On the Compatibility of the Reactivity–Selectivity Principle and the Ritchie N_+ Relationship

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Consideration of cross correlations existing within the framework of Ritchie's N_+ scale reveals that the variations in slope of the LFERs resulting from the treatment are sufficient to account for the range of selectivity ratios observed in this area of reactivity, and do not require any intrinsic link between reactivity (stability) and selectivity.

The question of the theoretical, molecular model to be attached to experimental observations of correlations between reactivity and selectivity, for which the best known statement is the reactivity–selectivity principle (RSP), remains the subject of considerable debate.[1–3] Within the field of aliphatic nucleophilic substitution, stability–selectivity relationships such as those of Schleyer[4] have been compared and contrasted[3,5,6] with the constant selectivities recorded by Ritchie, in his research into cation–anion combination reactions.[7] It has often been felt that some special explanation was needed for this apparent contradiction, but the possible compatibility of these results has been considered previously, in preliminary form.[8] A comprehensive and detailed argument is now presented, in which old data are reconsidered, and new data are incorporated, which supports, emphasizes, and extends the original conclusion.

Discussion

Ritchie's work has shown that, for a wide range of nucleophilic systems comprising nucleophile and solvent, reacting with various types of organic cations, the reaction rates can be correlated by one simple equation, the N_+ relationship, equation (1). Here k_{reaction} is the rate constant for reaction of a

$$\log k_{\text{reaction}} = N_+ + \log k_0 \qquad (1)$$

given cation with a given nucleophilic system, while k_0 is the rate constant for reaction of the cation with water in water (the reference reaction).† Ritchie found that benzenediazonium ions,[9,12–17] triarylmethyl cations,[9,16,18–20] and tropylium ions[9,21,22] obeyed this relationship. He extended its use to the reactions of nucleophiles with esters[10] and the nucleophilic aromatic substitution reactions of 2,4-dinitrohalogenobenzenes.[23] While acknowledging occasional failures of this relationship,[7,24,25,‡] it is impossible to ignore the overall generality and precision it exhibits. Other workers have shown it to be valid for ferrocenyl-stabilised cations[26] and for a wide range of co-ordinated cyclic π-hydrocarbons.[27,28]

It seems reasonable, therefore, to begin by assuming that the relationship expressed by equation (1) is correct. Let us then imagine a series of organic cations which obey the N_+ relationship, equation (1), exactly. Figure 1 shows the N_+ plots for three such cations reacting with three different nucleophilic systems. For each of these nucleophilic systems, it is further possible to imagine a parameter, p, against which the $\log k_{\text{reaction}}$ values for the series of cations would give a linear plot, as expressed in equation (2), where s is the slope of the correlation

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† N_+ values were originally calculated for the reactions of *p*-nitromalachite green cation;[9] in later work Ritchie modified his values by using an averaging procedure,[10] noting that reactions with water often gave anomalous results owing to general base catalysis.[10,11]

‡ Here the relatively very reactive trityl cation gives a log *k vs.* N_+ plot with a slope of 0.33. This may be due to reactions with more reactive nucleophiles approaching diffusion control. Moreover, some of the N_+ values used in the correlation are of uncertain status. For example, the solvent is 1 : 2 acetonitrile–water, while that for definition of N_+ values is water. Our opinion would be that these circumstances are indeed responsible for the deviation from the Ritchie correlation. On the other hand, it may well be a genuine example of the operation of reduced selectivity by a more reactive cation, as the authors point out, and in this regard, their further experiments, and those of others (see, for example, J. P. Richard, 'Breakdown of the N_+ Scale for the Reaction of Highly Unstable Ring-substituted 1-Phenyl-2,2,2-trifluoroethyl Carbocations,' ACS National Meeting, New Orleans, 1987) should prove to be of great relevance. Moreover, accentuating this alternative point of view, a referee writes as follows: 'The author is noted for his disbelief of the reactivity–selectivity principle, and this paper is therefore naturally biased towards his viewpoint. Nevertheless I feel it would be appropriate to present a more even-handed discussion.

'The gist of this paper is that since the reactivity–selectivity principle does not apply to some of Ritchie's data, we should therefore cease either to accept the principle or to use it at all. This strikes me as untenable. In coming to this conclusion the author notes that not all of Ritchie's data agree with equation (1), but these deviant data are apparently dismissed as being of no consequence. Thus the argument begins by assuming that equation (1) is correct, and then goes on to reach conclusions proving the assumption. Is this not a case of circular reasoning? If we accept that some of the Ritchie data do not conform to the reactivity–selectivity principle, but discount the extreme view that the principle is therefore defunct, does the paper then contribute anything further to that which Ritchie has already stated?

