The Relevance of Third-derivative Cross-interaction Coefficients in Hammett-type Treatments of Nucleophilic Substitution Reactions†

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Six nucleophilic substitution reactions of (Y)-phenylalkyl or (Y)-phenacyl (Z)-arenesulfonates with (X)-anilines or (X)-benzylamines are analysed in terms of a modified Hammett equation incorporating both second- and third-derivative cross-interaction coefficients. For five of the six reported analyses, the standard errors associated with the third-derivative value (ρ_{XYZ}) are large and the probabilities that the contribution to the overall analysis is statistically insignificant are very high (0.53–0.92). Although we confirm a previous report that the sixth system appears to have a marginally acceptable ρ_{XYZ} value, minor adjustments of six of the 48 rate coefficients (so as better to accommodate trends within the matrix of values) leads to improved correlations, an appreciably reduced ρ_{XYZ} (or ρ_{XYZ}^{in}) value, and a 0.45 probability that the term involving ρ_{XYZ} is not statistically significant. Extremely fast methanolyses of the more reactive 1-phenylethyl arenesulfonates are predicted and previously reported studies, by conventional techniques, of their reactions with anilines, in methanol as the solvent, need to be reevaluated.

It is well established that second-derivative cross-interaction coefficients are potentially capable of giving important information concerning reaction mechanism[1,2] and recently[3] we developed an improved procedure for arriving at these values, involving the use of internally generated substituent constants. For a Hammett treatment involving three substituents (X, Y and Z), it is possible to consider, in addition to the three possible mixed second-derivative coefficients (ρ_{XY}, ρ_{YZ} and ρ_{ZX}), a third-derivative coefficient (ρ_{XYZ}). Miller[4] has presented the appropriate eqn. (1) for threefold structural variation.

$$y = ax + bz + cw + dxz + ewx + fzw + gxzw + h \quad (1)$$

Excellent systems for studying this type of variation are nucleophilic substitution reactions, where it is possible to have aromatic rings with various substituents situated in the attacking nucleophile, attached directly or indirectly at the site of substitution, and in the leaving group [eqn. (2)].

$$\mathrm{XN + YRLZ \longrightarrow XNRY + LZ} \quad (2)$$

For treatments in terms of the Hammett equation, eqn. (1) can be expressed as eqn. (3),[5] where k_{XYZ} is the rate coefficient in

$$\log(k_{XYZ}/k_{HHH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_Z\sigma_Z + \rho_{XY}\sigma_X\sigma_Y + \rho_{YZ}\sigma_Y\sigma_Z + \rho_{ZX}\sigma_X\sigma_Z + \rho_{XYZ}\sigma_X\sigma_Y\sigma_Z + C \quad (3)$$

the presence of substituents X, Y and Z and k_{HHH} is the rate coefficient when X = Y = Z = H. ρ_X, ρ_Y and ρ_Z represent the appropriate first-derivative sensitivity parameters, ρ_{XY}, ρ_{YZ}, ρ_{ZX} and ρ_{XYZ} represent the appropriate second-derivative and third-derivative parameters, and C is a constant (residual) term.

Internal substituent constants[3,6] (σ_X^{in}, σ_Y^{in} and σ_Z^{in}) can be obtained using the technique previously reported;[3] for example, $\sigma_X^{in} = \log(k_{XHH}/k_{HHH})$. These internal substituent constants can be incorporated within eqn. (3) to give eqn. (4).

$$\log(k_{XYZ}/k_{HHH}) = \rho_X^{in}\sigma_X^{in} + \rho_Y^{in}\sigma_Y^{in} + \rho_Z^{in}\sigma_Z^{in} + \rho_{XY}^{in}\sigma_X^{in}\sigma_Y^{in} + \rho_{YZ}^{in}\sigma_Y^{in}\sigma_Z^{in} + \rho_{ZX}^{in}\sigma_Z^{in}\sigma_X^{in} + \rho_{XYZ}^{in}\sigma_X^{in}\sigma_Y^{in}\sigma_Z^{in} + C^{in} \quad (4)$$

