Selectivity and the Ritchie Equation

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The rates of addition of six primary amines to various electrophiles in aqueous solution have been analysed using a log *k*–log *k* type LFER treatment. Observed behaviour is in accord with the reactivity–selectivity principle and in quantitative agreement with previous work, questioning the validity of the Ritchie equation over large ranges of Lewis acidity. It is suggested that it is the range of electrophile stability considered, and not the intrinsic reactivity of the electrophiles themselves, which determines the degree of conformity to Ritchie type constant selectivity relationships.

The reactivity–selectivity principle, RSP, has been developed from a theoretical extension of the Hammond postulate[1] and predicts that selectivity will gradually decrease as the reactivity of a system increases. Although the RSP has been well reviewed[2,3] and, as Rappoport[4] comments, the concept of an inverse relationship between reactivity and selectivity is intuitively attractive, unequivocal experimental demonstrations of the RSP are rarer than might be supposed and the postulate has been strongly criticised.[3,5] As Ta-Shma and Rappoport have remarked,[6] the constant selectivity suggested by Ritchie's investigations into nucleophile–electrophile addition reactions in solution[7,8] has presented a serious problem to advocates of the RSP.[9] Ritchie has considered the reactivities of a series of neutral, and negatively and positively charged, nucleophiles, in various solvents, and he has concluded that rates of addition are adequately correlated by the LFER in eqn. (1),[8] where N_+ is

$$N_+ = \log \frac{k}{k_o} \qquad (1)$$

a constant for a particular nucleophile–solvent system, k is the second order rate constant of addition (first order for solvolyses), and $\log k_o$ is a constant for a particular electrophile.[8] The so-called Ritchie equation, eqn. (1), is adequately observed by stabilised triarylmethyl cations, aryldiazonium cations and tropylium ion derivatives.[8] Esters are also found to follow the Ritchie relation, although allowance must be made for the generally accepted two step substitution mechanism,[8] a procedure which Jencks has criticised.[10] Four 2,4-dinitrohalobenzene derivatives have also been found to combine with most nucleophiles at rates which are in approximate correspondence with eqn. (1), though azide and thiolate ions exhibit significant deviations.[11]

In 1976, Scott reported that, although the relative reactivities of a series of nucleophiles towards the 4,4′,4″-trimethoxytriphenylmethyl cation were in accord with the predictions of the N_+ scale, the observed slope parameter, of about 0.8, was lower than expected.[12] Scott therefore suggested the use of a modified Ritchie equation to correlate the reactivity behaviour of this electrophile, eqn. (2), where the S_+ parameter varies

$$\log \frac{k}{k_o} = S_+ N_+ \qquad (2)$$

according to the electrophile considered.[12] Although both Bunton[13] and Ritchie[14] have expressed doubts about the physico-chemical significance of S_+, further demonstrations of non-unity Ritchie slopes have accumulated recently, including N_+ correlations for the electrophiles picryl chloride,[15] $S_+ = 0.79$; acetyl chloride,[10] 0.47; the xanthylium ion,[16] 0.65, the trityl cation,[17] 0.39; *N*-methyl-*N*-nitrosotoluene-4-sulfonamide,[18] 2; and a series of 9-methylenefluorene derivatives,[19] 1.2.

Although slopes of less than unity for the reactive trityl and xanthylium ions may be attributable to the influence of diffusional limitation,[16,17] Scott,[12] McClelland[17] and Gandler[15] speculate that reduced gradients may be a manifestation of the RSP. Indeed, in a recent study into the addition reactions of primary alkylamines and an extensive series of triarylmethyl cations in aqueous solution, McClelland[20] has reported behaviour in accord with the RSP and concludes that amines do not adhere to a constant selectivity relation.[20] He has demonstrated that this behaviour may be characterised by a single second derivative cross correlation coefficient,[21] p_{xy}, defined over nine triarylmethyl cations, eqn. (3);[20] this

$$p_{xy} = \partial\left(\frac{\partial \log k}{\partial \mathrm{p}K_{\mathrm{R}^+}}\right) \Big/ \partial \mathrm{p}K_{\mathrm{a}} = \partial\left(\frac{\partial \log k}{\partial \mathrm{p}K_{\mathrm{a}}}\right) \Big/ \partial \mathrm{p}K_{\mathrm{R}^+} = 0.022 \pm 0.001 \qquad (3)$$

relationship extending into the stabilised cation region considered by Ritchie. In contrast, Richard[22] has recently studied the relative rates of alcohol addition to a series of 1-aryl-2,2,2-trifluoroethyl secondary carbocation derivatives and has proposed that selectivity is constant in the unreactive cation region ($p_{xy} = 0$), though it varies in accord with the RSP for more reactive electrophiles ($p_{xy} = +\mathrm{ve}$),[22] a dichotomy in reactivity behaviour which, as Richard comments, infers the presence of third derivative effects.[22]

