pattern), and a loss of a chlorine atom gives a peak at m/e 137. The base peak appears at m/e 121 which corresponds to a loss of CH_3Cl and an H atom from the molecular ion. On the basis of the fragmentation pattern, compound **15** is suggested to be the monochloro diene type compound of the structure shown previously.

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Prediction of Substituent Sensitivities (ρ_R^+) for Carbocations. Correlation with Charges or HOMO-LUMO Interactions

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A dual substituent parameter equation, using σ_I and σ_R^+ constants, is applied to substituent effect data from the solvolysis of 1-arylethyl derivatives to obtain ρ_R^+ values as a measure of the sensitivity to resonance effects at various positions. From a comparison of ρ_R^+ values with ^{13}C chemical shift data for stable arylcarbenium ions, it is concluded that the values of ρ_R^+ are proportional to the amount of charge developed at the site of substitution. The ρ_R^+ values are also discussed in relation to MO calculations of charge distribution and HOMO-LUMO interactions.

The interpretation of sensitivities to substituent effects indicated by ρ values in Hammett-type correlations has been a subject of continuing interest. For reactions such as the solvolysis of phenylcarbinyl derivatives in which carbocation intermediates are formed, the slope, ρ^+, of a plot of log k/k_0 against Brown σ^+ constants is usually interpreted as a measure of electron demand.[2] The negative sign of ρ^+ signifies that electron-donating substituents accelerate the reaction, and the magnitude of ρ^+ indicates the magnitude of the electron demand and the extent to which the substituents are able to interact with the electron-deficient reaction center.

Attempts to ascribe a quantum mechanical meaning to ρ^+ have led to distinct viewpoints. An interpretation based on charge is that electron demand is determined by the extent of positive charge development in the system and, specifically, that ρ^+ should depend on the amount of positive charge developed *at the site of substitution*.[3-6] Thus, charges obtained from MO calculations or some other measure of charge distribution in the carbocation should be sufficient to predict the trends of ρ^+ (eq 1, where a is the proportionality constant and b is the intercept).

$$\rho^+ = a\Delta q + b \qquad (1)$$

Another interpretation, based on perturbation theory, holds that the substituent effect can be described as an interaction between the HOMO of the substituent and the LUMO of the cation.[7-10] Jorgensen[10] suggested the use of an expression equivalent to eq 2, derived from second-order perturbation theory for the energy of the HOMO-LUMO interaction.

$$\rho^+ = a\frac{c^2}{E_L - E_H} + b \qquad (2)$$

Here the key factors are the delocalization of the LUMO, represented by c^2, the square of the appropriate LUMO coefficient, and the relative energies of the cation LUMO (E_L) and the substituent HOMO (E_H).

In this paper, we examine the suitability of eq 1 and 2 for predicting ρ_R^+ values in solvolysis reactions of 1-arylethyl derivatives. The ρ_R^+ values we will discuss in this context are those determined from application of a dual substituent parameter (DSP) equation (eq 3) which uses

$$\log k/k_0 = \rho_I\sigma_I + \rho_R^+\sigma_R^+ + i \qquad (3)$$

the parameters of Brownlee, Ehrenson, and Taft.[11] The DSP treatment is used because only the resonance effect, not the field (or inductive) effect, should be described by the second-order perturbation expression for the energy of the HOMO-LUMO interaction. The field effect would be accounted for by a separate electrostatic term in the full perturbation theory expression.[9a,12-15] Similarly, in

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(1) (a) Northeastern University. (b) Franklin and Marshall College.

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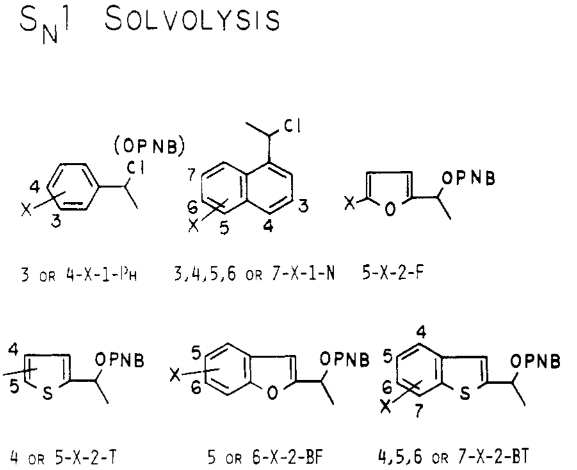