A statistically meaningful examination of third-derivative cross-interaction coefficients requires the precise determination of a large number of rate coefficients. A three-dimensional matrix can be established by studying all possible combinations with two substituents fixed and the third varied. In practice,[5,7–13] the number of determinations has varied between 48 and 80. The reported statistical treatments of reactions of the type expressed by eqn. (2) have involved a series of estimations of the second-derivative cross-interaction coefficients[1,2,5] for each of the individual third substituents. In all but one instance, the values have not varied widely as the third substituent is varied; however, for the reactions of indan-2-yl arenesulfonates with anilines in methanol at 55 °C, it was found[5] that not only do the second-derivative values vary widely with the nature of the third substituent but they also change sign. This behaviour was rationalized in terms of an appreciable third-derivative cross-interaction coefficient (ρ_{XYZ}).

We have taken the alternative statistical approach of applying the full equation, as presented by Miller [eqn. (1)], to the analysis of the second-order rate coefficients, using the form [eqn. (3) or (4)] appropriate for a modified Hammett equation treatment with either external or internally generated substituent constants, respectively.

Results and Discussion

The analyses of six previously reported systems are presented in Table 1 with use of eqn. (3) and in Table 2 with use of eqn. (4). The reactions are of 2-phenylethyl arenesulfonate with anilines in methanol[7] (reaction A) or with benzylamines in acetonitrile[8] (reaction B), of indan-2-yl arenesulfonates with anilines in methanol[5] (reaction C), and of, in methanol, phenacyl arenesulfonates with anilines[9] (reaction D), *N,N*-dimethylanilines[10] (reaction E), or benzylamines[11] (reaction F).

In terms of the correlation coefficient when external standards are used (Table 1), all of the reactions can be reasonably well correlated using only first-derivative terms (r_1 values of

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Table 1 Correlation using eqn. (3) of several reactions of anilines ($XC_6H_4NH_2$), *N*,*N*-dimethylanilines ($XC_6H_4NMe_2$), or benzylamines ($XC_6H_4CH_2NH_2$) with 2-phenylethyl, indan-2-yl, or phenacyl arenesulfonates ($YROSO_2C_6H_4Z$) in methanol or acetonitrile[a]

Reaction[b]	A (80)	B (80)	C (48)	D (48)	E (48)	F (48)
ρ_X	−1.11 ± 0.05	−0.57 ± 0.01	−1.36 ± 0.05	−2.01 ± 0.05	−1.95 ± 0.07	−0.77 ± 0.07
ρ_Y	−0.21 ± 0.02	−0.01 ± 0.01[c]	−0.40 ± 0.02	1.02 ± 0.02	1.06 ± 0.03	0.85 ± 0.03
ρ_Z	0.99 ± 0.02	1.18 ± 0.01	1.29 ± 0.02	1.27 ± 0.03	1.17 ± 0.03	1.00 ± 0.03
ρ_{XY}	−0.23 ± 0.12 (0.064)	0.01 ± 0.00 (0.860)	−0.04 ± 0.10 (0.686)	0.21 ± 0.11 (0.063)	0.17 ± 0.15 (0.246)	0.04 ± 0.15 (0.793)
ρ_{YZ}	0.14 ± 0.06 (0.0180)	0.01 ± 0.00 (0.656)	−0.08 ± 0.05 (0.102)	−1.00 ± 0.06	−0.92 ± 0.07	−0.59 ± 0.06
ρ_{ZX}	−0.64 ± 0.11	−0.13 ± 0.03	0.23 ± 0.11 (0.051)	0.33 ± 0.13 (0.018)	0.20 ± 0.16 (0.225)	0.01 ± 0.18 (0.943)
ρ_{XYZ}	0.08 ± 0.29 (0.775)	−0.04 ± 0.07 (0.574)	−0.52 ± 0.24 (0.039)	−0.12 ± 0.28 (0.678)	0.04 ± 0.35 (0.918)	0.24 ± 0.38 (0.533)
C	0.08 ± 0.07	−0.02 ± 0.02	0.04 ± 0.03	−0.03 ± 0.04	−0.06 ± 0.05	−0.01 ± 0.05
r_3[d]	0.9909	0.9994	0.9982	0.9978	0.9961	0.9919
r_2[e]	0.9909	0.9994	0.9980	0.9978	0.9961	0.9918
r_1[f]	0.9852	0.9991	0.9979	0.9777	0.9742	0.9722

