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HAMMETT ρ VALUES

ARE THEY AN INDEX OF TRANSITION STATE CHARACTER?

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Abstract—The reactivity-selectivity principle states that reactivity and selectivity amongst a series of similar reactions should correlate inversely. Yet this is rarely found to be the case when the selectivity index is the Hammett ρ value for a reaction series. This observation then calls into question the practice of using ρ as an index of transition state character insofar as "early" vs "late" transition states are concerned. Or, if ρ *is* considered as a transition state index, the practice of assigning progressively later (more product-like) transition states to slower reactions must be questioned, despite a multitude of non-LFER observations to the contrary. In resolving this paradox, we focus attention on differences in efficiency of charge transmission from reaction centre to substituent between similar reaction series. For a few reactions where sufficient data are available, it is found that once raw ρ values are corrected for variation in transmission efficiency, they indeed follow the order predicted by the reactivity-selectivity principle.

It is almost a tenet of organic chemistry that substrates or substrate sets displaying high reactivity towards a given reagent should exhibit a low degree of intramolecular or intermolecular selectivity, and vice versa. The expectation of this inverse relationship forms the basis of the reactivity-selectivity principle (RSP).[1-3] Recently the veracity of the principle has been questioned, principally by Johnson,[4-7] with particular reference to linear free energy relationships such as the Hammett equation.[4] The ρ value for a reaction series is of course a direct measure of intermolecular selectivity and should, according to the RSP, correlate inversely with the intrinsic reactivity of members of the series when two or more similar sets of suitably substituted aryl substrates react with a common reagent (Fig. 1). Johnson claims that this expectation has not been realised, and that constant selectivity despite changes in reactivity is apparently the rule as far as Hammett correlations are concerned[4] (Fig. 2).

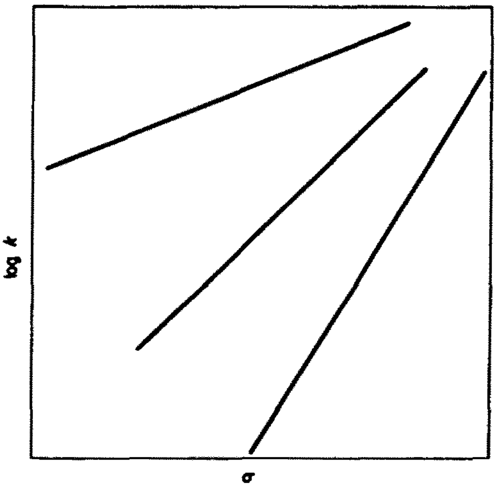


Fig. 1. A hypothetical situation wherein three similar Hammett series comply with the RSP.

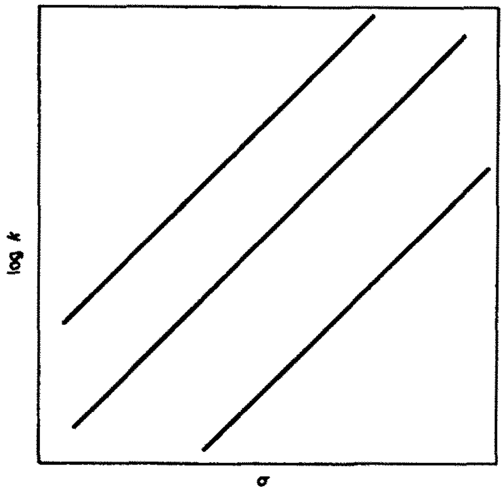


Fig. 2. An illustration of the situation commonly met with in practice (see Ref. 4 for examples).

A corollary of the RSP is that a substituent which stabilizes products relative to reactants and in lowering the energy of the transition state relative to reactants increases the reactivity, should lead to the transition state occurring earlier on the reaction coordinate (more reactant-like), and vice versa for substituents which destabilize products relative to reactants. The extension from the RSP to the corollary concerning transition state structures is not implicit in the RSP itself, but such considerations form the basis of the alternative Bell–Evans–Polanyi (BEP),[8] Hammond–Leffler,[9] or Extended Hammond[10] postulates, each of which leads to the prediction of RSP behaviour. In view of the frequently ignored constraints imposed in the original Hammond treatment, which often lead to misuse,[11] we will refer to this concept as the BEP. Thus in an ionic reaction, if the Hammett ρ is a measure of substituent stabilization of charge at the reaction centre in the transition state vs that in the initial state, it should also be an index of transition state character, but Johnson's observations lead him to also cast doubt on this.[4]

Indeed, he and others[12] question whether the BEP and the existence of linear $\log k$ vs σ plots are compatible in that reactivity and thus transition state character should be continually changing along a given reaction series so long as ρ is not zero. This paradox has however been nicely resolved by Pross,[2] who points out that the BEP considers only transition state structural changes parallel to the reaction coordinate, and is thus not appropriate for multicentre reactions. Of greater relevance are Thornton's rules wherein substitutent interactions with stable (perpendicular) modes are also considered,[13,14] and if roughly equal substituent effects on parallel and perpendicular modes are postulated,[15] constant length of the reacting bond nearest to the substituent can be understood.[2] This then allows rationalization of constant ρ within a Hammett series. However we may still write in terms of early and late transition states with the understanding that we are referring to bond length *ratios* of partial bonds and not absolute lengths. For instance, in the transfer in eqn (1),

$$A-B+C \longrightarrow A...B...C \longrightarrow A+B-C \quad (1)$$

substitution in C (to give C^1) such that the transition state and B – C product are stabilized will, if equal parallel and perpendicular perturbations are allowed, have no effect on the B...C bond length, but will shorten the A...B partial bond to give A..B...C^1 as the resultant. In terms of the bond length ratio, this is an earlier transition state than the symmetrical species in eqn (1). The use of two-dimensional "energy profiles" for multicentre reactions is thus seen to be misleading if understanding at an advanced level is required, since the substituent effect manifested perpendicular to the reaction coordinate is altogether ignored in such diagrams. We shall not consider this point further however, except to remark that curvature has been detected in two Hammett series involving proton transfers,[16] and this may be understood in terms of the Marcus theory of proton transfer.[17] We take it for granted that transition state character does change with changing σ in a Hammett series in view of the extensive isotope effect evidence to this effect.[18] Some cases where hydrogen isotope effects are relatively insensitive to reactivity changes[19] can however be understood at least qualitatively in terms of Marcus theory[20] or in other ways.[21] Other criticisms of Johnson's views have been published, with reference to specific issues.[22]

The slopes of Hammett plots

One case which will not be dealt with extensively is that where a given set of *m*- and *p*-substituted ArX compounds is treated with a set of reagents $R_1, R_2 \ldots$ of a similar type. Rho values which do not accord with the predictions of the RSP are sometimes observed, and the apparently anti-BEP consequences have been examined. One rationalization of anomalies was couched in terms of variable steric requirements of the reagents,[23] but the theory was developed in terms of parallel effect domination of geometric change, and Thornton has now allowed at least an equal role to perpendicular effects in appropriate cases.[15] However the general theme of the argument should retain its validity since an increase in the steric requirements of C in an eqn (1) transfer should by itself lead to an overall looser transition state when viewed in terms of perpendicular effects, i.e. one that is neither more product-like nor more reactant-like, so that steric and electronic effects on the parallel mode will remain important, yielding anti-BEP results in some cases. For instance, hindered bases are kinetically more effective in deprotonating methylcreatininium ion than is expected on the basis of their p*K*'s.[24] The relevant hydrogen isotope effects are however smaller than expected, which could mean that the proton is more transferred than when unhindered bases of the same kinetic basicity are employed.