'The author also fails to mention the fact that Ritchie *et al.* believe that the failure of the reactivity–selectivity principle with some of their data arises because they are reacting extremely reactive cations with nucleophiles. The rate data which they obtain are therefore a measure of some property of the nucleophiles alone, which they believe to be desolvation. They have also pointed out that the anomalous reactivity order for the nucleophiles also supports this view. A balanced argument would draw attention to this special reason for the failure of the RSP.'

In respect of these comments it will be extremely interesting to see if the Ritchie equation maintains its integrity, or if systematic deviations are noted which enforce its modification to include parameters which define a dependence of reactivity on selectivity. Again, however, we emphasise that if one accepts the assumption of the validity of equations (1) and (2), then the conclusions detailed in this paper inevitably follow, and that, to the best of the senior author's knowledge, here and in ref. 8, are the first time they have been pointed out.

It is also possibly relevant to mention that if indeed the rate data obtained by Ritchie are a measure of some property of the nucleophiles alone, all the cations following equation (1) would react at the same rate; this is not observed to be the case.

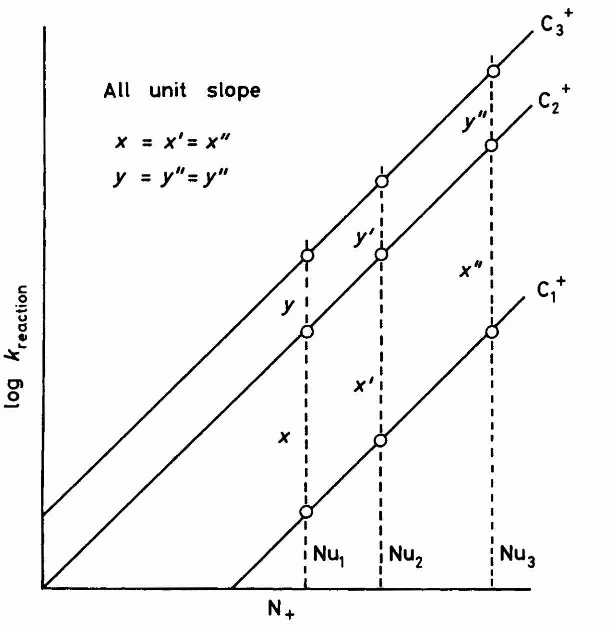

Figure 1. Perfect N_+ plots for three hypothetical cations, C_1^+, C_2^+, and C_3^+ reacting with three nucleophilic systems, Nu_1, Nu_2, and Nu_3

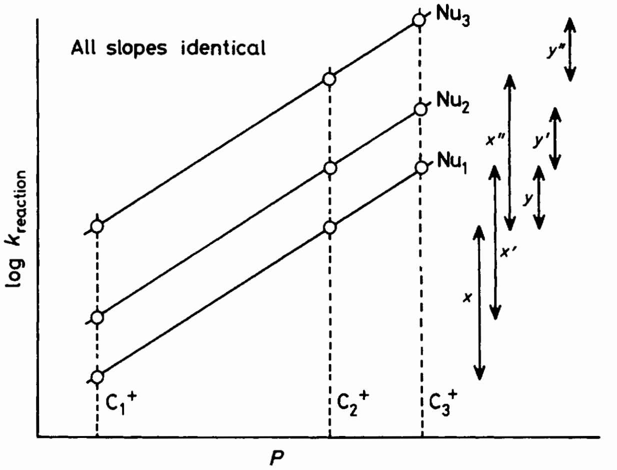

Figure 2. Hypothetical plots against parameter p for the systems in Figure 1. Note that the slopes must be identical if $x = x' = x''$ and $y = y' = y''$

which is of the form of a general free-energy relationship (LFER).

$$\log k_{reaction} = sp + \text{constant}. \qquad (2)$$

Such a set of parameters, p, would probably be Hammett σ values, when s would be equivalent to ρ, or represent some other property such as pK_a, or a set of $\log k$ values for reactions with a different nucleophilic system. Figure 2 shows the plots for the three nucleophilic systems and cations used in Figure 1, plotted against some such hypothetical parameter p, for which equation (2) holds true. This clearly demonstrates that, if the N_+ relationship is followed precisely by the three cations, then the slopes of these plots must all be the same. That is, the Cordes coefficient $C^{29,30}$ in equation (3) is infinitely large. Thus, for a