[a] The ρ values and C value are reported with associated standard errors. Probabilities in excess of 0.0001 that the term governed by the quoted parameter is not statistically significant in the overall correlation are given (below) in parentheses. [b] The reactions are coded as A–F, the values in parentheses are the numbers of k_{XYZ} values incorporated for the systems: A, $XC_6H_4NH_2$ + $YC_6H_4CH_2CH_2OSO_2C_6H_4Z$ in MeOH at 65 °C (ref. 7); B, $XC_6H_4CH_2NH_2$ + $YC_6H_4CH_2CH_2OSO_2C_6H_4Z$ in MeCN at 65 °C (ref. 8); C, $XC_6H_4NH_2$ + indan-2-yl arenesulfonates in MeOH at 55 °C (ref. 5); D, $XC_6H_4NH_2$ + $YC_6H_4COCH_2OSO_2C_6H_4X$ in MeOH at 45 °C (ref. 9); E, $XC_6H_4NMe_2$ + $YC_6H_4COCH_2OSO_2C_6H_4X$ in MeOH at 55 °C (ref. 10); F, $XC_6H_4CH_2NH_2$ + $YC_6H_4COCH_2OSO_2C_6H_4X$ in MeOH at 45 °C (ref. 11). [c] Probability of 0.170 that the $\rho_Y\sigma_Y$ term is not statistically significant. [d] Correlation coefficient for use of eqn. (3). [e] Correlation coefficient for use of eqn. (3), with omission of the third-derivative term. [f] Correlation coefficient for use of eqn. (3), with omission of all of the second- and third-derivative terms.

Table 2 Correlation using eqn. (4) of several reactions of anilines ($XC_6H_4NH_2$), *N*,*N*-dimethylanilines ($XC_6H_4NMe_2$), or benzylamines ($XC_6H_4CH_2NH_2$) with 2-phenylethyl, indan-2-yl, or phenacyl arenesulfonates ($YROSO_2C_6H_4Z$) in methanol or acetonitrile[a]

Reaction[b]	A (80)	B (80)	C (48)	D (48)	E (48)	F (48)
ρ_X^{in}	1.01 ± 0.01	0.93 ± 0.03	1.03 ± 0.03	1.01 ± 0.01	1.00 ± 0.01	1.00 ± 0.01
ρ_Y^{in}	1.01 ± 0.03	−0.13 ± 0.10	1.24 ± 0.06	1.00 ± 0.01	0.99 ± 0.01	1.00 ± 0.01
ρ_Z^{in}	1.01 ± 0.01	1.00 ± 0.01	0.99 ± 0.01	1.01 ± 0.01	1.00 ± 0.01	1.02 ± 0.01
ρ_{XY}^{in}	−0.62 ± 0.12	−0.45 ± 0.80 (0.574)	−0.04 ± 0.21 (0.852)	−0.10 ± 0.03	−0.09 ± 0.02	−0.11 ± 0.03 (0.001)
ρ_{YZ}^{in}	−0.48 ± 0.07	0.11 ± 0.20 (0.595)	0.20 ± 0.10 (0.050)	−0.79 ± 0.02	−0.80 ± 0.02	−0.87 ± 0.01
ρ_{ZX}^{in}	0.36 ± 0.02	0.19 ± 0.05 (0.001)	−0.13 ± 0.06 (0.025)	−0.13 ± 0.03	−0.11 ± 0.02	−0.15 ± 0.03
ρ_{XYZ}^{in}	−0.29 ± 0.27 (0.291)	1.15 ± 1.00 (0.253)	−0.93 ± 0.37 (0.017)	0.05 ± 0.06 (0.393)	0.03 ± 0.04 (0.473)	0.07 ± 0.07 (0.358)
C	−0.01 ± 0.02	−0.02 ± 0.02	−0.02 ± 0.03	−0.03 ± 0.04	−0.01 ± 0.02	0.00 ± 0.01
r_3[c]	0.9994	0.9988	0.9987	0.9994	0.9996	0.9999
r_2[d]	0.9994	0.9987	0.9985	0.9994	0.9996	0.9999
r_1[e]	0.9964	0.9985	0.9983	0.9791	0.9763	0.9749

[a] See footnote *a* to Table 1. [b] See footnote *b* to Table 1. [c] Correlation coefficient for use of eqn. (4). [d] Correlation coefficient for use of eqn. (4), but with omission of the third-derivative term. [e] Correlation coefficient for use of eqn. (4), but with omission of the three second-derivative terms and the third-derivative term.

