PERKIN 2

Application of the aromatic ring parameter (I) to solvolyses of β-arylalkyl toluene-*p*-sulfonates

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The specific rates of solvolysis of a variety of β-arylalkyl toluene-*p*-sulfonates, where the solvolyses proceed with anchimeric assistance (a k_Δ pathway), are shown to be very well correlated by a Grunwald–Winstein treatment involving Y_{OTs} and I (the aromatic ring parameter), previously successfully applied to k_c solvolyses of substrates with aryl groups at the α-carbon. A recently proposed alternative treatment, using Y_{OTs} in conjunction with Y_Δ [a scale derived from 2-methyl-2-(*p*-methyoxyphenyl)propyl toluene-*p*-sulfonate solvolyses], is shown to be equivalent to use of Y_{OTs} plus I; the sensitivity coefficients from the two treatments can be readily interconverted. Three methods (similarity models of type Y_{BnX}, use of Y_X plus I and use of Y_X plus $Y_{\Delta\mathrm{X}}$ have now been proposed for treatment of dispersion in Grunwald–Winstein plots due to the presence in the substrate of conjugated π electrons. The relative efficiencies of these three methods are discussed.

Recently, there has been considerable interest in the dispersion observed in Grunwald–Winstein plots for benzylic and related derivatives and three modes of treatment of this dispersion in terms of free energy relationships have been proposed.

Liu and co-workers have proposed the development of similarity models and have put forward a series of Y_{BnX} scales[1–5] for use in eqn. (1), in place of Y_X, when the substrate is

$$\log (k/k_0)_{\mathrm{RX}} = mY_\mathrm{X} + c \qquad (1)$$

benzylic. In the simple (one-term) Grunwald–Winstein equation,[6,7] expressed as eqn. (1); k and k_0 are the specific rates of solvolysis of a substrate (RX) in a given solvent of ionizing power Y_X and in 80% ethanol, respectively; m is the sensitivity to changes in Y_X value; and c is a constant (residual) term. Bentley *et al.*[8] have suggested the use of the specific rates of solvolysis of *p*-methoxybenzyl chloride as a similarity model for benzylic chloride solvolyses.[9–11] When nucleophilic assistance from the solvent is also present, this can be treated by use of eqn. (2). In

$$\log (k/k_0)_{\mathrm{RX}} = lN + mY_\mathrm{X} + c \qquad (2)$$

eqn. (2), l represents the sensitivity to changes in solvent nucleophilicity (N), with the N_T scale, based on solvolyses of the *S*-methyldibenzothiophenium ion,[12] being recommended.[13]

A major disadvantage of similarity models is the difficulty in choosing a suitable model. It must be established that the chosen standard substrate solvolyses by one mechanism in all of the solvents under consideration.[11,14,15] A second disadvantage is that, even if a Y_X scale (usually based on solvolyses of an adamantyl derivative[7]) already exists, it is necessary to construct a brand new Y_{BnX} scale for the appropriate leaving group X. Indeed, with the two restrictions being combined, one must have available a matrix of values, dealing not only with an appropriate similarity model R group but also with each different leaving group X which could be involved in a given study.

In an attempt to overcome the severe limitations of the similarity model approach, a new parameter called the aromatic ring parameter (I) has been put forward. This parameter, with an appropriate sensitivity h, is introduced into eqn. (1) to give eqn. (3). If solvent nucleophilicity is also a relevant factor, the lN term can be added to give eqn. (4), paralleling the movement

$$\log (k/k_0)_{\mathrm{RX}} = mY_\mathrm{X} + hI + c \qquad (3)$$

$$\log (k/k_0)_{\mathrm{RX}} = lN + mY_\mathrm{X} + hI + c \qquad (4)$$

from eqn. (1) to eqn. (2). The use of eqn. (3) involves only the scales of Y_X values, already available for most leaving groups in a wide range of solvents,[7] and the sensitivity h to a parameter I,[9] whose use is independent of both the nature of the leaving group and the structure of the R group. The contribution from the hI term is considered to arise from a combination of effects involving changes in solvation of the aromatic rings and variations in ion-pair return, relative to the corresponding changes induced by solvent variation for the aliphatic standard substrates (usually adamantane derivatives).[10]