However, when a common reagent R undergoes reaction of a common type with similar but different sets of *m*- and *p*-substituted aryl series, ArX, ArY,..., differential steric interactions between reagent and substituents will be absent, whilst differential interactions between R and X, Y,... may be negligible. The discrepancy between the frequently observed behaviour depicted in Fig. 2, and the behaviour expected on the basis of simple application of the RSP and the BEP (Fig. 1) must be rationalized without recourse to steric effects if one holds to the belief that transition state character is a function of reactivity and is determinant of selectivity. A simple example will suffice to show that use of the observed Hammett ρ value can be grossly misleading as far as assessment of transition state character is concerned, when systems in the present category are considered.

The ρ value for alkaline hydrolysis of ethyl benzoates, $ArCO_2Et$, is 2.54 whilst that for arylacetates $ArCH_2CO_2Et$ is 0.824.[25] This could naively be taken as an example of the operation of the RSP, since $PhCH_2CO_2Et$ is 17 times more reactive than $PhCO_2Et$ towards alkaline hydrolysis.[25] Would it then be in order to take the next step and assert that the $PhCO_2Et/OH^-$ transition state possessed a higher degree of negative charge at the reaction centre (more product-like, or rather, more tetrahedral intermediate-like) on the basis of the ρ values and the relative reactivities?

It would most definitely not be in order. If it is accepted that the ρ for the $ArCO_2Et$ series is a measure of the amount of negative charge able to be stabilized by electron-withdrawing groups, it does not follow that ρ for the $ArCH_2CO_2Et$ series is a similar measure, for even were the amount of charge the same, it would not be transmitted to the ring substituents with equal efficiency, since the extra methylene in the latter series acts as a damping group.[26] Yet an examination of Johnson's review[4] reveals that in many cases where anti-BEP behaviour is claimed, the transmission efficiencies are most unlikely to be equal, meaning that the several ρ values are not indexes of reaction centre charges. Pross has also commented on this fact.[2]

It is the purpose of the present paper to develop a simple methodology to allow correction of raw Hammett ρ values for variable transmission factors. The corrected ρ values should then reflect transition state charges and structures, and only then should they be used in deciding whether or not the BEP corollary to the RSP has any validity. If this is the case the RSP itself must be generally valid, with the proviso that the raw Hammett ρ value, while existing as an operational measure of selectivity, may not always have theoretical significance as far as transition state structures are concerned. Finally, the method is applied to the distressingly few examples for which suitable experimental results are available.

Evaluation of transmission efficiencies. The ionization of benzoic acids in water, eqn (2) is the model reaction for the evaluation of σ constants.[27] The substituent constant

$$\mathrm{ArCO_2H} \longrightarrow \mathrm{ArCO_2^-} + \mathrm{H^+}(\rho_0{}^{m}) \qquad (2)$$

$\rho_0{}^{m}$ is arbitrarily assigned a value of 1.00 for this purpose. The σ values can then be used to obtain $\rho_x{}^0$ for a rate series, eqn (3) in which the reaction centre being modified is directly bonded to the ring. The latter proviso

$$\mathrm{ArX} + \mathrm{R} \longrightarrow \mathrm{ArY} + \mathrm{S}(\rho_x{}^0) \qquad (3)$$

is made so as to ensure equality of transmission effects, but in the general case we must write eqn (4) in

$$\rho(\text{obs.}) = \tau\rho_c \qquad (4)$$

which ρ_c is an index of the amount of charge generated at the reaction centre upon reaction, and τ is a transmission coefficient expressing the relative efficiency with which that charge is transmitted to the substituents. We set ρ_c and τ equal to unity for the model reaction (eqn 2), so if $\tau = 1$ for eqn (3) also, then $\rho_x{}^0$ will be $\rho_c{}^0$, a direct measure of the fractional charge on the reaction centre in the transition state, relative to an assumed value of unity for benzoate ion.

Now we insulate the ring and the reaction centre in eqn (3) by a non-reacting group G, which exerts no extra steric effects (eqn 5). If τ_G is the transmission coefficient for G, then

$$\mathrm{ArGX} + \mathrm{R} \longrightarrow \mathrm{ArGY} + \mathrm{S}(\rho_x{}^G) \qquad (5)$$

$\rho_c{}^G$ as a measure of the transition state charge is given by eqn (6), where $\rho_x{}^G$ is the observed ρ value based on the benzoic acid σ scale. Thus in comparing reaction series (3)

$$\rho_x{}^G = \tau_G\rho_c{}^G \qquad (6)$$

and (5) from the point of view of the respective transition state charges, the parameters for comparison must be $\rho_x{}^0$ and $\rho_x{}^G/\tau_G$, so that evaluation of τ_G is required.

Consider the ionization of the carboxylic acids $\mathrm{ArGCO_2H}$ in water (eqn 7), where the observed ρ value, $\rho_G{}^M$, is based on the benzoic acid σ scale. By analogy with the benzoic

$$\mathrm{ArGCO_2H} \longrightarrow \mathrm{ArGCO_2^-} + \mathrm{H^+}(\rho_G{}^M) \qquad (7)$$

acid series, ρ_c for this process is assumed to be unity, since unit negative charge is generated in both series, and so τ_G can be simply evaluated via eqn (4) as eqn (8). Thus

$$\tau_G = \rho_G{}^M \qquad (8)$$

$\rho_c{}^G$ is given by eqn (9) as the ratio of the observed ρ value

$$\rho_c{}^G = \rho_x{}^G/\rho_G{}^M \qquad (9)$$

for the reaction series and the observed ρ value for a model carboxylic acid ionization, both ρ values being based on benzoic acid σ constants. Thus in general, eqn (9) may be used to obtain ρ_c as in index of transition state charge development. Thus, returning to the earlier example,

$$\rho_c = \frac{\text{obs. } \rho \text{ for reaction in question}}{\text{obs. } \rho \text{ for suitable carboxylic acid ionization}} \qquad (9)$$

$\mathrm{ArCO_2H}$ ionization would be used as the suitable model reaction for hydrolysis of $\mathrm{ArCO_2Et}$ esters, whilst $\mathrm{ArCH_2CO_2H}$ ionization ($\rho_G{}^M = 0.56$)[25] would be used as the model for ester hydrolysis in the $\mathrm{ArCH_2CO_2Et}$ series. In this way the methylene damping factor may be taken into account, assuming that it remains constant, and hopefully the respective ρ_c values will then provide information as to relative transition state structures. We shall return to these specific examples later.