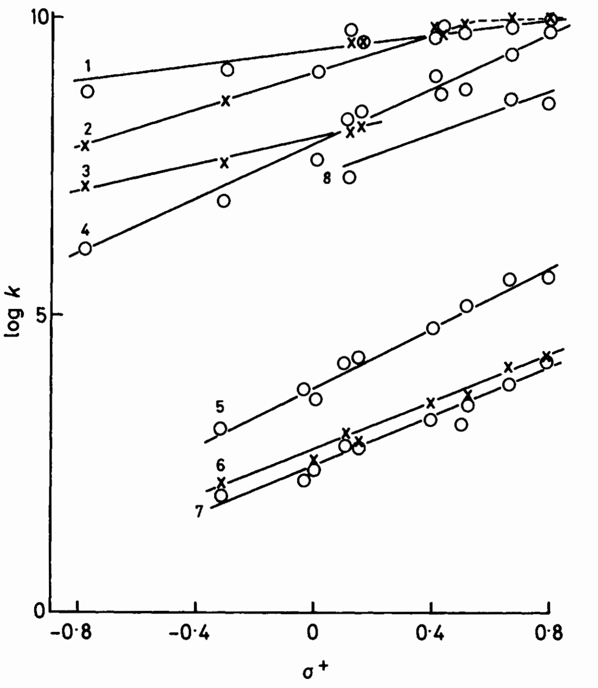

Figure 3. Reactions of nucleophiles with substituted benzene diazonium ions correlated with σ^+ values: (1) PhS^-(MeOH): substituents = p-NO_2, p-CN, p-PhCO, p-CO_2H, m-Cl, p-Cl, p-Br, H, p-Me, p-OMe; (2) N_3^-(DMSO): substituents = p-NO_2, p-CN, p-PhCO, p-CO_2H, m-Cl, p-Br, p-Cl, H, p-Me, p-OMe; (3) CN^-(DMSO): substituents = p-Br, p-Cl, p-Me, p-OMe; (4) N_3^-(MeOH): substituents = p-NO_2, p-CN, p-PhCO, p-CO_2H, m-Cl, p-Cl, p-Br, H, p-Me, p-OMe; (5) $OH^-(H_2O)$: substituents = p-NO_2, p-CN, m-CF_3, m-Cl, p-Cl, p-Br, H, p-CO_2^-, p-Me; (6) $PhSO_2^-$(MeOH): substituents = p-NO_2, p-CN, m-CF_3, m-Cl, p-Cl, p-Br, H, p-Me; (7) $CN^-(H_2O)$: substituents = p-NO_2, p-CN, m-CF_3, p-PhCO, m-Cl, p-Cl, p-Br, H, p-CO_2, p-Me; (8) $SO_3^{2-}(H_2O)$; substituents = p-NO_2, p-CN, p-Cl

$$\delta\sigma^+/\delta(d \log k/dN_+) = \delta N_+/\delta\rho = C = \text{infinity} \qquad (3)$$

series of cations following, for example, the Hammett–Brown equation,[31] equation (4), all the ρ values would be the same

$$\log k = \rho\sigma^+ + \log k_0. \qquad (4)$$

regardless of changes in nucleophile and/or solvent. However, the key point is that it has been demonstrated innumerable times (certainly too numerous to require referencing) that these are the very factors which do indeed cause ρ to vary!

It must be stressed that the paradox which thus arises can be instantly resolved by refusing to accept the legitimacy of equation (1), or equation (2), as expressed in for example the form of equation (4), or both.

As we have taken care to detail above, however, the majority of chemists would accept the validity of equation (1) in a large number, if not all, of such systems. They would also certainly agree that equations of the form of equation (4) would have variable slope values for different nucleophile systems, even if there was some argument about the exact form they should take.* It therefore seems relevant to at least inquire if the paradox can be resolved in an alternative manner. This alternative method is demonstrable by using actual experimental data for systems which have been shown to follow the N_+ relationship. From these data, a variety of plots can be constructed for which equation (2) is a general expression.