0.972–0.999). For reactions A through C, only modest improvements result from incorporation of second-derivative terms. However, appreciable improvements are noted for the reactions of the phenacyl derivatives (reactions D through F) with the corresponding r_1 values of 0.972–0.978 increasing, on incorporation of second-derivative cross-interaction terms, to 0.992–0.998 (r_2 values). Finally, virtually no increases in correlation coefficient ($\leqslant 0.0002$) are observed for the analyses on moving from r_2 values to r_3 values [r_3 values based on full eqn. (3), and incorporating both second- and third-derivative terms]. This is consistent with previous claims by Lee[1,2] that in most instances the contribution from the $\rho_{XYZ}\sigma_X\sigma_Y\sigma_Z$ term can be neglected. Indeed, for five of the six systems, the ρ_{XYZ} values obtained from the eqn. (3) analyses have associated standard errors larger than the value and extremely high probabilities that the $\rho_{XYZ}\sigma_X\sigma_Y\sigma_Z$ term is not statistically significant (0.53 to 0.92). Only in the previously mentioned case of reaction C is the probability (0.04) marginally acceptable and the value of −0.52 ± 0.24 apparently meaningful (in good agreement with the value of −0.53 calculated by Lee *et al.*[5]). It should be pointed out, however, that on incorporation of higher-derivative terms only very modest increases in correlation coefficient are observed (r_1 = 0.9979; r_2 = 0.9980; r_3 = 0.9982).

When internally generated substituent constants are employed (Table 2), the correlations are in five instances improved. For this approach to be advantageous, there is the requirement that, for two substituents being hydrogen, reasonable variations in rate coefficient must accompany variation of each of the third substituents. For reaction B, Table 1 indicates a ρ_Y value of −0.01 ± 0.01 and, accordingly, the σ_Y^{in} values are essentially constant. It is not surprising, therefore, that the calulated ρ_Y^{in} value is far removed from unity (−0.13 ± 0.10), indicative of an inconsistent data set.[3] Again, in five instances (except for reaction C) ρ_{XYZ}^{in} values have associated with them a relatively

Table 3 Adjustments made to second-order rate coefficients for the reactions of (Y)-indan-2-yl (Z)-arenesulfonates with (X)-anilines in methanol at 55.0 °C

Substituents			$k_2/10^{-5}$ dm^3 mol^{-1} s^{-1}	
X	Y	Z	Reported[a]	Adjusted[b]
H	H	H	5.52	6.3
H	H	*p*-Cl	13.3	14.4
p-Cl	Br	*p*-CH_3	1.39	1.24
p-OCH_3	NO_2	*p*-CH_3	4.10	4.55
p-Cl	NO_2	*p*-CH_3	0.90	0.81
p-Cl	NO_2	*p*-NO_2	12.1	13.8

[a] From ref. 5. [b] Based on a consideration of the detailed nature of the rate coefficient variation upon variation in turn of each of the three substituents. The adjustments identified were in each case indicated by the trends within all three of the possible variations (of X, Y and Z); for further discussion, see the text.

large standard error and a high probability that the term incorporating the $\rho^{\text{in}}_{\text{XYZ}}$ value is not statistically significant (0.25–0.47).

For reaction C, the $\rho^{\text{in}}_{\text{XYZ}}$ value of -0.93 ± 0.37 can be converted, using eqn. (5), into a ρ_{XYZ} value of -0.65 ± 0.26, in

$$\rho_{\text{XYZ}} = \rho^{\text{in}}_{\text{XYZ}}\rho_{\text{X}}\rho_{\text{Y}}\rho_{\text{Z}} \qquad (5)$$

reasonable agreement with the value presented in Table 1. It is also to be noted that, despite a reasonably large value of -0.40 for ρ_{Y}, the $\rho^{\text{in}}_{\text{Y}}$ value (1.24 ± 0.06) is appreciably removed from unity, indicative of inconsistency in the data set.[3] Independent of the Hammett treatment of the data, we have examined the trends within the second-order rate coefficients, considered as a three-dimensional matrix, such that each determination must take a reasonable position within each of three series of rate coefficients (with two of the three substituents kept constant and the third varied). Six were found which deviated in a consistent manner in all three of the series from their ideal positions by 8–12% of their value; these are presented in Table 3.