Results and Discussion

Thus, the current understanding of the variation of selectivity with reactivity in nucleophile–electrophile addition reactions is rather confused, a point amply illustrated if one attempts to define the magnitude of the cross correlation coefficient[21] directly applicable to the revised Ritchie relation [eqn. (2)], as shown in eqn. (4).

$$p_{xy}' = \partial S_+ / \partial \log k_o \qquad (4)$$

A plot of S_+ against $\log k_o$ is shown in Fig. 1 for the majority of the electrophiles discussed above. As may be ascertained, no systematic dependence of selectivity with reactivity is discernible. Depending on the electrophile pair selected, RSP, anti-RSP and constant selectivity relationships may be constructed, by employing a similar method to that described by Johnson.[23]

The current state of confusion regarding the relationship between reactivity and selectivity may arise from a lack of

Table 1 Second order nucleophile–electrophile addition rate constants, log *k*, for the reactions of amines with a series of triphenylmethyl cation, T^+; tropylium ion, Tr^+; and 2,4-dinitrobenzene, D; derivatives, and 2,4-dinitrophenyl acetate, DNPA; 1-acetoxy-4-methoxypyridinium perchlorate, AMPP; and acetyl chloride, AC[a]

	NH_2NH_2	CH_3–[b]	^-OOC–[b]	$^-OOCCH_2NHCO$–[b]	EtOOC–[b]	$^+H_3NCH_2$–[b]	CF_3–[b]
4,4′-$(NMe_2)_2$-T^+	1.60[c]	0.81[c]	0.95[c]	0.28[c]	−0.01[c]	−0.06[c]	−0.96[c]
4-NO_2-4′,4″-$(NMe_2)_2$-T^+	1.61[c]			0.34[c]			
4,4′-, 4″-$(MeO)_3$-T^+	4.97[d]	4.39[e]					
T^+	7.32[f]		7.20[f]				6.43[f]
4-NMe_2-C_6H_4-Tr^+	3.48[c]	3.45[c]	3.71[c]	3.11[c]	2.73[c]	2.32[c]	1.62[c]
Tr^+	5.48[c]			5.15[c]	4.45[c]	4.40[c]	3.86[c]
1-F-D	−0.39[g]		−0.78[g]	−1.48[g]	−1.49[g]		−2.81[g]
1-Cl-D	−2.80[g]		−3.40[g]	−4.20[g]			
1-I-D	−3.20[g]		−3.70[g]	−4.50[g]			
1-Cl-6-NO_2-D	0.96[h]			−0.19[h]		−0.82[h]	−1.91[h]
DNPA	2.48[i]	2.07[i]					
AMPP	3.91[i]	3.42[i]			2.45[i]	2.16[i]	
AC	5.18[j]	4.92[j]				4.11[j]	3.68[j]

[a] In water at 25 °C, except where indicated otherwise. Units are $dm^3\ mol^{-1}\ s^{-1}$. [b] R-CH_2NH_2, R as indicated. [c] 23 °C, ref. 24. [d] Ref. 12. [e] Ref. 25. [f] 20 °C, 33% aqueous acetonitrile solution, ref. 17. [g] Ref. 11. [h] Ref. 15. [i] Ref. 26. [j] Ref. 10.

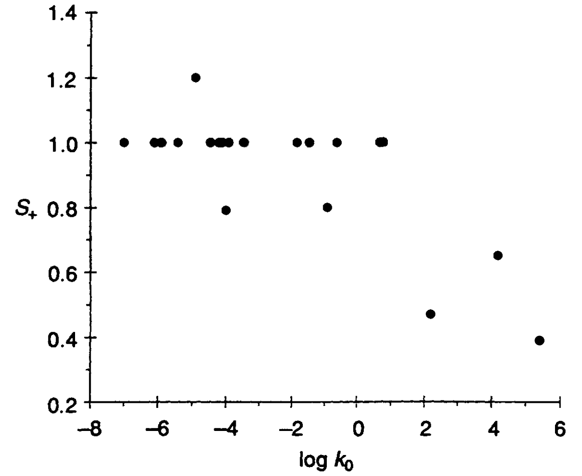

Fig. 1 A plot of S_+ against log k_o over various electrophile types, as discussed in the text