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* A number of approaches have been made to improving the Hammett equation, notably the Yukawa–Tsuno equation,[32] the Taft equation[33] and the Jencks–Young equation.[34]

Table 1. ρ Values for plots of log k_{reaction} against σ^+ for benzenediazonium ions

No.[a]	Nucleophilic system	ρ Value[b] (corr. coeff.)	No. of points
1	$PhS^-(MeOH)$[c]	0.79 (0.933)	10
2	$N_3^-(Me_2SO)$[d]	1.63 (0.981)	8
3	$CN^-(Me_2SO)$[d]	1.11 (0.991)	4
4	$N_3^-(MeOH)$[c]	2.36 (0.988)	10
5	$OH^-(H_2O)$[e]	2.54 (0.994)	9
6	$PhSO_2^-(MeOH)$[f]	2.04 (0.987)	8
7	$CN^-(H_2O)$[e]	2.05 (0.984)	10
8	$SO_3^{2-}(H_2O)$[g]	1.99 (0.986)	3

[a] See Figure 3. [b] See also ref. 8. [c] Ref. 16. [d] Ref. 9. [e] Ref. 15. [f] Ref. 12. [g] Ref. 17.

Table 2. Slope values for plots of log k_{reaction} against log $k_{P(OBu)_3}$ values for co-ordinated cyclic π-hydrocarbons[a]

No.[b]	Nucleophile[c]	Slope (corr. coeff.)	No. of points
1	PBu_3	1.05 (0.974)	7
2	$P(4\text{-}MeC_6H_4)_3$	1.36 (0.968)	5
3	PPh_3	1.34 (0.970)	13
4	C_5H_5N	1.05 (0.984)	5
5	Imidazole	1.62 (0.978)	4
6	$PhNH_2$	1.34 (0.999)	3
7	$P(C_2H_4CN)_3$	1.06 (0.999)	3
8	$P(OPh)_3$	1.18 (0.999)	3

[a] Data taken from ref. 27. [b] See Figure 4. [c] Acetone, acetonitrile, or nitromethane as solvent; see ref. 27.

Table 3. Slope values for plots of log k_{reaction} against pK_{R^+} values for tropylium ions

Nucleophilic system	Slope (corr. coeff.)	No. of points
$H_2O(H_2O)$[a]	−0.70 (0.977)	5
$OH^-(H_2O)$[a]	−0.73 (0.966)	5
$MeOH(MeOH)$[b]	−0.99 (0.984)	5
$MeO^-(MeOH)$[b]	−0.70 (0.979)	4

[a] Ref. 21; see also ref. 8. [b] Ref. 22; see also ref. 8.

Table 4. ρ Values for plots of log k_{reaction} against σ^+ for triarylmethyl cations

Nucleophilic system	ρ Value (corr. coeff.)	No. of points
$OH^-(H_2O)$[a]	0.57 (0.996)	4
$H_2O(H_2O)$[a]	0.42 (0.941)	4
$CN^-(H_2O)$[a]	0.51 (0.993)	3
$CN^-(DMSO)$[b]	0.72 (0.999)	3
$MeO^-(MeOH)$[b]	0.82 (0.996)	5
$CN^-(DMF)$[b]	0.71 (0.999)	3
$HOCH_2CH_2S^-(H_2O)$[c]	0.58 (0.996)	4

[a] Ref. 19. [b] Ref. 18. [c] Ref. 20.