Figure 1. Arylethyl systems used in solvolysis studies.

a treatment based on charges, the resonance portion of the substituent effect is expected to be proportional to the amount of charge delocalized to the site of substituent attachment, with the field effect treated as a separate electrostatic effect.[16-19] The use of the simple ρ^+ value from a correlation with σ^+ constants is justifiable only if the balance of field/inductive and resonance interactions is nearly constant among the compared systems, as may be approximately valid in a series of phenylcarbenium ions but is certainly not true in variously substituted arylcarbenium ions (vide infra).

A crucial aspect of this examination is the comparison of ρ_R^+ values from the solvolysis of 1-arylethyl chlorides and p-nitrobenzoates with ^{13}C chemical shift response slopes[20,21] for the corresponding stable arylcarbenium ions. The ^{13}C data will be used as a measure of charge distribution which is independent of methods of MO calculations and population analysis.

Results

Substituent effect data are available for the S_N1 solvolysis of 1-arylethyl p-nitrobenzoates from the work of Noyce et al.[17,22-24] and from that of Tsuno et al.[25-27] for 1-arylethyl chlorides. The systems, as shown in Figure 1, include monosubstituted 1-phenylethyl chlorides (3- or 4-X-1-Ph), 1-(1-naphthyl)ethyl chlorides (3-, 4-, 5-, 6- or 7-X-1-N), 1-(2-benzothienyl)ethyl p-nitrobenzoates (4-, 5-, 6- or 7-X-2-BT), 1-(2-benzofuryl)ethyl p-nitrobenzoates (5- or 6-X-2-BF), 1-(2-furyl)ethyl p-nitrobenzoates (5-X-2-F), and 1-(2-thienyl)ethyl p-nitrobenzoates (4- or 5-X-2-T).

Table I. Application of the DSP Equation (Eq 3) to Solvolysis of 1-Arylethyl Chlorides and p-Nitrobenzoates

substituted (X) π system[a]	solvol condit[b]	ρ_I	ρ_R^+	n[c]	SD/RMS[d]	ref[e]
3-X-1-Ph	A	−4.55	−1.13	7	0.150	25
4-X-1-Ph	A	−5.60	−6.15	8	0.063	25
3-X-1-N	A	−5.21	−0.72	5	0.104	26
4-X-1-N	A	−5.20	−5.22	6	0.033	26
5-X-1-N	A	−3.07	−1.24	6	0.147	27
6-X-1-N	A	−2.48	−0.79	4	0.054	27
7-X-1-N	A	−3.06	−2.16	6	0.104	27
4-X-2-BT	B	−4.51	−2.25	4	0.100	17
5-X-2-BT	B	−3.78	−1.44	5	0.033	17
6-X-2-BT	B	−3.95	−3.36	4	0.015	17
7-X-2-BT	B	−3.89	−1.04	4	0.113	17
5-X-2-BF	B	−3.70	−1.53	5	0.025	24
6-X-2-BF	B	−4.03	−3.50	5	0.007	24
5-X-2-F	C	−6.97	−8.54	5	0.017	22
5-X-2-T	C	−7.38	−7.45	6	0.095	23
4-X-2-T	C	−8.76	−3.75	3	f	23

[a] See the beginning of the Results section for notation of substituted systems. [b] Solvolysis conditions of leaving group, solvent, and temperature: (A) Cl, 80% acetone, 45 °C; (B) OPNB, 80% ethanol, 75 °C; (C) OPNB, 80% ethanol, 25 °C. [c] Number of data points. [d] Measure of goodness of fit. A value less than 0.100 indicates an excellent fit and 0.10–0.20 indicates acceptable fits. See ref 11 and R. D. Topsom, *Prog. Phys. Org. Chem.*, 12, 1 (1976). [e] Source of data. [f] Insufficient data to define.