appreciation of the more subtle aspects of the Ritchie equation. To illustrate this point, we present a revised analysis of nucleophile–electrophile combination rate constants. In line with McClelland's investigation,[20] we have considered the reactions of a single nucleophile type in a single solvent; primary amines in aqueous solution. Rate constants corresponding to nucleophile–electrophile addition are available from a variety of sources and are listed in Table 1. Most of the kinetic measurements considered are at 23–25 °C in water at low ionic strength. Although some of the rate data fall slightly outside these criteria, it is anticipated that the Pfluger method of analysis adopted, see below, will minimise potential discrepancies. Due to gaps in the experimental data, it is impossible to construct meaningful Brönsted correlations for the majority of the various electrophiles listed in Table 1. It is possible, however, to measure selectivities in these combinations by constructing log *k*–log *k* plots, or Pfluger[27] type correlations, of the available kinetic measurements. Both McClelland[20,28] and Mayr[29] have had some success in correlating nucleophile–electrophile addition rates on the basis of log *k*–log *k* LFER treatments, a general representation of which being shown in eqn. (5); where *k* is the second order rate constant of addition

$$\log k = a \log k_o + \log c \qquad (5)$$

of a nucleophile with a series of electrophiles, k_o is the rate constant of electrophile combination with a reference nucleophile system (a measure of Lewis acidity which Richard[22] has also employed) and *a* and log *c* are slope and intercept parameters, the latter being related to the reactivity of the nucleophile considered. Here, we adopt eqn. (5) and employ hydrazine as our standard nucleophile, simply as rate data is comparatively plentiful. Thus, eqn. (5) becomes eqn. (6); where

$$\log k = a_{hy} \log k_{hy} + \log c_{hy} \qquad (6)$$

k_{hy} is the second order rate constant for hydrazine-electrophile addition in aqueous solution, $k_{NH_2NH_2(H_2O)}$.

McClelland's investigations suggest that primary amine–triarylmethyl cation combinations in aqueous media involve an initial nucleophile desolvation step.[20] Similar mechanisms have been put forward by Johnson[30] and Jencks[31] for the reactions of pyridines and alkoxides, respectively. In these mechanisms, the Lewis base desolvation step is independent of the nature of the electrophile considered. Thus, the value of a_{hy} is expected not to be influenced by nucleophile desolvation, although the magnitude of log c_{hy} will be diminished by the free energy required to expose the reactive lone pair, prior to combination.

The results of a least squares analysis of the experimental data, using eqn. (6), are shown in Table 2. Correlations are generally excellent, contradicting the notion that the α-effect nucleophile hydrazine is not a suitable reference Lewis base. A series of log *k*–log *k* plots for the six primary alkylamines are shown in Fig. 2, the correlation being expanded along the *y* axis by plotting log *k* + pK_a, rather than log *k*, against log k_{hy}. The pK_a term is introduced solely to reduce clutter in Fig. 2 and is expected to bear a linear relation to primary amine–electrophile addition rates over the six amines. This expectation is supported by the observation that a plot of the nucleophilicity parameter log c_{hy} with amine pK_a is reasonably linear. Excluding ethylamine, the remaining five primary alkylamines conform to the good Brönsted type correlation described in eqn. (7).

$$\log c_{hy} = 0.62 \pm 0.06\, pK_a - 6.32 \pm 0.45\, (0.987) \qquad (7)$$

All five Lewis bases fall on this LFER if the standard deviations of log c_{hy}, Table 2, are considered. The log c_{hy} parameter calculated for ethylamine falls about 1 log unit below that predicted by eqn. (7). A similar discrepancy has been reported by Ritchie in his correlations of N_+ against pK_a over several primary alkylamines.[8] The deviation may arise as ethylamine is expected to be particularly strongly solvated, it being the most basic amine considered in this study. As might

Table 2 Values of a_{hy} and log c_{hy} from eqn. (6) for a series of amines, and details of the electrophiles considered[a]