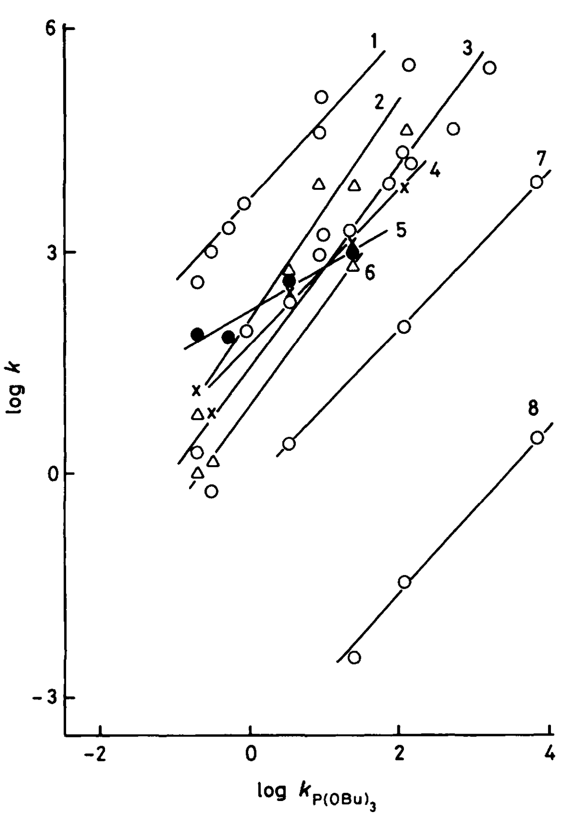

Figure 4. Reactions of nucleophiles with co-ordinated cyclic π-hydrocarbons correlated with log $k_{P(OBu)_3}$ values: (1) PBu_3: substrates = $Fe(CO)_3(C_6H_7)^+$, $Mn(CO)_2(NO)(6\text{-}PhC_6H_6)^+$, $Mn(CO)_2(NO)(6\text{-}MeC_6H_6)^+$, $Mn(CO)(NO)(PPh_3)(C_6H_7)^+$, $Fe(Cp)(C_7H_8)^+$, $Cr(CO)_3(C_7H_7)^+$, $Fe(CO)(NO)(PPh_3)(C_4H_4)^+$; (2) $P(4\text{-}MeC_6H_4)_3$: substrates = $Fe(CO)_3(C_6H_7)^+$, $Fe(CO)_3(2\text{-}MeOC_6H_6)^+$, $Mn(CO)_2(NO)(6\text{-}MeC_6H_6)^+$, $Mn(CO)_2(NO)(C_7H_9)^+$, $Cr(CO)_3(C_7H_7)^+$; (3) PPh_3: substrates = $Fe(CO)_3(C_6H_7)^+$, $Fe(CO)_3(2\text{-}MeOC_6H_6)^+$, $Mn(CO)_2(NO)(6\text{-}PhC_6H_6)^+$, $Mn(CO)_2(NO)(6\text{-}MeC_6H_6)^+$, $Mn(CO)(NO)(PPh_3)(C_6H_7)^+$, $Mn(CO)_2(NO)(C_7H_9)^+$, $Fe(C_6H_6)_2^{2+}$, $Ru(C_6H_6)_2^{2+}$, $Os(C_6H_6)_2^{2+}$, $Mn(CO)_2(PPh_3)(C_7H_8)^+$, $Cr(CO)_3(C_7H_7)^+$, $Fe(CO)_2(NO)(C_4H_4)^+$, $Fe(CO)(NO)(PPh_3)(C_4H_4)^+$; (4) C_5H_5N: substrates = $Fe(CO)_3(C_6H_7)^+$, $Fe(CO)_3(2\text{-}MeOC_6H_6)^+$, $Mn(CO)_2(NO)(6\text{-}PhC_6H_6)^+$, $Mn(CO)_2(NO)(6\text{-}MeC_6H_6)^+$, $Mn(CO)_2(NO)(C_7H_9)^+$; (5) imidazole: substrates = $Fe(CO)_3(2\text{-}MeOC_6H_6)^+$, $Mn(CO)_2(NO)(6\text{-}MeC_6H_6)^+$, $Mn(CO)_2(NO)(C_7H_9)^+$, $Fe(Cp)(C_7H_8)^+$; (6) $C_6H_5NH_2$: substrates = $Fe(CO)_3(2\text{-}MeOC_6H_6)^+$, $Mn(CO)_2(NO)(6\text{-}PhC_6H_6)^+$, $Mn(CO)_2(NO)(6\text{-}MeC_6H_6)^+$; (7) $P(C_2H_4CN)_3$: substrates = $Mn(CO)_2(NO)(C_7H_9)^+$, $Mn(CO)_3(C_7H_8)^+$, $Mn(CO)_2(PPh_3)(C_7H_8)^+$; (8) $P(OPh)_3$: substrates = $Fe(CO)_3(C_6H_7)^+$, $Fe(CO)_3(2\text{-}MeOC_6H_6)^+$, $Mn(CO)_3(C_7H_8)^+$

Table 1 and Figure 3 give the results for Hammett–Brown σ^+ plots using data for benzenediazonium ions, and illustrate that the ρ values are by no means constant. For co-ordinated cyclic π-hydrocarbons, log k_{reaction} values can be plotted against log k values for reaction with $P(OBu)_3$; the results are shown in Table 2 and Figure 4. Results for tropylium ions are collected in Table 3, and data for limited series of triarylmethyl cations are listed in Table 4. Within each of these four sets of correlations exists considerable variations in slope parameters, as expected from the range of solvents and reagents used.