An alternative is to apply different but proportional σ scales. For the benzoic acids, σ is defined by eqn (10)

$$\sigma = (1/\rho_0{}^M)\log K/K_0 \qquad (10)$$

with $\rho_0{}^M = 1.00$. For the $\mathrm{ArGCO_2H}$ model series we define a new σ_G scale via eqn (11), which means setting $\rho_G{}^M = 1.00$. Reactions

$$\sigma_G = \log K^G/K_0{}^G \qquad (11)$$

in the eqn (3) series are then correlated with the benzoic acid σ to obtain $\rho_x{}^M$, as before. Reactions in the eqn (5) series are correlated with σ_G and thus the observed ρ is equal to ρ_c, and is not contaminated by the transmission coefficient. In modifying the σ scale from literature data, eqn (12) is the appropriate expression for σ_G, where σ pertains to benzoic acid ionization, and the ρ values on the right hand side are based on the benzoic acid σ values on the right hand side are based on the benzoic acid σ scale. Both of the alternatives

$$\sigma_G = \frac{\rho \text{ for suitable model ionization}}{\rho \text{ for benzoic acid ionization}} \times \sigma \qquad (12)$$

for cancelling out the effects of variable transmission have been discussed from the point of view of substituent effects in heterocyclic reactions,[28,29] a question that we will consider later.

Consideration of substituent effect transmission is not novel.[30-33] However none of the previous treatments has as its aim the evaluation of ρ parameters for the purpose of elucidating transition state structures. In the following sections we examine some reaction series in seeking the inverse correlation between ρ_c and intrinsic reactivity demanded by the RSP and the BEP.

The observed ρ values quoted are based throughout on the McDaniel and Brown benzoic acid σ scale,[27] since "sliding"[34] or "best-value"[25] σ scales are inappropriate in the present context. Values of $\rho_G{}^M$ for various model acid ionizations are shown in Table 1 ($\mathrm{H_2O}$ solvent) and Table 2 (50% $\mathrm{EtOH/H_2O}$).

RESULTS AND DISCUSSION

E2 eliminations. One relevant paper not discussed by Johnson[4] concerns a multiple substitution investigation of the *E*2 reactions of 2-arylethyl arenesulphonates (eqn 13).[48]

$$\mathrm{XC_6H_4CH_2CH_2OSO_2C_6H_4Y} + t\text{-}\mathrm{BuO^-} \longrightarrow$$
$$\mathrm{XC_6H_4CH{=}CH_2} + \mathrm{YC_6H_4OSO_2^-} + t\text{-}\mathrm{BuOH}. \qquad (13)$$

Table 1. Acidities and Hammett ρ values for ionization of carboxylic acids in water at 25°

Acid series	$\rho_G{}^M$	pK_a[a]	Ref.[b]
2-Furanyl	1.396	3.128	36
$ArOCH_2CO_2H$	0.341	3.17	37
2-Thienyl	1.223	3.53	29
$ArSCH_2CO_2H$	0.300	3.567	38
o-Methylbenzoic	1.22	3.90	39
$ArCO_2H$	1.00	4.20	25
$ArCH_2CO_2H$	0.562	4.31	25
$ArCH{=}CHCO_2H$ (*trans*)	0.466	4.438	40
$ArCH{=}CHCO_2H$ (*cis*)	0.643	—	40
trans-2-Arylcyclopropyl	0.182	4.57	41
$ArCH_2CH_2CO_2H$	0.212	4.709	25

[a] Acidity of parent (unsubstituted) member of series.
[b] Some ρ values and acidities have been taken from compilations in Refs. 25, 27, 30, 31 and 35.

Table 2. Acidities[a] and Hammett ρ values for ionization of carboxylic acids in 50% (vol./vol.) EtOH–H_2O at 25°

Acid series	$\rho_G{}^M$	pK_a[a,b]	Ref.
$ArC{\equiv}CCO_2H$	0.69	3.40	42
2-Thienyl	1.677	5.15	29
2,6-Dimethylbenzoic	1.40	5.18	43
$ArCH{=}CHCO_2H$ (*cis*)	0.77[c]	5.22	44
p-$ArC_6H_4CO_2H$[d]	0.437	5.66	25
$ArCH{=}CHCO_2H$ (*trans*)	0.68	5.68	44
$ArCO_2H$	1.57	5.75	- 25,45
o-Methylbenzoic	1.672	5.76	46
trans-2-Arylcyclopropyl	0.473	5.783	47
$ArCH_2CH_2CO_2H$	0.344	5.887	47
cis-2-Arylcyclopropyl	0.436	6.331	47

[a] Apparent pK_a values.
[b] Apparent pK_a of parent (unsubstituted) acid.
[c] *Para*-substituents only.
[d] In 50% *n*-$BuO(CH_2)_2OH$–H_2O, in which solvent ρ for the $ArCO_2H$ series is 1.42 (Ref. 25).

Table 3. *E*2 rates and ρ parameters for reactions of 2-arylethyl arenesulphonates, $XC_6H_4CH_2CH_2OSO_2C_6H_4Y$, with t-BuOK in t-BuOH at 40° (Ref. 48)

Substrate series	ρ_x	k_0, l mol^{-1} s^{-1} (X = H)
$ArCH_2CH_2OSO_2C_6H_4NO_2(p)$	2.03	4.17×10^{-2}
$ArCH_2CH_2OSO_2C_6H_4Br(p)$	2.36	1.20×10^{-2}
$ArCH_2CH_2OSO_2Ph$	2.50	6.17×10^{-3}
$ArCH_2CH_2OSO_2C_6H_4Me(p)$	2.49	4.01×10^{-3}
	ρ_y	k_0, l mol^{-1} s^{-1} (Y = H)
m-$ClC_6H_4CH_2CH_2OSO_2Ar$	0.94	4.72×10^{-2}
p-$ClC_6H_4CH_2CH_2OSO_2Ar$	1.01	2.07×10^{-2}
m-$MeOC_6H_4CH_2CH_2OSO_2Ar$	1.06	9.77×10^{-3}
$PhCH_2CH_2OSO_2Ar$	1.08	6.17×10^{-3}
p-$MeC_6H_4CH_2CH_2OSO_2Ar$	1.24	1.99×10^{-3}
p-$MeOC_6H_4CH_2CH_2OSO_2Ar$	1.24	1.17×10^{-3}

The measured selectivities ρ_x (Y constant) and ρ_y (X constant) clearly decrease with increasing reactivity which, for the ρ_x series, is taken as the rate constant for the X=H compound for each Y, and for the ρ_y series, is taken as the rate constant for the Y=H compound for each X. Data are given in Table 3. Three points require emphasis. The first is that the order of ρ values is as expected for the degree of carbanionic charge in the transition state[14,15,49] (more for electron-withdrawing groups on the β-carbon; and more for poorer leaving groups). The second is that the k_0 values are valid measures of intrinsic reactivity in that there is no cross-over of Hammett plots in either of the ρ_x and ρ_y series. Thus any rate constant for the substituted compounds could have been used as a measure of reactivity. Thirdly, there is no real need in this system to consider transmission factors, so that the observed ρ values may validly be compared.

Yano and Oae[50] have reported results for eliminations from $ArGCH_2CH_2CH_2Br$ compounds using t-BuOK/t-BuOH. For G = O, $\rho = 0$, (non-selective reaction) whilst for G = S, $\rho = 0.37$. In accordance with the RSP the oxygen compounds are some 2.5 times more reactive than the sulphur compounds. Transmission factors need not be considered here either since the appropriate model reactions, the respective ionizations of $ArOCH_2CO_2H$ and $ArSCH_2CO_2H$ exhibit almost identical ρ values (Table 1).