Table II. LUMO Coefficients and Energies and HOMO-LUMO Interaction[a]

	CNDO/2			SCF-π		
position	c^2	$-E_L$	$c^2/(E_L - E_H)$	c^2	$-E_L$	$c^2/(E_L - E_H)$
C_3-1-Ph	0.0003	7.59	0.0004	0.0007	8.51	0.0010
C_4-1-Ph	0.1700	7.59	0.2394	0.1613	8.51	0.2338
C_3-1-N	0.0008	6.96	0.0006	0.0015	8.05	0.0013
C_4-1-N	0.2260	6.96	0.1687	0.2195	8.05	0.1909
C_5-1-N	0.0470	6.96	0.0351	0.0588	8.05	0.0511
C_6-1-N	0.0001	6.96	0.0001	0.0001	8.05	0.0001
C_7-1-N	0.0526	6.96	0.0393	0.0600	8.05	0.0522
C_4-2-BT	0.0642	7.10	0.0535	0.0563	8.20	0.0563
C_5-2-BT	0.0020	7.10	0.0017	0.0020	8.20	0.0020
C_6-2-BT	0.0664	7.10	0.0553	0.0592	8.20	0.0592
C_7-2-BT	0.0006	7.10	0.0005	0.0002	8.20	0.0002
C_5-2-BF	0.0045	7.26	0.0043	0.0011	8.30	0.0012
C_6-2-BF	0.0709	7.26	0.0682	0.0631	8.30	0.0701
C_5-2-F	0.1925	7.59	0.2711	0.2035	8.57	0.3230
C_5-2-T	0.1969	7.49	0.2431	0.1714	8.38	0.2090
C_4-2-T	0.0059	7.49	0.0073	0.0118	8.38	0.0144

[a] Calculated by using best-fit value of E_H. E_H is −8.3 eV in CNDO/2 and −9.2 eV in SCF-π.

We have applied eq 3 to these data to obtain a ρ_R^+ value for each aryl position investigated (Table I). The ρ_R^+ values range from −0.72 to −8.54. The data were obtained under three sets of conditions, so that not all of the ρ_R^+ values are strictly comparable, but the differences in conditions should have only a minor effect. The solvent influence should be negligible, since a plot of log k/k_0 for 1-phenylethyl chlorides in 80% ethanol at 45 °C against the corresponding values of log k/k_0 in 80% acetone at 45 °C has a slope of 1.01 ± 0.01.[28] Values of ρ for solvolysis reactions have previously been shown to be insensitive to the leaving group, be it p-nitrobenzoate, chloride, or to-

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Table III. ^{13}C Response Slopes and Calculated Δq for Arylcarbenium Ions

position	^{13}C response slope	Δq SCF-π	Δq CNDO/2 total	Δq CNDO/2 π	Δq CNDO/2 regional
C_3-1-Ph	0.197	0.042	−0.022	−0.025	0.039
C_4-1-Ph	1.000	0.200	0.140	0.242	0.199
C_3-1-N	0.112	0.019	−0.048	−0.065	0.011
C_4-1-N	1.052	0.225	0.170	0.298	0.221
C_5-1-N	0.152	0.084	0.061	0.093	0.094
C_6-1-N	0.081	0.043	−0.003	−0.001	0.041
C_7-1-N	0.301	0.107	0.072	0.115	0.112
C_4-2-BT	0.322	0.075	0.069	0.100	0.105
C_5-2-BT	0.163	0.042	−0.005	−0.002	0.040
C_6-2-BT	0.605	0.117	0.080	0.137	0.124
C_7-2-BT	0.082	0.026	−0.009	−0.022	0.032
C_5-2-BF	0.181	0.045	−0.003	0.002	0.045
C_6-2-BF	0.832	0.118	0.087	0.150	0.133
C_5-2-F	1.564	0.264	0.176	0.306	0.261
C_5-2-T	1.986	0.232	0.136	0.288	0.209
C_4-2-T	0.491	0.040	−0.029	−0.041	0.044