What is therefore of fundamental importance is that the N_+ relationship expresses the constant selectivity observed for these cations over the wide reactivity range encompassed by such correlations, while within them there is sufficient scatter over much shorter ranges of reactivity to allow for the variations in slopes, and thus selectivities, as described and calculated above. It is in consequence quite clearly the variation in slope of the resultant LFERs that accounts for the range of selectivity ratios observed in this area of reactivity, and not any intrinsic link between reactivity (or stability) and selectivity.* Why then

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* A referee writes as follows: 'I am not sure what is meant by this statement. Changes in reactivity may or may not cause changes in the selectivity, but any such change will be reflected in the slopes of the LFER. Thus, it is wrong to imply that the changes in the selectivity ratios arise from variation in the slope of LFER; they are the same thing. What is important to point out is that specific effects that lead to variation in the rate have a greater effect on slopes when incurred over a short reactivity range, than when measured over a large change in reactivity.'

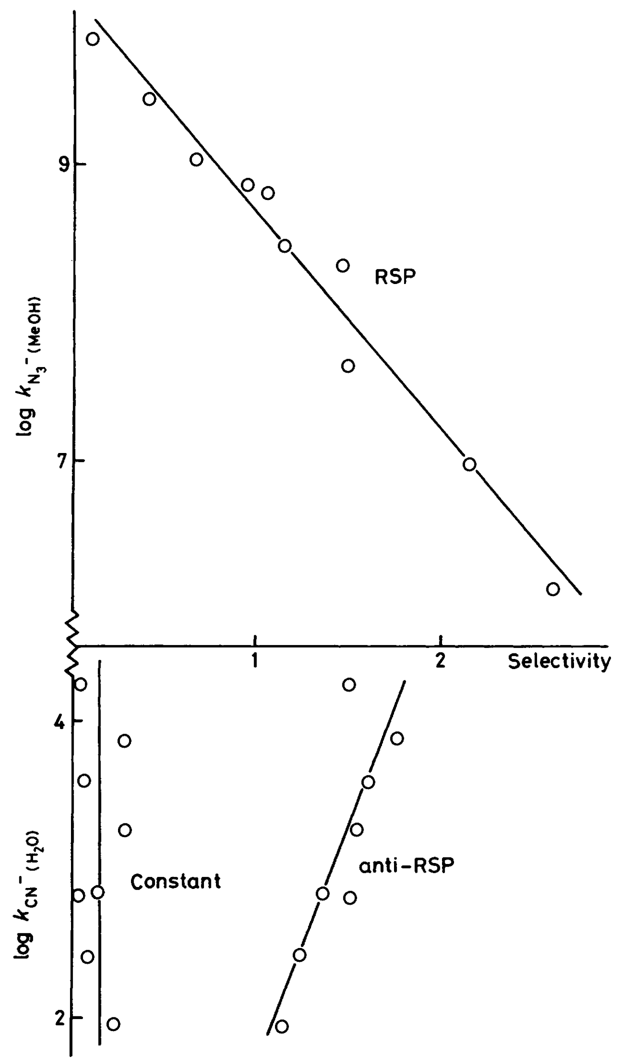

Figure 5. Reactivity–selectivity plots for benzenediazonium ions: RSP, $\log k_{N_3^-(MeOH)}$ *vs.* $\log [k_{PhS^-(MeOH)}/k_{N_3^-(MeOH)}]$; anti-RSP, $\log k_{CN^-(H_2O)}$ *vs.* $\log [k_{OH^-(H_2O)}/-k_{CN^-(H_2O)}]$; constant selectivity, $\log k_{CN^-(H_2O)}$ *vs.* $\log [k_{PhSO_2^-(MeOH)}/k_{CN^-(H_2O)}]$

should it be otherwise for any other area of aliphatic nucleophilic substitution, where, for example, reaction proceeds on cations which represent high energy intermediates, rather than stable reactants?

