F bond (*i.e.*,  $+\Delta C$ ) decrease  $\delta$  (*i.e.*, deshield and shift the resonance downfield). The positive  $d^E$  indicates that those substituents that increase the tendency to bond electrostatically (*i.e.*,  $+\Delta E$ ) increase  $\delta$  (*i.e.*, shields and shifts the resonance upfield). These shift contributions are in the direction expected from theoretical evaluation<sup>18</sup> of <sup>19</sup>F shifts which relate the paramagnetic contribution to p-orbital electron populations and  $\Delta E$ . The ( $d^C + d^E$ ) approximation shows the electrostatic effect dominates.

The <sup>19</sup>F chemical shifts of several multiply substituted fluorobenzenes are given in Table 5. These shifts are calculated by summing the  $\Delta E^X$  and  $\Delta C^X$  contributions from the substituents and using the  $d^E$ ,  $d^C$ , and  $\Delta\chi^H$  values from the fit in Table 4. The major discrepancies, again, involve 4-X, conjugative substituents. The deviations parallel those found for the analogous 4-X substituents in Table 4.

## Conclusions

The examples discussed in this paper indicate limitations on the use of 4- $\Delta C$ , 4- $\Delta E$  parameters in making correlations. In six-membered aromatic rings, 4- $\Delta E$  and 4- $\Delta C$  constants apply to the prediction of the changes in electron density at the atom para to the substituent. When other mechanisms involving the ring  $\pi$ -system influence the chemistry or the spectroscopy, contributions from these effects can cause the  $\Delta E$ - $\Delta C$  substituent constant correlation to fail.

Correlations with the nonconjugative  $\Delta E$  and  $\Delta C$  substituents not only provide acceptable data fits but also provide new interpretations of data that have been historically difficult to analyze. Our correlations do not show the U-shaped structure as is the case with the associated Hammett plots, but when significant lone pair  $\pi$ -conjugation or hyperconjugation is present, we also find deviations, *i.e.*, the  $\pi$ -plus effect. The patterns in these deviations have suggested additional bonding interactions complicating the chemistry of lone pair conjugative substituents. The chemistry treated in this study further illustrates the advantage of the  $\Delta E$ - $\Delta C$  analyses as a tool to spot deviant systems thereby enabling one to look for patterns in these deviant systems and to provide for their interpretation. The connection of  $\Delta E$  and  $\Delta C$  to the  $E$ - $C$  based solvation minimized enthalpy data set has the

(17) Botto, R. E.; Roberts, J. D. *J. Org. Chem.* 1979, 44, 140.

(18) For a summary of this work, see: Drago, R. W. *Physical Methods in Chemistry*, 2nd ed.; Saunders Publishing: Philadelphia, PA, 1992.

potential to take substituent constant analyses to a higher level of understanding of the chemical system.

### Experimental Section

The data were fit to eq 3 using reported values for  $\Delta E^X$  and  $\Delta C^X$  and a simplex-based multiple linear regression computer program that includes a weighting parameter  $n$  where  $n = 1/\text{weight}$ . In all instances of the examples considered here, the entire experimental data set is fit less accurately than the experimental error.

When a poor fit is obtained for the entire data set, the deviations from the fit by the individual substituents are examined to see if a pattern exists. Once a suspected pattern is perceived, in this case  $\pi$ -bonding to substituent lone pairs, all of these substituents are given low weight (high  $n$  value) and the data refit. If the remaining substituents fit well, quantitative support for the suspected complication is found. Other possible explanations and combinations of omitted substituents can also be tried until the most logical explanation for the pattern in the deviations is found. In general, this procedure leads to an interpretation of the data which may not be unique. As more systems and more substituents are studied other models may be found that have more universal utility. The quality of the fit is measured by the absolute value of the average deviation,  $\bar{x}$ , between the calculated and measured value. The % fit (% F) is given by the ratio of the average deviation to the range expressed as a percentage. The range is defined as the difference between the

largest and the smallest experimental values. A 2% fit is excellent and 5-6% fit is considered to be good. A table of substituent constants may be found in ref 1a.

**Treatment of Literature Data. Table 1.** In the  $\text{Me}_3\text{N}$ ,  $\text{RCH}_2\text{Cl}$  system the 4-OCH<sub>3</sub>, 4-CH<sub>3</sub>, and 4-Br substituents were omitted from the initial fit. A good fit resulted, and the rate constants for the omitted groups were then calculated from the resulting  $d^E$  and  $d^C$  parameters. For the  $\text{C}_5\text{H}_5\text{N}$ ,  $\text{RCH}_2\text{Br}$  reaction all hyperconjugative and all lone pair conjugative substituents were omitted from the fit. The remaining substituents were weighted according to the literature<sup>1b</sup> recommendation. A good fit resulted, and the rates for the LPC substituents were calculated with the resulting  $d^E$  and  $d^C$  parameters. The resulting values are indicated in parentheses in the tables. For the solvolysis of  $\text{RCH}_2$  tosylate the LPC substituents were omitted from the correlation and their values calculated from the resulting  $d^E$ ,  $d^C$ , and  $\Delta\chi^H$  parameters using reported 4-X substituent constants.

**Table 2.** The equilibrium constants are reported to one or two significant figures implying an error limit of  $\pm 0.5$ . The parent hydrogen compound is reported to one decimal point as 5.5 implying an error of  $\pm 0.1$ . For  $K_{\text{add}}$  the 4-OCH<sub>3</sub> substituents was omitted from the fit.

**Tables 3 and 4.** Potential hyperconjugative and LPC substituents were omitted from the fit and the procedure described above for Table 1 was employed.

**Table 5.** The calculated values were obtained by summing the reported substituent constant values and calculating the shift with  $d^E = 34.55$ ,  $d^C = -3.86$ ,  $\Delta\chi^H = 0.133$ .