Table IV. Linear Least-Squares Fitting of ρ_R^+ vs. Predictors of Resonance Effects

$$\rho_R^+ = aP + b$$

predictor (P)	a	b	SD[a]	SD/RMS[b]
^{13}C response slope	−4.14	−0.78	0.74	0.288
$c^2/(E_L - E_H)$, CNDO/2	−24.1	−1.35	0.81	0.314
$c^2/(E_L - E_H)$, SCF-π	−22.9	−1.33	0.85	0.332
$\Delta q(\pi)$, SCF-π	−28.3	−0.17	0.94	0.366
Δq(regional), CNDO/2	−28.8	−0.06	1.04	0.406
$\Delta q(\pi)$, CNDO/2	−16.8	−1.49	1.26	0.492
Δq(total), CNDO/2	−28.0	−1.62	1.42	0.552

[a] Standard deviation of regression. [b] SD divided by RMS, root mean square of the data, indicates goodness-of-fit (see ref 11).

sylate.[19] The effect of temperature may be slightly larger: Tsuno et al. report a decrease of $|\rho|$ by 0.20 units between 25 and 45 °C for 1-phenylethyl chlorides.[29]

The LUMO coefficients and energy levels obtained for the arylcarbenium ions in CNDO/2 and SCF-π calculations are listed in Table II. Details of the MO calculations have been described previously.[20,21] Also listed are the values of $c^2/(E_L - E_H)$ for use in eq 2, based on the value of E_H which allows the best fit with the ρ_R^+ data (for CNDO/2, $E_H = -8.3$ eV; for SCF-π, $E_H = -9.2$ eV).

In Table III are listed values relevant to the charge model of resonance effects. In the first column are the experimental slopes of the ^{13}C chemical shift responses at the various positions in arylcarbenium ions.[20,21] The ^{13}C chemical shift response for a particular position is found by plotting the ^{13}C chemical shift for that position in a series of arylcarbenium ions vs. the ^{13}C chemical shift at the para position in the analogous series of phenylcarbenium ions. The slopes of the ^{13}C chemical shift responses may be considered as being indicative of the relative amounts of charge developed at each position in the formation of arylcarbenium ions from neutral precursors.[20,21] Calculated values from SCF-π and CNDO/2 calculations are also given in Table III for the change in charge (Δq) at each position for the change from neutral arene to arylcarbenium ion, $Ar \rightarrow ArCH_2^+$.

The results of the linear correlations of ρ_R^+ with the various predictors (P) of sensitivity to resonance effects are given in Table IV.

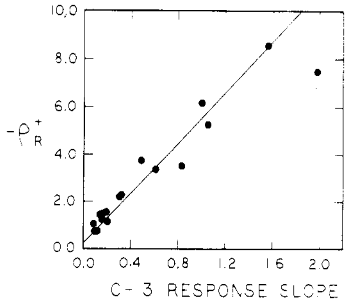

Figure 2. Plot of ρ_R^+ vs. ^{13}C response slope. The line shown is the correlation line, omitting the point at upper right, which is for the 5-position of thiophene (C_5-2-T).

Discussion

On the basis of the correlations in Table IV, the best predictor of ρ_R^+ values for the 16 positions in various arylethyl systems is the slope of the ^{13}C chemical shift response at the corresponding position in stable arylcarbenium ions. The ρ_R^+ values are plotted vs. the ^{13}C response slopes in Figure 2. The correlation between ρ_R^+ values and response slopes is independent of any theoretical model, whether it is a theory of ^{13}C shifts, a theory of kinetic substituent effects, or a molecular orbital theory of charge distribution.

Assuming that the application of the DSP equation leads to a good separation of polar and resonance effects, the ρ_R^+ values are expected to show the importance of π electronic interactions. In the two models considered here, the importance of π resonance interactions is determined either by the change in charge at the site of substituent attachment or by the HOMO–LUMO interaction. There is no reason to expect that ^{13}C shifts would be related to the term describing the HOMO–LUMO interaction, except insofar as the charge distribution is determined by the coefficients of the LUMO. On the other hand, for series of carbon atoms in very similar molecular environments, there have been repeatedly demonstrated correlations between ^{13}C shifts and electronic charge.[21] The ^{13}C response slopes in hydrocarbon arylcarbenium systems were shown to correlate well with calculated charges, and the best correlation was with SCF-π charges.[21] Thus, the π charge distribution seems likely to be the connecting link between ^{13}C response slopes and ρ_R^+ values.