Nucleophile	pK_a[b]	a_{hy}	log c_{hy}[c]	r[d]	n[e]
NH_2NH_2	8.2	1.00[f]	0.00[f]	1.000[f]	13
CH_3–[g]	10.97	1.07 ± 0.09	−0.69 ± 0.33	0.987	6
^-OOC–[g]	9.76	1.05 ± 0.03	−0.39 ± 0.12	0.998	6
$^-OOCCH_2NHCO$–[g]	8.25	1.12 ± 0.04	−1.13 ± 0.10	0.997	8
EtOOC–[g]	7.9	1.03 ± 0.09	−1.28 ± 0.30	0.989	5
$^+H_3NCH_2$–[g]	7.42	1.15 ± 0.06	−1.92 ± 0.23	0.995	6
CF_3–[g]	5.84	1.23 ± 0.04	−2.74 ± 0.17	0.998	7

[a] Using data from Table 1. [b] Ref. 26. [c] $dm^3\ mol^{-1}\ s^{-1}$. [d] Correlation coefficient. [e] Number of data pairs. [f] Reference. [g] R-CH_2NH_2, R is as indicated.

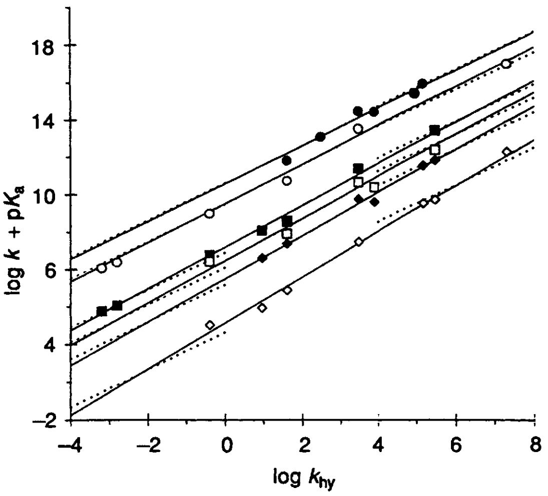

Fig. 2 log k–log k correlations of log k + pK_a (see text) *versus* log k_{hy} for six primary alkylamines, using data from Table 1; $EtNH_2$, ●; $^-OOCCH_2NH_2$, ○; $^-OOCCH_2NHCOCH_2NH_2$, ■; $EtOOCCH_2NH_2$, □; $^+H_3NC_2H_4NH_2$, ◆; $CF_3CH_2NH_2$, ◇. The solid lines have slopes defined by eqn. (8) and the dashed lines describe constant selectivity relationships.

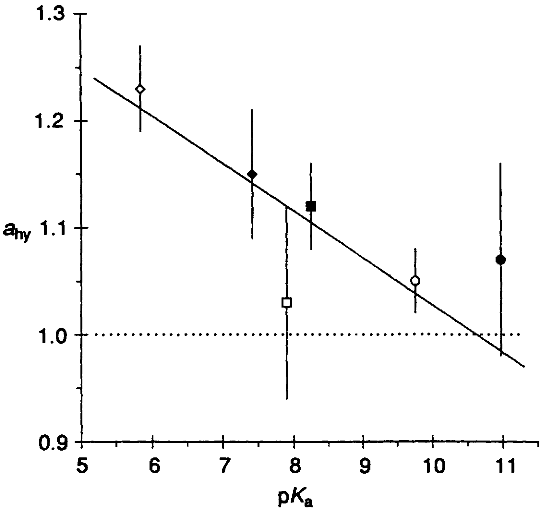

Fig. 3 A plot of a_{hy}, including standard deviations, against pK_a for six primary amines in aqueous solution (symbols have the same definition as in Fig. 2). The solid line has a slope of −0.046, while the dashed line corresponds to behaviour in accord with the Ritchie relation.

be expected, the α-effect nucleophile hydrazine falls about 2 log units above the correlation in eqn. (7).

A plot of a_{hy} against primary amine pK_a, Fig. 3, reveals that there is some correspondence between the two quantities, the constant selectivity predicted by the Ritchie equation being shown for comparison. Four nucleophiles, $^-OOCCH_2NH_2$, $^-OOCCH_2NHCOCH_2NH_2$, $^+H_3NC_2H_4NH_2$ and $CF_3CH_2NH_2$, define the linearity in eqn. (8).