It is possible, following the method of Bordwell,[35] to construct reactivity–selectivity plots from these data, which exhibit any desired form, either of apparent RSP or anti-RSP character, or constant selectivity. This is demonstrated in Figures 5 and 6 for Ritchie's data on benzenediazonium ions[12,15,16] and for the more recent data from Sweigart and co-workers[27] for co-ordinated cyclic π-hydrocarbons. It is not necessary to predict a limiting value of unity for the selectivity factors; crossovers of the LFERs lead to inversion of selectivities, as seen for $\log (k_{PPh_3}/k_{C_5H_5N})$ in Figure 6. In precisely the same way, a closely related example[36] concerns the addition of diarylcarbenium ions to alkenes. Variation in slope of the resultant LFERs gives rise to apparent RSP, anti-RSP, and constant selectivity behaviour. Also of significance here is the fact that the selectivity ratios calculated from the individual LFERs are precisely those, within experimental error, which arise directly from the corresponding competitive reaction between alkene and electrophile pairs.[37]

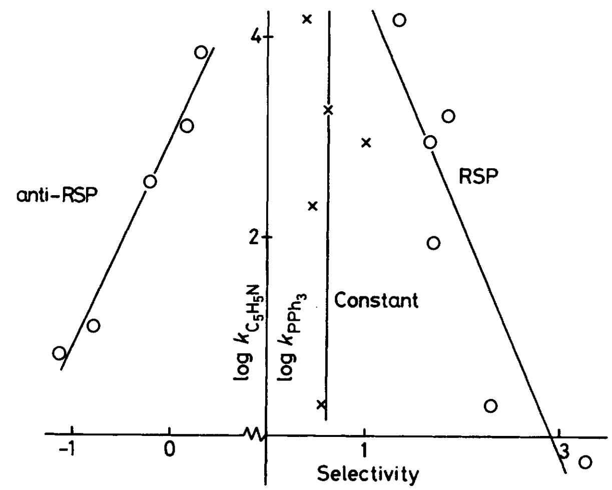

Figure 6. Reactivity–selectivity plots for co-ordinated cyclic π-hydrocarbons: RSP, $\log k_{PPh_3}$ *vs.* $\log (k_{PBu_3}/k_{PPh_3})$; anti-RSP, $\log k_{C_5H_5N}$ *vs.* $\log (k_{PPh_3}/k_{C_5H_5N})$; constant selectivity, $\log k_{PPh_3}$ *vs.* $\log [k_{P(4-MeC_6H_4)_3}/k_{PPh_3}]$. The selectivity factors for the plots in Figures 5 and 6 were calculated from the difference in log rate constants for each reaction. Where these reactions are measured in different solvents, the selectivity factor obtained cannot directly correspond to the result of a competition experiment, which uses a common solvent

Conclusion

As Ritchie stated in a recent review,[7] the 'N_+ relationship is certainly not the final work on nucleophilic reactivity.' However, any theory relating to nucleophilic reactivity must still be able to incorporate the N_+ relationship as it stands at present, as well as the varying stability–selectivity behaviour. Recognising that reactivity–selectivity plots result from changes in the slope of LFERs, and not from any intrinsic link between the two properties, would help to simplify arguments in this complex region of chemistry. In recent years, Jencks has examined the reactions of 1-arylethyl cations, and has concluded[38] that changes in mechanism and diffusion-controlled reactions of intermediate cations allowed a full interpretation of the results. Independently, Ta-Shma and Rappoport reached the same conclusions[3] from their re-examination of trapping studies on solvolysis reactions performed by many workers. While continuing to use the term 'reactivity–selectivity relationship' in an illustrative fashion, these workers appear close to agreement with Arnett[2] and Bordwell, that the use of the RSP as a predictive or interpretative tool should be discontinued, a view we have also shared for some time.[8,39] Discussion now seems to be centred on the question of whether the principle exists at all, or whether it exists, but is frequently and systematically masked by other influences, particularly by those at work within two-dimensional energy surfaces of Albery–More O'Ferrall–Jencks form. In this regard, we agree completely with the statement of Arnett,[2] that 'nothing more is gained by inferring the transition state on a complex hyperspace from a plot of $\Delta G\ddagger$ *vs.* $\Delta G°$ than is available from the linear free-energy correlation itself which, moreover, has true predictive value.' Of course, in the limiting case that no experimental demonstration of the existence of the reactivity–selectivity principle exists at all, then in that event the existence of the principle itself becomes a philosophical rather than a scientific question,[40,*] associated with the impossibility of ever proving a negative proposition.

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* Various sources may be found for contrasting views from 'only that which is observable is significant' to 'in principle it is quite wrong to try founding a theory on observable data alone. In reality the very opposite happens. It is the theory which decides what we can observe.'

Acknowledgements

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