The situation is markedly different when elimination from $ArGCH_2CH_2Cl$ (t-BuOK/t-BuOH) is considered.[51] For G = O, $\rho = 1.33$, and for G = S, $\rho = 1.98$. Yet the more selective sulphur compounds are the more reactive, by a factor of 550 for Ar = Ph. This is definitely an anti-RSP phenomenon if the observed ρ values are taken as the relative ρ_c parameters as was done above. However the heteroatoms are now bonded directly to a reacting atom, the β-carbon, whereas this is neither the case in the $ArGCH_2CH_2CH_2Br$ system, nor in the model reactions. It is reasonable to assume that C_β in the *E*2 transition state will be carbanionic,[14,15,49] and direct resonance interaction between it and the heteroatom is now permitted. d-Orbital resonance has been involved to explain the greater reactivity of the sulphur compounds; the same phenomenon would lead to sulphur being the better transmitter of C_β charge to the ring substituents.[51] Thus the near equality of τ_G values for the model acid ionizations, ensured by the methylene group interposed between the ring and the reaction centre, is clearly not appropriate in the present system, and direct application of the RSP is invalid. While MO calculations suggest that *d*-orbital resonance stabilization of the $HSCH_2^-$ carbanion is unimportant,[52] the results of measurements of carbon acid acidities in DMSO strongly suggest that divalent sulphur stabilizes adjacent carbanionic charges by some sort of a conjugative effect.[53]

The *E*2 reactions of 5-substituted 2-(2-thienyl) ethyl bromides and tosylates; Th–CH_2CH_2X where Th = 5 - substituted - 2 - thienyl and X = Br, OTs; may be compared with those of ring-substituted 2-arylethyl bromides and tosylates; $YC_6H_4CH_2CH_2X$. The observed ρ parameters and k_0 values (for unsubstituted compounds) are shown in Table 4. With the aid of data in Table 1, ρ_c values may be calculated using eqn (9), and these are also tabulated. Thus while ρ_{obs} values exhibit no relationship with regard to k_0 values, ρ_c increases as k_0 decreases, in accordance with the BEP.

Diphenyldiazomethane esterifications. The rate-determining step in the esterification of carboxylic acids by diphenyldiazomethane (DDM) has been established as simple proton transfer.[56] In Tables 5 and 6 are shown observed

$$ArGCO_2H + Ph_2CN_2 \longrightarrow ArGCO_2CHPh_2 + N_2$$

ρ values for various relay groups G, and second-order

Table 4. Rate constants and Hammett ρ values for $E2$ elimination from 2-thienylethyl and 2-arylethyl bromides and tosylates with NaOEt–EtOH at 50°

	10^3k_0[a]	ρ_{obs}[b]	ρ_c[c]	Ref.
2-Thienylethyl bromides	9.46	2.12	1.74	54
2-Arylethyl bromides	3.42	1.97	1.97	55*a*
2-Thienylethyl tosylates	1.32	2.485	2.03	54
2-Arylethyl tosylates	1.05	2.27[d]	2.27	55*b*

[a] For unsubstituted compound, in $1\ \text{mol}^{-1}\ \text{s}^{-1}$.

[b] Based on benzoic acid $\text{p}K_a$'s in H_2O.

[c] Obtained by dividing ρ_{obs} by 1.223 (thienyl series) and 1.00 (2-arylethyl series) (see Table 1).

[d] At 30°, likely to be a little smaller at 50°.

Table 5. Rate constants[a] and Hammett ρ_{obs} values for esterification of carboxylic acids by DDM in EtOH at 30°

Acid series	ρ_{obs}	k_2^0	ρ_c[b]	Ref.
2-Furanyl–CO_2H	0.932[c]	6.82	0.67	36
$ArOCH_2CO_2H$	0.247	6.60	0.72	57
$ArCH_2CO_2H$	0.390	1.08	0.69	57
$ArCO_2H$	0.917	0.991	0.92	45, 57, 58
trans-$ArCH{=}CHCO_2H$	0.403	0.972	0.86	57
o-Methylbenzoic	0.940	0.939	0.77	46
$ArCH_2CH_2CO_2H$	0.212	0.735	1.00	57

[a] For parent (unsubstituted) acid, in $1\ \text{mol}^{-1}\ \text{min}^{-1}$.

[b] Based on ρ_G^M values in H_2O (Table 1).

[c] At 24.85°.

Table 6. Rate constants[a] and Hammett ρ_{obs} values for esterification of carboxylic acids by DDM in EtOH at 30°

Acid series	ρ_{obs}	k_2^0	ρ_c[b]	Ref.
$ArC{\equiv}CCO_2H$	0.310	19.6	0.45	59
2,6-Dimethylbenzoic	0.685	3.64	0.49	43
p-$ArC_6H_4CO_2H$	0.208	1.00	0.48	57
$ArCO_2H$	0.917	0.991	0.58	45, 57, 58
trans-$ArCH{=}CHCO_2H$	0.403	0.972	0.59	57
o-Methylbenzoic	0.940	0.939	0.56	46
$ArCH_2CH_2CO_2H$	0.212	0.735	0.61	57

[a] For parent (unsubstituted) acid, in $1\ \text{mol}^{-1}\ \text{min}^{-1}$.

[b] Based on ρ_G^M values in 50% EtOH/H_2O (Table 2).

rate constants for Ar = Ph, which are taken for the moment as measures of intrinsic reactivity. There is no relationship between ρ_{obs} and k_2^0. However when ρ_c values are calculated in the usual way using acid ionization ρ_G^M values in H_2O (Table 5) and EtOH/H_2O (Table 6), there is a general trend in that ρ_c exhibits an overall increase as reactivity decreases, as required by the BEP. Thus the degree of proton transfer appears to become less extensive as reactivity increases. Over the range of acid strengths available the Brönsted plot of $\log k_2^0$ vs $\text{p}K_a$ is however linear (slope = − 0.6), whereas curvature would be expected were gross changes in transition state character occurring. Such curvature is clearly apparent in the Brönsted plot resulting from deployment of a far wider range of acid strengths.[16b] The linearity of the present plots argues against intrusion of steric effects except perhaps for *o*-methylbenzoic acid, which is markedly less reactive than expected (while 2,6-dimethylbenzoic acid is normal). It is noteworthy that the reactivity-selectivity data for *o*-methylbenzoic acid in Tables 5 and 6 are somewhat anomalous.

The almost perfect inverse correlation of k_2^0 and ρ_c is unfortunately undermined by two observations. The first concerns the reactivity range, which is small—only 46-fold from the fastest to the slowest reaction considered. The second is that the plots of $\log k$ vs σ for each acid series exhibit a number of crossovers within the σ range (*p*-Me to *p*-NO_2) employed. Thus it is somewhat misleading to insist that k_2^0 is a satisfactory reactivity index, as a different order of reactivities could be obtained were *p*-methyl- or *p*-nitro-substituted acids employed as standards for obtaining reactivity indexes. Nonetheless when we consider the extremes—the $ArCH_2CH_2CO_2H$ series on the one hand and $ArC{\equiv}CCO_2H$ series on the other—we find no crossover within the σ range and, as shown in Fig. 3, an anti-RSP pattern when the unadjusted Hammett plots are viewed. When the respective σ scales are adjusted to give σ_G values according to eqn (12) the result shown in Fig. 4 is in accordance with the RSP. There is no practical possibility of a crossover. The anomalously high ρ_{obs} for the $ArC{\equiv}CCO_2H$/DDM series is thus seen to be a consequence of the acetylenic moiety being a better transmitter of reaction centre charge than is the $-CH_2CH_2-$ group.