The correlation between ρ_R^+ values and ^{13}C response slopes (Table IV) is better than either the correlation of ρ_R^+ with calculated charges (Table IV) or the correlation of ^{13}C response slopes with calculated charges.[20] From this we conclude that the ρ_R^+ values and response slopes, both derived from experiment, generally represent the charge distribution more accurately than do the MO calculations. However, we noted previously that the ^{13}C response slope for C_5 in the 2-thienylcarbenium ion series is unusually large and deviates considerably from a correlation with calculated charges.[20] In Figure 2, the C_5-2-T point also deviates considerably from the general correlation between response slopes and ρ_R^+. If the C_5-2-T point is eliminated, the correlation improves significantly ($a = -4.98$, $b = -0.48$, SD/RMS = 0.207). The deviation is again in the direction which suggests that the ^{13}C response slope exaggerates the amount of charge reaching the C_5 position. Thus, there is at least one exception to the generalization that ρ_R^+ values and ^{13}C response slopes are measures of relative charge densities, although this exception seems clearly to involve the ^{13}C chemical shifts.[20]

The correlation between ρ_R^+ and ^{13}C response slopes is seen as support for the view that the resonance portion of the substituent effect is proportional to the amount of

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Table V. Correlation of $\rho_R{}^+$ vs. Resonance Predictors for Individual Ring Systems

predictor	a	b	SD	SD/ RMS
(a) 4,5,6,7-X-2-Benzothienyl System ($n = 4$)				
$\Delta q(\pi)$, SCF-π	−25.4	−0.37	0.02	0.018
^{13}C response slope	−4.43	−0.72	0.08	0.067
$\Delta q(\pi)$, CNDO/2	−12.8	−1.34	0.33	0.267
Δq(regional), CNDO/2	−21.2	−0.43	0.38	0.302
Δq(total), CNDO/2	−20.0	−1.35	0.48	0.379
$c^2/(E_L - E_H)$, SCF-π	−28.2	−1.19	0.54	0.433
$c^2/(E_L - E_H)$, CNDO/2	−29.8	−1.19	0.56	0.446
(b) 3,4,5,6,7-X-1-Naphthyl System ($n = 5$)				
^{13}C response slope	−4.58	−0.47	0.24	0.113
$c^2/(E_L - E_H)$, CNDO/2	−26.6	−0.73	0.33	0.153
$c^2/(E_L - E_H)$, SCF-π	−23.6	−0.63	0.40	0.185
$\Delta q(\pi)$, SCF-π	−23.0	0.17	0.43	0.196
Δq(regional), CNDO/2	−22.3	0.11	0.61	0.281
$\Delta q(\pi)$, CNDO/2	−12.9	−0.89	0.70	0.322
Δq(total), CNDO/2	−20.8	−0.98	0.85	0.393

charge developed at the site of substitution. Why then, in correlations (Table IV) of $\rho_R{}^+$ with theoretically derived quantities, are the correlations with the HOMO–LUMO expression better than the correlations with calculated charges? Is $c^2/(E_L - E_H)$ really a better predictor than Δq, so that we would only need more accurate MO calculations to show that the HOMO–LUMO approach is better than any measure of the charge distribution, including ^{13}C response slopes, in representing the sensitivity to resonance effects? Our answers to these important questions are that the HOMO–LUMO expression is not a better *predictor* of $\rho_R{}^+$ values and that the correlations are misleading because E_H is treated as an adjustable parameter. Further, the definition of E_H as a constant is not justifiable theoretically.

The use of eq 1 is not strictly a *prediction* of the trends of $\rho_R{}^+$ when E_H is treated as an adjustable parameter, because then the value of E_H and hence the values of $c^2/(E_L - E_H)$ are not known until the statistical fitting of the data is carried out. The value of E_H determined by the best fit will be different for each collection of data considered. Moreover, with E_H as a third adjustable parameter it is difficult to compare meaningfully the quality of the correlation to the quality of correlations where only two parameters, the slope and intercept, are optimized in the fitting procedure.