$$a_{hy} = -0.046 \pm 0.002\,\mathrm{p}K_a + 1.49 \pm 0.01\ (0.999) \qquad (8)$$

Upon the incorporation of error bars into Fig. 3, the standard deviations reported by the linear least squares analysis, it is found that the remaining two amines, $EtOOCCH_2NH_2$ and $EtNH_2$, also fall on the LFER slope–reactivity correlation. The magnitude of the gradient in eqn. (8) requires that eqn. (9) is

$$p_{xy}'' = -\partial\left(\frac{\partial \log k}{\partial \log k_{hy}}\right)\Big/\partial \mathrm{p}K_a = -\partial\left(\frac{\partial \log k}{\partial \mathrm{p}K_a}\right)\Big/\partial \log k_{hy} = -\partial\beta_{nuc}/\partial \log k_{hy} = 0.046 \pm 0.002 \qquad (9)$$

valid, where p_{xy}'' is a second derivative cross correlation coefficient.[21] Jencks[21] has strongly supported the idea that non-zero correlation coefficients of this type correspond to shifts in transition state position, a notion endorsed recently by Richards.[22] The positive value for p_{xy}'' recorded here suggests that the degree of nitrogen–electrophile bond formation gradually lessens as the reactivity of the Lewis acid increases. This places less positive charge on the amine nitrogen in the transition state and consequently reduces the sensitivity of reaction rates to changing amine pK_a, in line with the predictions of the RSP.[20] Thus, eqn. (9) predicts a decrease in β_{nuc} of around 0.5 on going from 2,4-dinitroiodobenzene to the trityl cation, Table 1.

The second derivative cross correlation coefficient reported here may be contrasted with that reported by McClelland in his primary amine–triarylmethyl cation addition study,[20] p_{xy}, eqn. (3). Using pK_{R^+} values[32] for the four triarylmethyl cations considered here, Table 1, we calculate that $\partial \log k_{hy}/-\partial \mathrm{p}K_{R^+}$ = 0.45 ± 0.07, this comparing very well with the value of this quantity which may be determined from the ratio p_{xy}/p_{xy}'' = 0.48 ± 0.04. The results of McClelland's study[20] and this work are thus in agreement.

The behaviour recorded here may also be couched in terms of Lee's methodology, eqn. (10),[32] where k_{ij} is the second order

$$\log k_{ij} = p_{ij}X_iX_j + p_iX_i + \mathrm{p}_jX_j + \text{constant} \qquad (10)$$

rate constant of combination, the p terms are correlation coefficients, and X_i and X_j are structure–reactivity parameters corresponding to the two reagents (usually pK_a or σ type parameters). Lee's approach has been employed successfully to correlate the reactivity behaviour of numerous reaction types.[32] Combining eqns. (6), (7) and (8) suggests that, if X_i = pK_a and X_j = log k_{hy}, $p_{ij} = -0.046$, $p_i = 0.62$ and $p_j = 1.49$.

Paradoxically, most of the rate data employed in this analysis of reactivity and selectivity, Table 1, has been correlated by the Ritchie equation. Since N_+ and amine pK_a bear a linear relation to each other,[8] eqn. (9) may be rewritten as eqn. (11).

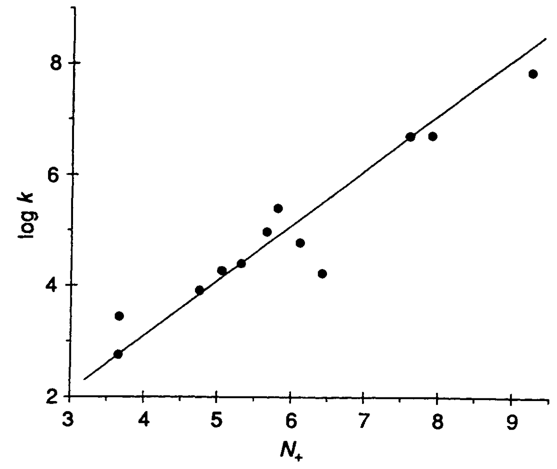

Fig. 4 A Ritchie plot for the 4,4′,4″-trimethoxytriphenylmethyl cation, employing rate data from Table 3. The solid line possesses unit slope.

Table 3 Second order rate constants for nucleophile addition to the 4,4′,4″-trimethoxytriphenyl cation, and corresponding N_+ values[a]

Nucleophile	log *k*	N_+[b]
$EtNH_2$	4.39[c]	5.31
Piperidine	4.78[c]	6.11
Imidazole	2.75[c]	3.66
NH_2NH_2	4.97[d]	5.66
$HONH_2$	4.26[d]	5.05
HO^-	3.91[e]	4.75
$4\text{-}CH_3C_6H_4O^-$	5.40[e]	5.80
$CF_3CH_2O^-$	4.23[f]	6.42
SO_3^{2-}	6.71[d]	7.90
N_3^-	6.70[e]	7.60
CN^-	3.43[e]	3.67
$HOCH_2CH_2S^-$	7.86[g]	9.24[h]