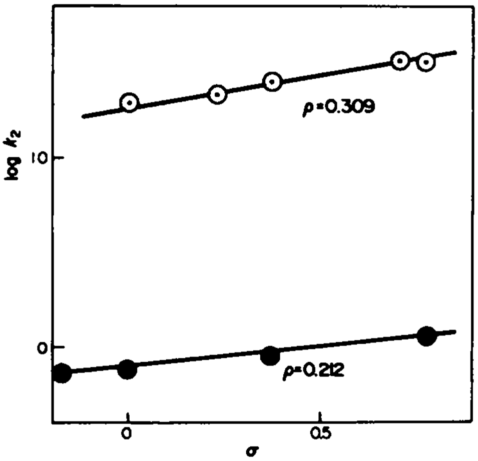


Fig. 3. Hammett plots for reactions of DDM with $ArC{\equiv}CCO_2H$ (○) and $ArCH_2CH_2CO_2H$ (●). The lines will intersect at $\sigma = -16.2$, whence $\log k_2 = -3.7$.

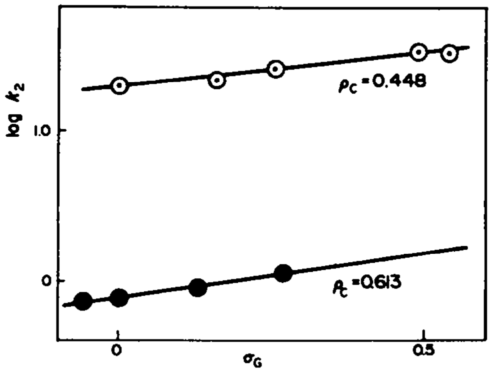


Fig. 4. Modified Hammett plots of $\log k$ vs σ_G values (via Tables 2 and 5) for reactions of DDM with $ArC{\equiv}CCO_2H$ (○) and $ArCH_2CH_2CO_2H$ (●). The lines will intersect at $\sigma_G = 8.5$, whence $\log k_2 = 5.1$.

Ester hydrolysis. A reasonable amount of relevant data is available on the alkaline hydrolysis of ethyl esters in 87.8% EtOH/H_2O. Values of ρ_{obs} and k_2^0 are shown in Tables 7 and 8. As usual, ρ_{obs} and k_2^0 show no correlation. Values of ρ_c are again calculated, but these too fail to correlate inversely with k_2^0. We do not believe however that this demonstrates the invalidity of our general postulate. Instead it seems that carboxylic acid ionization is not a satisfactory model reaction for assessment of transmission effects in ester hydrolysis. The obvious reason for this is that whilst acid pK_a values and $\rho_G{}^M$ values do not reflect primary steric effects to any extent, the rates of alkaline ester hydrolysis are sensitive to steric as well as transmitted electronic effects. Indeed the Taft derivation of polar substituent constants relies on this fact.[64]

Table 7. Rates[a] of alkaline hydrolysis of ethyl esters of carboxylic acids in 87.8% EtOH/H_2O at 30°, and Hammett ρ values

Acid series	ρ_{obs}	$k_2^{0\,a}$	$\rho_c{}^b$	Ref.
$ArOCH_2CO_2H$	1.10	0.53	3.23	60
$ArCH_2CO_2H$	0.824	1.54×10^{-2}	1.46	61
$ArCH_2CH_2CO_2H$	0.635	5.78×10^{-3}	2.99	41*b*, 62
trans-ArCH=$CHCO_2H$	1.301	1.90×10^{-3}	2.79	40
trans-2-Arylcyclopropyl	0.812	1.38×10^{-3}	4.46	41*b*
cis-ArCH=$CHCO_2H$	1.122	1.07×10^{-3}	1.75	40
$ArCO_2H$	2.545	8.89×10^{-4}	2.54	25

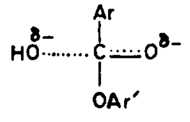
[a] For Ar = Ph, in l mol^{-1} s^{-1}.
[b] Based on $\rho_G{}^M$ values in H_2O (Table 1).

Table 8. Rates[a] of alkaline hydrolysis of ethyl esters of carboxylic acids in 87.8% EtOH/H_2O at 30°, and Hammett ρ values

Acid series	ρ_{obs}	$k_2^{0\,a}$	$\rho_c{}^b$	Ref.
ArC≡CCO_2H	1.10[c]	$8.00\times10^{-3\,d}$	1.59	59
$ArCH_2CH_2CO_2H$	0.635	5.78×10^{-3}	1.85	41*b*, 62
trans-ArCH=$CHCO_2H$	1.301	1.90×10^{-3}	1.92	40
trans-2-Arylcyclopropyl	0.812	1.38×10^{-3}	1.72	41*b*
cis-ArCH=$CHCO_2H$	1.122	1.07×10^{-3}	1.46	40
p-$ArC_6H_6CO_2H$	0.600	9.06×10^{-4}	1.37	63
$ArCO_2H$	2.545	8.89×10^{-4}	1.62	25
cis-2-Arylcyclopropyl	1.014	9.11×10^{-5}	2.32	41*b*

[a] For Ar = Ph, in l mol^{-1} s^{-1}.
[b] Based on $\rho_G{}^M$ values in 50% EtOH/H_2O (Table 2).
[c] At 10°, likely to be lower at 30°.
[d] At 20°.

One other ester hydrolysis example is at odds with the RSP. The alkaline hydrolyses of substituted phenyl benzoates, $YC_6H_4COOC_6H_4Z$ in 33% MeCN/H_2O have been subjected to a multiple substituent study.[65] The ρ values obtained by variation of Y are independent of the identity of Z and therefore of intrinsic reactivity, and likewise, ρ_z values are independent of Y. These results are in contrast to the *E*2 multiple substitution pattern mentioned earlier.[48] Assuming that the rate-determining step is nucleophilic attack at carbonyl carbon, the transition state will resemble 1. The Thornton rules[13] predict that electron-donating groups (EDG) able to interact with the carbonyl carbon will cause lengthening of both partial bonds, and electron-withdrawing groups (EWG) will shorten both bonds. Substitution will therefore have little if any effect on transition state structure in the



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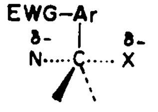
reactant-like: product-like dimension because of a cancellation effect[13] and it is therefore little wonder that manifestations of the RSP are not observed, since the BEP is not appropriate to this situation. One is reminded of the analogous situation of S_N2 reactions at benzylic carbon. Transition states 2 (tight) and 3 (loose) are



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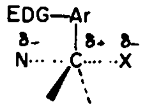