One way to put the correlations on an equal basis for comparison is to limit the comparison to substituent effect data for several positions within the same arylcarbenium ion system. In this situation, only c^2 is important in eq 2, because E_L will be a constant that applies to all positions in any particular arylcarbenium ion, and hence the value of E_H will not affect the quality of the correlation as measured by SD/RMS. Correlations of $\rho_R{}^+$ are summarized in Table V for the 2-benzothienyl system (four $\rho_R{}^+$ values) and for the 1-naphthyl system (five $\rho_R{}^+$ values). For the 1-naphthyl system, the HOMO–LUMO expression is hardly superior to SCF-π charges, and in the 2-benzothienyl system, correlations with charges are distinctly better.

Another more general approach to put the correlations on an equal basis would be to use a theoretical value for E_H instead of treating it as an adjustable parameter. Jorgensen noted in his treatment that the best-fit E_H was similar to the theoretical E_H for the HOMO of benzene.[10] However, there actually is no logical choice of a constant value for E_H, because E_H should not be a constant. In the perturbation theory of substituent effects, the substituent effect occurs due to the interaction of a substituent HOMO with the LUMO of the cation. In order for each substituent to have a different effect, the energy level must differ for each substituent HOMO. Thus, the perturbation expression should be written (eq 4) such that it accounts for

$$\rho_R{}^+\sigma_R{}^+ = a\frac{c^2}{E_L - E_H} + b \qquad (4)$$

the complete resonance effect, $\rho_R{}^+\sigma_R{}^+$, and not just $\rho_R{}^+$. In eq 4, neither E_L nor E_H are constants; E_L and c^2 account for variations in the cations to which the substituents are attached, and E_H accounts for variations in the substituents. In other words, $c^2/(E_L - E_H)$ is not, in theory, analogous to $\rho_R{}^+$ in describing the sensitivity to substituent effects, because it also includes E_H which serves a purpose analogous to that of substituent constants, $\sigma_R{}^+$.

We consider the prediction of ρ values through the use of eq 2 to be an incorrect extension of second-order perturbation theory, despite its moderate success in correlating the data. This conclusion does not challenge the validity of the HOMO–LUMO theory of substituent effects itself, only the extension to ρ values. When E_H is forced to be constant, it may be that eq 2 works as an approximate measure of sensitivity to resonance effects because of the dominance of the c^2 factor. Correlation of all 16 $\rho_R{}^+$ values with c^2 alone is not as successful as with eq 2 (with c^2 from CNDO/2, SD/RMS = 0.448; with SCF-π c^2, SD/RMS = 0.433). However, it is not clear whether eq 2 is somewhat more successful because E_L correctly modifies the influence of c^2, with the best fit value of E_H resembling an average E_H value, or simply because of E_H as an additional adjustable parameter gives the incorrectly derived expression the "looseness" that allows it to correlate a limited set of data.

We conclude, for substituted aryl systems, that sensitivity to resonance effects as measured by $\rho_R{}^+$ is proportional to the amount of charge developed at the site of substitution. We recognize the proportionality between resonance effects and charge development is likely to be valid only for substituents attached to sp^2-hybridized carbons in π-delocalized cations. In the case of substituents on a phenyl ring, the $\rho_R{}^+$ value will reflect the amount of charge delocalized into the ring from the reaction center, but this will not necessarily be proportional to the total charge at the reaction center. The charge must be located in an orbital suitable for overlap with the appropriate phenyl orbitals in order for charge stabilization by resonance to occur. There are likely to be cases, such as σ-delocalized ions, in which only a portion of the total charge at a carbon atom could possibly be involved in resonance interactions with the directly attached group.[9a] In the case of substituents directly attached to such ions and not attached to an intervening phenyl group, it is probably necessary to apply perturbation theory (in a manner analogous to eq 4, treating the entire resonance effect) to come to an understanding of the substituent effect.[9]

It is also important to note that although we have used ^{13}C chemical shift data to draw conclusions about charge distributions, the data have been carefully restricted to sp^2 carbons remote from the carbenium center. At these remote positions, it is reasonable that the dominant influences on ^{13}C chemical shifts are resonance and polarization influences on the π-electron distribution.[21,30,31]

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