[a] In water at 25 °C. [b] Values from ref. 8, except where indicated. [c] Ref. 25. [d] Ref. 12. [e] Ref. 34. [f] Ref. 35. [g] Ref. 36. [h] Defined using $N_+ = \log k_{HOCH_2CH_2S^+(H_2O)} - \log k_{OH^+(H_2O)} + 4.75$ (ref. 8) and rate data for the reactions of the 4-dimethylaminophenyltropylium ion from ref. 37.

$$p_{xy}''' = -\partial\left(\frac{\partial \log k}{\partial \log k_{hy}}\right)\Big/\partial N_+ = -\partial\left(\frac{\partial \log k}{\partial N_+}\right)\Big/\partial \log k_{hy} > 0 \quad (11)$$

Thus, the slopes of Ritchie plots composed solely of data for primary amines are expected to decrease smoothly in magnitude with increasing electrophile reactivity in accordance with the RSP, over the 10^{11} reactivity range investigated. Over narrower electrophile reactivity ranges, however, it is apparent that the decrease in selectivity with increasing reactivity is small enough to permit a constant selectivity relationship to represent adequately reactivity behaviour, as is clearly demonstrated by the dashed lines in Fig. 2. Thus, it is the range of electrophile reactivities considered, and not the intrinsic reactivities of the electrophiles themselves, which will determine the degree to which constant selectivity Ritchie type relationships are obeyed, a notion considered previously.[2] Since early investigations into nucleophile–electrophile addition reactions primarily concerned the reactivities of stabilised cations, due to limitations in available experimental techniques, N_+ values are primarily defined on the basis of these reactions, though, as Fig. 2 demonstrates, constant selectivity relationships may also be adequately obeyed by reactive Lewis acids, though, of course, the corresponding N_+ values will be different.

The effects of the RSP on Ritchie plots are further hidden as Ritchie correlations rarely consider structurally related nucleophiles exclusively. As Johnson has discussed,[23] when many disparate nucleophilic systems are considered, LFER gradient parameters, such as a_{hy} and ρ^+, bear no systematic relation with nucleophile reactivity and the unit slope Ritchie equation is upheld, though with some random scatter. This is clearly demonstrated if one constructs an N_+ correlation for the 4,4′,4″-trimethoxytriphenylmethyl cation, Fig. 4, using kinetic data for a greater diversity of Lewis bases than that considered by Scott,[12] Table 3. A linear least squares analysis of this correlation yields eqn. (12), the slope being effectively unity

$$\log k = 1.03 \pm 0.10\,N_+ - 0.80 \pm 0.54\,(0.953) \quad (12)$$

within experimental error, as predicted by the Ritchie equation.[8] There is a considerable scatter, however, Fig. 4, questioning the true applicability of Ritchie's N_+ scale to reactive electrophiles.

Thus, this kinetic analysis suggests that the slopes of Ritchie plots are expected to be dependent on the nature of the nucleophiles employed in their construction and that the S_+ parameter is, therefore, not a reliable indicator of electrophile selectivity, this being the most likely origin of the observed non-systematic variation of S_+ with electrophile reactivity, Fig. 1. Moreover, we find no evidence for curvature in the log *k*–log *k* correlations we have constructed, Fig. 2, and we conclude, therefore, that the observed applicability of the Ritchie equation over narrow reactivity ranges of stabilised electrophiles, and the apparent RSP relationships described in this paper and in McClelland's study,[20] do not represent a dichotomy in reactivity behaviour. Rather, the former is a reasonable approximation of the latter. Thus, there is no requirement to invoke the concept of non-zero third derivative correlation coefficients to rationalise reactivity behaviour in these systems, in contrast to Richard's proposition.[22] It may be noted that Richard has used only four data readings to reach his conclusion,[22] while Lee has commented that at least sixteen rate constants are required before even *second* derivative correlation coefficients may be defined quantitatively.[32]

Finally, we note that a recent and extensive log *k*–log *k* type study of approximately 1600 rate constants by Exner[33] has concluded that the RSP applies in only roughly half of the 100 reaction series investigated. Although the two studies consider very different reaction systems, it is clear from our analysis (based largely on data previously accepted to follow a constant selectivity relationship) that the balance between a demonstration of general adherence to the predictions of the RSP, and adherence to constant selectivity relationships, can be relatively fine, and may be tipped either way by the inclusion, or omission, of relatively few kinetic measurements. We are satisfied that the broad data set of 51 rate constants employed in this study minimises this possibility.

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