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respectively indicated for EWG and EDG.[66] and the gradual switch from one to the other is generally marked by the observation of U-shaped Hammett plots.[67] The plots in the phenyl benzoate hydrolyses are however linear, and this may result from the inability of transition state 1 to exhibit the same degree of bond length flexibility—the extension of the C=O bond is restricted to the C–O^- single bond length in the tetrahedral intermediate, since the carbonyl oxygen does not depart as does the S_N2 leaving group X. Giese has made a similar point with respect to the reactions of anilines with benzenesulphonyl chlorides.[3]

Vinyl ether hydrolyses. The acid-catalysed hydrolyses of aryl vinyl ethers, ArOCH=CH_2 and aryl vinyl thioethers, ArSCH=CH_2 have been studied by McClelland.[68] The respective ρ values are −2.06 and −1.77, and yet the more selective O-ethers are more reactive than the thioethers by a factor of about 10. Even when the small $\rho_G{}^M$ difference between the $ArOCH_2CO_2H$ and $ArSCH_2CO_2H$ model series (Table 1) is taken into account, the thioethers remain the more selective. But as with an *E*2 case discussed earlier, these model reactions are not appropriate to the reactions in question. In the latter the heteroatoms are bonded to a reacting atom, in that if the mechanism is A-S_E2 involving rate-limiting protonation of carbon,[69] the intermediates will resemble oxonium ions, Ar$\overset{+}{O}$=CH–CH_3 and sulphonium ions, Ar$\overset{+}{S}$=CH–CH_3 respectively. The fact that the latter are more stable would account for the greater reactivity in the thioether series. However, neither the oxygen nor the sulphur atoms appear to be capable of allowing direct resonance transmission of charge to the ring substituents since log *k* for both series correlates with σ rather than σ^+.[68] Hence the reactivity pattern is distorted by direct involvement of the "insulating" groups.

Electrophilic aromatic substitution. Reactivity-selectivity patterns in such reactions have been extensively discussed.[22,70] We intend focussing our attention on the chlorination of substituted benzenes and thiophenes, a system quoted by Johnson[4] as an example of the negation of the RSP. Plots of log k_2 for positional chlorination vs the Brown–Okamoto σ^+ constants (t-cumyl chloride scale, $\rho_0{}^M = -4.54$)[71] are shown in Fig. 5 for chlorination of benzenes[72] and thiophenes[73] in HOAc.

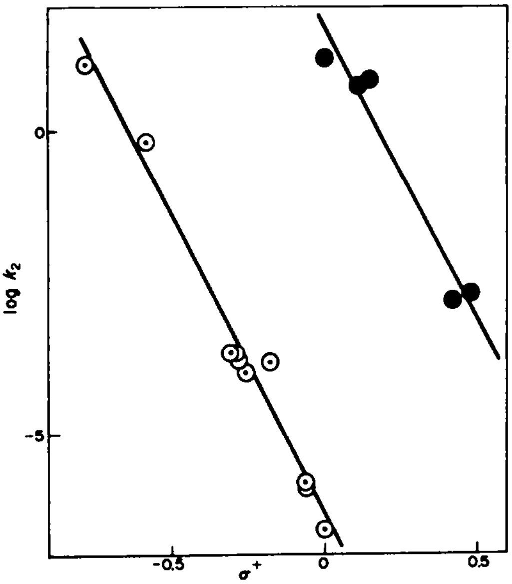

Fig. 5. Plots of $\log k_2$ vs σ^+ for reaction of Cl_2 in HOAc with monsubstituted benzenes (○) and with the 2-position of 5-substituted thiophenes (●)- $\sigma_p{}^+$ values are employed in the latter series.

Despite the fact that the thiophenes are some 10^7 times more reactive than the benzenes, the plots are almost parallel, yielding ρ^+ values of -9.64 and -9.93 respectively. However this is not necessarily an anti-RSP phenomenon, as the ability of thiophene vs benzene to transmit charge to the substituents has been neglected.† In resolving the anomaly we call on our earlier treatment.

What is required is a thiophene σ^+ scale, and for consistency this could be obtained from solvolysis rates of substituted 2-thienyl analogoues of t-cumyl chlorides. Unfortunately no such data are available and so an alternative model series must be sought.

The t-cumyl chloride, $ArCMe_2Cl$, series appropriate for benzene ring substitution has a ρ^+ (defined) of -4.54.[71] This is practically solvent independent.[74] It is also independent, within reason, of leaving group identity since the corresponding p-nitrobenzoates, $ArCMe_2OPNB$, give $\rho^+ = -4.72$.[75] On going from tertiary to secondary systems the ρ^+ value increases markedly: $\rho^+ = -5.79$ for ArCH(Me)Cl in 80% $EtOH/H_2O$;[76] $\rho^+ = -5.74$ for ArCH(Me)OPNB in 70% acetone $-H_2O$[77] (2-point plot): but appears to remain insensitive to solvent and leaving group variation. It is therefore reasonable to adopt a $\rho_G{}^M$ value of -5.77 for solvolysis of benzenoid 1-arylethyl compounds.

Rate constants for the solvolysis of 4- and 5- substituted 1-(2-thienyl) ethyl p-nitrobenzoates, ThCH(Me)OPNB, in 80% $EtOH/H_2O$ are correlated by the t-cumyl chloride σ^+ constants, giving $\rho^+ = -6.93$.[78] This value can then serve as $\rho_G{}^M$ for electrophilic reactions in the thiophene nucleus. From eqn (12) we may now derive a $\sigma_G{}^+$ scale for thiophene substituents by multiplying t-cumyl chloride σ^+ constants by $(-6.93/-5.77) = 1.20$. Alternatively, the ρ^+ value for thiophene chlorination, based on t-cumyl chloride σ^+ constants, must be divided by 1.20, in an electrophilic analogy to eqn (9) in order to cancel variable transmission effects. Thus the ρ^+ value of -9.93 for chlorination of benzenes must logically be compared with a value of $(-9.64)/1.20 = -8.03$ for thiophenes. No crossover of rates in a sensible rate range occurs. In these terms, the RSP holds, and the transition state for thiophene chlorination is more reactant-like.

These two series in fact constitute part of an extended selectivity relationship between benzene and thiophene reactions.[79,80] The reactivity of the 2-position of thiophene, relative to a single position in benzene, is shown in Table 9 as a function of ρ^+ for the benzene reactions. If the latter is viewed as an index of the amount of positive charge on the ring in transition states, it is to be expected that the thiophene: benzene rate ratio should decrease as ρ^+ decreases. A general trend of this type is found. Thus the observed ρ^+ value for thiophene chlorination is artificially enhanced by the superiority of the thiophene nucleus as a transmitter of positive charge, a fact that also emerges from other types of study.[81]

We may briefly consider Johnson's query[4] as to why an LFER should remain linear over the enormous reactivity range shown in the chlorination of benzenes (4.5×10^7 from p-H to p-OMe in HOAc) with yet a progressively changing transition state structure. The question may be answered in two ways. Firstly, the σ^+ scale is itself based on rates, and if the structures of the t-cumyl choride solvolysis transition states are substituent-dependent, this may carry over into other rate processes involving σ^+ correlations, with a tendency towards suppression of intrinsic curvature (see Ref. 2, p. 81). Alternatively, if electrophilic chlorination is considered as a concerted process, with simultaneous heterolytic making of an aromatic carbon–chlorine bond and breaking of the Cl–Cl bond (so that the intermediate is an areneonium chloride ion-pair):