Recalculation, using eqn. (3), with substitution of these adjusted values leads to the following parameters: $\rho_{\text{X}} = -1.35 \pm 0.05$; $\rho_{\text{Y}} = -0.41 \pm 0.02$; $\rho_{\text{Z}} = 1.29 \pm 0.02$; $\rho_{\text{XY}} = -0.14 \pm 0.10$ (0.193); $\rho_{\text{YZ}} = -0.03 \pm 0.05$ (0.499); $\rho_{\text{ZX}} = 0.22 \pm 0.11$ (0.063); $\rho_{\text{XYZ}} = -0.19 \pm 0.25$ (0.448); $C = -0.01 \pm 0.04$ ($r_3 = 0.9982$). The only value appreciably changed from those presented in Table 1 is the one for ρ_{XYZ} which falls from -0.52 ± 0.24 to -0.19 ± 0.25, with a corresponding increase in the probability that the contribution from the term including this parameter is statistically insignificant from 0.04 to 0.45. Similar conclusions result from the use of internally generated σ^{in} values within eqn. (4). The values obtained are: $\rho^{\text{in}}_{\text{X}} = 1.03 \pm 0.03$; $\rho^{\text{in}}_{\text{Y}} = 1.03 \pm 0.03$; $\rho^{\text{in}}_{\text{Z}} = 1.00 \pm 0.01$, $\rho^{\text{in}}_{\text{XY}} = -0.27 \pm 0.13$ (0.053); $\rho^{\text{in}}_{\text{YZ}} = 0.07 \pm 0.06$ (0.280); $\rho^{\text{in}}_{\text{ZX}} = -0.13 \pm 0.05$ (0.009); $\rho^{\text{in}}_{\text{XYZ}} = -0.28 \pm 0.25$ (0.271), $C^{\text{in}} = 0.01 \pm 0.02$ ($r_3 = 0.9992$). What is particularly noteworthy about this recalculation is that the $\rho^{\text{in}}_{\text{Y}}$ value is reduced to a value of very close to unity, suggesting that inconsistencies present in the data set used for the original calculation (reaction C of Table 2) have been removed.

We wish to emphasize that we are not recommending that sets of data be 'smoothed' prior to calculation of the various Hammett-type parameters. Our purpose is merely to demonstrate that relatively minor adjustments, of about 10%, of only six of the 48 rate coefficients, despite leading to only very minor changes in first- and second-derivative values, lead to an appreciable change in the third-derivative cross-interaction value. Indeed, the ρ_{XYZ} value changes sufficiently for what appears initially to be a minor but identifiable contribution to the linear free energy relationship to become negligible. Lee has previously emphasized[2] the need for rate coefficients of relatively high precision for calculation of second-derivative cross-interaction values. The present analyses show that values of even higher accuracy will be needed if one wishes to attempt a meaningful (low standard error and low probability that the associated term is statistically insignificant) evaluation of the magnitude of third-derivative cross-interaction coefficients (ρ_{XYZ} or $\rho^{\text{in}}_{\text{XYZ}}$).

We have also analysed two series of second-order rate coefficients for reactions claimed to be those of (X)-anilines[12] or (X)-*N*,*N*-dimethylanilines[13] with (Y)-1-phenylethyl (Z)-arenesulfonates in methanol. There are, however, extremely strong indications that the more reactive of these substrates would undergo methanolysis much too rapidly for any appreciable reaction with added amines, at the rates indicated, to be possible. Clearly, a series of arenesulfonates was studied but it appears highly unlikely that they could have been 1-phenylethyl derivatives. Evidence supporting this viewpoint follows.