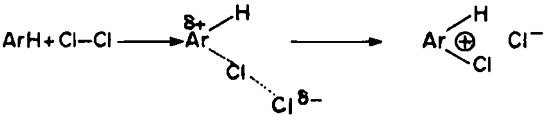

Table 9. Electrophilic reactions[a] of benzene and thiophene

Reaction	ρ^{+b}	$\log(k_2/k_{Ph})^c$
Bromination	−12.1	9.70
Chlorination	−9.6	7.11
Protodetritiation	−8.5	7.38
Solvolysis of ArCH(Me)OPNB	−5.8	4.8
Protodeboronation	−5.2	5.93
Iododeboronation	−4.7	3.83
Protodesilylation	−4.8	3.70
Isom. of *cis*-ArCH=CHPh	−3.3	2.55
Rearr. of arylpropenylcarbinol	−2.9	1.70
Pyrolysis of $ArCH(OAc)CH_2Ph$	−0.66	0.52

[a] References to original data sources in Ref. 79.

[b] For reactions of substituted benzenes.

[c] Reactivity of the 2-position of thiophene, relative to a single position in benzene. A limited amount of data for the 3-position of thiophene follows the same general trend.[79]

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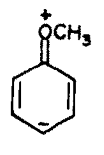
†Since benzene is the reference substrate for the benzene series and thiophene is the reference substrate for the thiophene series, the σ^+ of the –S– group in the latter relative to =CH– in the former is not an issue here. The evaluation of σ^+ for heteroatoms in fact requires the assumption that ρ for the benzenoid series is equal to ρ for the heterocyclic series, and since this is not generally the case, it is not surprising that such σ^+ values often vary from reaction to reaction.[28,80] This may be seen as a manifestation of RSP effects.

application of the revised Thornton rules[15] leads to the conclusion that substitution in the ring will change neither the length nor the polarity of the C–Cl partial bond. Substitution on the ring will therefore not change to any great extent the amount of electron deficiency generated there in the transition state.

It is appropriate at this point to discuss heteroaromatic reactivity in solvolyses leading to carbocationic intermediates. Solvolysis of 2-ThCH(Me)OPNB compounds in 80% EtOH/H_2O are slower than those of the corresponding 2-furanyl compounds, 2-FnCH(Me)OPNB, but the respective ρ^+ values (t-cumyl chloride scale) are -6.93 and -7.44.[78,82] This is again an anti-RSP order, but it can again be rationalized in terms of unequal transmission efficiencies. MO calculations by Forsyth and Noyce[83] (CNDO/2) show that while ρ^+ is not a reactivity index for solvolysis of such heteroaromatic compounds, it correlates directly with the amount of charge transmitted to the substituted position upon ionization. The furanyl system is calculated to be a better transmitter than is the thienyl system, and it is noteworthy that furans are more reactive than thiophenes in electrophilic heteroaromatic substitution reactions.[80,84]

The rho value for Cl_2 chlorination *meta* to R in monosubstituted benzenes (HOAc solvent) is about -10.[72] For chlorination *meta* to R in the more reactive *p*-RC_6H_4NHAc series, $\rho = -5.3$.[85] At first sight, this is an example of the RSP in operation, but two factors may mitigate against this. Firstly the entering chlorine may be subject to extra steric pressures in the acetanilide series, since it attacks *ortho* to the acetamido group. Secondly, an electron-withdrawing R group may modify the electronic effects of the –NHAc group, so that σ_0^+ may be larger and variable. The effect will then be to reduce the observed ρ value.[85] In other words, the –NHAc group attenuates the substituent effects of the R groups (variable transmission).

We conclude the section on aromatic substitution by remarking on a statement of Johnson[4] concerning initial state energies. In considering initial state resonance hybrids of anisole and nitrobenzene as S_E substrates, **4** and **5**, he remarks that the form **4** effectively "starts off" anisole further along the reaction coordinate. This statement is demonstrably wrong. Resonance delocalization of electrons is a stabilizing phenomenon and if **4** and **5** are significant contributors to the structure of anisole and nitrobenzene they will stabilize *both* molecules relative to benzene.[86] Thus in energy terms they will be handicapped relative to benzene, and despite the fact that we are dealing with an EDG vs an EWG, the handicaps will be in the same direction. Initial state differentiation is thus impossible, and only when the initial state charge distribution is polarized by the approach of an electrophile do the groups show differing behaviour as to the energetic consequences. Anisole is more reactive and nitrobenzene less reactive than benzene. Energies of initial states are important in the context of the BEP,[11] and explicit consideration of them will be given in the next section.



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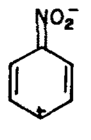

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Solvolysis and carbocations. Stability-selectivity relationships in solvolysis leading to carbocations and carbocationic ion-pairs have been adequately discussed elsewhere;[2,87] the Hammett equation aspect having little relevance. The specific reactions we intend to discuss are exemplified in eqn (13). What effects do variations in R_1 and R_2 have on reactivity and the Hammett rho?

$$\mathrm{Ar}-\underset{R_2}{\overset{R_1}{\mathrm{C}}}-\mathrm{X} \longrightarrow \mathrm{Ar}-\underset{R_2}{\overset{R_1}{\mathrm{C}^+}} + \mathrm{X}^- \qquad (13)$$

In general terms we may identify several factors that may influence the magnitude of ρ; amongst these are:

(i) The amount of positive charge generated on C_α as a result of $C_\alpha - X$ heterolytic stretching in the transition state (a BEP effect),

(ii) The amount of nucleophilic solvent assistance provided,[88]

(iii) The degree of nucleophilic participation by neighbouring groups,[89]

(iv) The extent to which R_1 and R_2 sterically prevent the plane of the ring from becoming perpendicular to the axis of the developing *p*-orbital in the carbocation-like transition state. A perpendicular conformation is essential for maximum charge delocalization and transmission to ring substituents.[90,91]

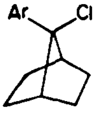
If through variation of R_1 and R_2 we seek the RSP inverse correlation of ρ and intrinsic reactivity we must be certain that factors (ii)–(iv) are either absent or constant. The way in which steric inhibition of delocalization, factor (iv), may complicate the issue is amply illustrated by the results of solvolyses (unassisted S_N1) of *p*-$YC_6H_4CR_1R_2OPNB$ compounds,[92] shown in Table 10. The apparent selectivity order, **6** > **7** > **8** > **9** bears no relationship to the reactivity order of **6** > **8** > **7** > **9** for the Y = H and Y = OMe derivatives, nor to that of **8** > **9** > **6** > **7** for Y = CF_3. If we extrapolate the $\log k - \sigma^+$ plots to $\sigma^+ = 2.00$ for a hypothetical EWG, the reactivity order, **9** > **8** > **7** > **6** now shows the inverse relationship with the ρ values. And only in this last case is delocalization of the developing positive charge on C_α into the ring unimportant as a significant transition state stabilization factor, so that ring conformation differences now become unimportant. The position of the transition state on the reaction coordinate is then seen to depend largely on the amount of initial state steric strain relief attending ionization[93]—destabilization of the initial state achieves a lower barrier height and an earlier transition state in BEP terms in the same way as does the more usually discussed stabilization of products.[11]