A study of the background solvolysis of a compound believed to be 1-phenylethyl *p*-nitrobenzenesulfonate (nosylate, ONs) in methanol led to reports[12] of a specific rate of 2.89×10^{-4} s^{-1} at 25.0 °C and a negative $\Delta S^{\neq}$ value of unusually high magnitude (-51.9 cal mol^{-1} K^{-1}). In contrast, for the ethanolysis of 1-phenylethyl toluene-*p*-sulfonate (tosylate, OTs), Hoffmann[14] reported a $\Delta S^{\neq}$ value of -6.8 cal mol^{-1} K^{-1} and specific rates which allow an interpolated value of 83×10^{-4} s^{-1} at 25.0 °C to be estimated. After conservative estimates of factors of ten for the ONs/OTs rate ratio[15] and for transfer from ethanol to methanol (based on data for 1-phenylethyl chloride solvolyses[16]), we can estimate from Hoffmann's measurements a specific rate for solvolysis of 1-phenylethyl nosylate in methanol at 25.0 °C of 0.83 s^{-1}, corresponding to a half-life of slightly less than 1 s and about 3000 times higher in value than the reported[12] specific rate.

Extremely strong support for Hoffmann's determinations has been presented recently in a study, using rapid kinetics techniques, of 1-phenylethyl methanesulfonate (mesylate, OMs) solvolysis.[17] In particular, the ethanolysis at 25.0 °C has a specific rate of 42.7×10^{-4} s^{-1}, which converts into a predicted value for the tosylate of 77×10^{-4} s^{-1} when a recommended[18] OTs/OMs rate ratio of 1.8 is applied. Further, the reported[17] $\Delta S^{\neq}$ value of -2.5 cal mol^{-1} K^{-1} is nicely consistent with the value reported by Hoffmann for the tosylate.

For reactions in 93% acetone, Shiner has claimed that 1-(*p*-methoxyphenyl)ethyl chloride reacts about 10^6 times faster than 1-phenylethyl chloride.[19] Even if this ratio is applied to the apparently low specific rate for methanolysis of the parent nosylate reported by Lee *et al.*,[12] a specific rate corresponding to a half-life for methanolysis of 1-(*p*-methoxyphenyl)ethyl nosylate at 25 °C of about 2.4×10^{-3} s is predicted, obviously incompatible with a study by conventional techniques of reaction with an added nucleophile. We also mention that, while 1-phenylethyl tosylate[20] and 1-phenylethyl mesylate[21] have been reported to decompose rapidly at room temperature and it is recommended that the mesylate be kept in solution,[17] the members of the series of arenesulfonates studied by Lee *et al.* were isolated by routine procedures. Accordingly, we postpone the presentation of our analyses of these studies[12,13] until the detailed nature of the substrates involved is clarified.

Conclusions

Six nucleophilic substitution reactions involving threefold variation of substituents [eqn. (2)], previously analysed in terms of a series of correlations involving combinations of first- and second-derivative terms, are analysed in terms of a modified Hammett-type equation involving the three first- and the three mixed second-derivative terms in conjunction with the third-derivative term involving all three series of substituents. Analyses were carried out using either externally [eqn. (3)] or internally generated [eqn. 4)] substituent constants.

For five reactions, the third-derivative cross-interaction coefficient was clearly negligible, as indicated by a standard error comparable to or larger than its value, only an extremely small increase in the value for the overall correlation coefficient on incorporating the third-derivative term into the linear free energy relationship, and a high probability that the term incorporating the third-derivative parameter is not statistically significant. The sixth reaction was confirmed, using the rate coefficients presented, to have a significant value for the third-derivative cross-interaction. However, relatively small adjustments (based on expected trends in the various possible series of second-order rate coefficients) of from 8–12% for six of the 48 rate coefficients (Table 3) lead to the ρ_{XYZ} and ρ^{in}_{XYZ} coefficients assuming characteristics similar to those observed for the other five reactions. This modified analysis throws considerable doubt upon the only evidence put forward to date suggesting that nucleophilic substitution reactions can have a significant value for the third-derivative cross-interaction coefficient.

Literature values for the specific rates of solvolysis of 1-phenylethyl sulfonate esters suggest an extremely fast methanolysis of (Y)-1-phenylethyl (Z)-arenesulfonates when Y is electron supplying and Z is electron withdrawing. Accordingly, bimolecular reaction, in methanol as the solvent, with anilines or *N*,*N*-dimethylanilines would be overwhelmed by the rapid background methanolysis.

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