Brown *et al.* have reported that in solvolyses of *p*-nitrobenzoates with $R_1 = Me$,[75,94] the reactivity order is R_2 = cyclopropyl > phenyl > Me > *i*-Pr, whilst the ρ values are respectively -2.78, -3.23, -4.72, -4.76. On the surface this would seem to be a nice RSP pattern, but the order of ρ values is in the order of decreasing electron demand by the R_2 groups, and gives little if any information regarding the relative structures of the transition states. Furthermore, the McManus and Harris treatment suggests that the cyclopropyl and *i*-Pr ρ values are distorted by steric inhibition of delocalization.[90] Of more import is the study of solvolysis of 1-arylcycloalkyl chlorides **10**–**13**.[95] Rate constants for Ar = Ph and ρ

Table 10. Solvolyses of $(p\text{-}YC_6H_4)CR_1R_2OPNB$ substrates in 70% acetone/H_2O at 100°

Compound	R_1	R_2	ρ^a	$k(Y = OMe)^b$	$k(Y = H)^b$	$k(Y = CF_3)^b$	$k(Y = EWG)^{b,c}$
6	Me	Me	−3.74	1.42	1.48×10^{-3}	8.97×10^{-6}	5.3×10^{-11}
7	Neopen.	Neopen.	−2.91	4.52×10^{-2}	2.79×10^{-4}	4.15×10^{-6}	2.1×10^{-10}
8	t-Bu	Neopen.	−2.64	1.48×10^{-1}	1.20×10^{-3}	3.62×10^{-5}	6.3×10^{-9}
9	t-Bu	t-Bu	−1.30	7.55×10^{-4}	1.38×10^{-5}	1.25×10^{-5}	2.1×10^{-7}

[a] Based on $ArCMe_2Cl$ σ^+ scale.
[b] In s^{-1}.
[c] For a hypothetical electron-withdrawing group having $\sigma^+ = 2.00$.



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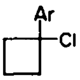

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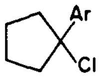

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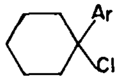

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values are shown in Table 11. A nice RSP pattern appears, and steric effects are judged not to complicate the issue.[90] Although for Ar = Ph, 11 > 13 in reactivity, the Ar = p-MeC_6H_4 compounds are almost equally reactive. This is explained[95] in terms of substituent-induced changes in transition state character: for Ar = Ph the two transition states will be relatively product-like, and as 11 gains much relief of initial state angle strain (not present in 13) in achieving such a configuration, its enhanced reactivity is understandable. But when Ar = p-MeC_6H_4, the two transition states will occur earlier on the reaction coordinate so 11 will not be able to relieve angle strain to the same extent, and so looses its reactivity advantage. For Ar = p-$MeSC_6H_4$, the reactivity order is actually reversed, and becomes 13 > 11.

Table 11. Reactivities and selectivities of 1-arylcycloalkyl chlorides in 90% acetone/H_2O (Ref. 93)

Compound	$10^4k_1\,(s^{-1})^a$	ρ
12	72.3	−4.10
11	0.274	−4.48
13	0.196	−4.65
10	3.98×10^{-4}	−5.64

[a] For Ar = Ph, at 25°.

The ρ values for ethanolysis of 1-adamantyl and 2-adamantyl arenesulphonates are equal although compounds in the former series are some 10^5 times more reactive,[96] and Johnson has cited this as an anti-RSP example.[4] However, the rate effect is attributed to relief of initial state steric compressions in the 1-adamantyl series[96,97] and while this by itself should engender an earlier transition state and a lower ρ value, the fact that the tertiary 1-adamantyl cation cannot achieve desirable coplanarity[98] without expenditure of considerable bond and angle distortion may push the transition state further in the product direction, so that the 1- and 2-adamantyl transition states may end up with the same degree of charge development.

We discuss now the interesting case of solvolyses of substituted 2-(1-azulyl)ethyl tosylates, 1-$AzCH_2CH_2OTs$.[99] In HOAc the aryl participation pathway (Fk_Δ) is dominant, and by comparing the ρ value with those for acetolysis of $ArC(Me)_2CH_2OBs$ (neophyl) and $ArCH_2CH_2OTs$ (Fk_Δ component) compounds, the authors concluded (i) that a single reaction constant applies to acetolysis of β-arylethyl derivatives when the leaving group is attached to primary carbon, and (ii) that ρ obtained from substituent effect data cannot yield any information concerning early vs late formed transition state structures. If this is so, the arguments of the present paper are invalid. However the solvolyses investigated exhibited several strange features. Firstly $\log k$ for solvolysis of 1-$AzCH_2OTs$ compounds correlated linearly with pK_a values[100] of the corresponding 1-$AzCo_2H$ acids in 50% $EtOH/H_2O$. Since the pK_a values correlated linearly with the normal $\sigma_p{}^0$ Hammett constants, *irrespective of substituent position*, so were the solvolysis $\log k$ values best correlated with $\sigma_p{}^0$, irrespective of substituent position. The fact that no σ^+ dependence is observed in this participatory process is strange, since a σ^+ correlation is observed for the Fk_Δ acetolyses of neophyl brosylates[101] and 2-phenylethyl tosylates,[102] whilst the normal Hammett σ scale correlates the acidities of $ArCH_2CH_2CO_2H$ compounds[25] but σ^+ does not. Before the RSP-related contentions of McDonald *et al.* can be accepted, further light needs to be cast upon these irregularities in substituent constant behaviour.

We eschew examination of substituent-induced variation of solvolysis sensitivity to solvent polarity[93] on the grounds that Johnson's treatment shows the Winstein–Grunwald m-value to be a function of a solvent-dependent ρ,[103] and therefore outside the scope of this paper. Furthermore, m values for solvolysis of ring-substituted $Ar_2CHOPNB$ compounds in $EtOH/H_2O$ mixtures show no dependence of m on substituents that can be reasonably interpreted in terms of carbocation stabilities,[104] and it may well be that variable amounts of solvent assistance[105] are distorting the m values.

Summary and conclusion. We agree with Johnson's basic contention that the automatic equation of reactivity and selectivity is misleading.[4] In pointing out that observed Hammett ρ values for related reaction systems are often measures of more than simple selectivities, and in correcting some of these to remove extraneous influences we have found examples which negate his claim that "selectivity is independent of reactivity, from which the theoretical deduction may be made that transition state structure is independent of reaction rate; the same conclusion may be drawn from isotope studies". Some of our examples are featured in Johnson's review, others eluded his attention, and the selection of papers quoted in Ref. 18 is sufficient to refute his inference that isotope effects are *always* insensitive to reactivity.

We conclude that the Hammett relationship and the RSP are interwoven, but that more care than has previously been employed is needed before RSP relationships and the related question of transition state structure can be derived from Hammett series. In this context we draw attention to the recent work of Pryor on Hammett relationships in free radical reactions.[106] He has shown that naive application of the ρ values can often have contradictory results as far as assignment of transition state polarities (nucleophilic vs electrophilic radicals) is concerned and that substituents can often affect bond dissociation energies to the point where transition state properties are obscured.

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