It has been found that, for many purposes, the calibrated h/m ratio is a more useful quantity than the h values themselves. For example, in the similarity model approach, the important consideration is not similarity in structure but similarity in h/m ratio.[9,15] The I scale was developed from a comparison of the solvolyses, in a wide range of solvents, of the *p*-methoxybenzyldimethylsulfonium ion[9] and the 1-adamantyldimethylsulfonium ion.[16] The main advantage of using $\mathrm{R{-}X^+}$ cations, with a neutral molecule leaving group, is that the leaving-group effects are minimized and one can concentrate on other factors: here the dispersion in Gunwald–Winstein plots and previously[12,17] solvent nucleophilicity. Treatments in terms of the hI parameter within eqn. (3) or, occasionally, eqn. (4) have been very successfully applied to the solvolyses of benzyl, benzhydryl, naphthylmethyl and anthrylmethyl toluene-*p*-sulfonates (tosylates), chlorides, bromides and *p*-nitrobenzoates.[9,11,15,18] The solvolyses of the benzhydryldimethylsulfonium ion have been very successfully treated[19] in terms of a combination of I values[9] and Y^+ values.[7,16] Also, the relatively mild dispersions observed[20] in solvolyses of allylic and propargylic chlorides (aryl group replaced by a vinyl or acetylenic group) have led to excellent correlations with use of eqn. (3), with (as one would expect) reduced h values.

Lee and co-workers have recently[21] given strong support to the use of eqn. (3), including arguments based on use of the standard AMI procedure, as implemented in the MOPAC ver-

Table 1 Correlation of the specific rates of solvolysis of neophyl tosylates using the Grunwald–Winstein approach and various combinations of $Y_{\mathbf{OTs}}$, $N_{\mathbf{T}}$ and I parameters; including the indirectly determined [*via* eqn. (5)] values for m and h (designated as m' and h')[a]

Compound[b] m' h' (n')	n[b]	l[c]	m[c]	h[c]	c[d]	r[e]	F[f]
1A	38		0.50 ± 0.03		−0.04 ± 0.23	0.9518	347
0.52 0.65			0.52 ± 0.01	0.59 ± 0.05	−0.08 ± 0.11	0.9891	791
(standard)[g]		−0.15 ± 0.03	0.42 ± 0.03		−0.11 ± 0.18	0.9689	269
		−0.03 ± 0.03 (0.32)	0.53 ± 0.02	0.65 ± 0.08	−0.07 ± 0.11	0.9894	528
1H	37		0.65 ± 0.03		−0.04 ± 0.24	0.9661	490
0.65 0.62			0.66 ± 0.01	0.62 ± 0.06	−0.07 ± 0.12	0.9916	997
(45)		−0.16 ± 0.04	0.56 ± 0.03		−0.10 ± 0.19	0.9781	376
		0.02 ± 0.03 (0.57)	0.67 ± 0.03	0.66 ± 0.09	−0.06 ± 0.12	0.9917	652

[a] Specific rates at 45.0 °C, from ref. 23; values in parentheses are the probabilities that the associated term is not statistically significant (reported if greater then 0.005). [b] For structure, see text; n is the number of solvents with use of eqn. (3) and n' is the number of solvents with use of eqn. (5). [c] With associated standard error. [d] Residual (constant) term, accompanied by the standard error of the estimate. [e] Correlation coefficient. [f] The F-test value. [g] By definition: $m_{\mathbf{c}} = 0.00$ and $m_{\Delta} = 1.00$.

sion 6. Liu has suggested[22] that an 'obvious drawback' in using eqn. (3) is that a rather large standard error is frequently associated with the h value. However, it is not meaningful to compare this value with the standard error of m values obtained by use of eqn. (1). It is reasonable to compare the standard error associated with the m of the $mY_{\mathbf{BnX}}$ term with that associated with the m of the $mY_{\mathbf{X}}$ term of eqn. (3); for 22 benzylic solvolyses, Liu quotes very similar values of less than 0.05 and less than 0.07, respectively (for similar magnitude m values).

Fujio, Tsuno and co-workers have carried out a very thorough study of solvent effects upon solvolyses of several tosylate esters in which there is the possibility of incorporating a 1,2-migration of an aryl group, so as to give an appreciable anchimeric assistance.[23–25] Dispersion was found in the Grunwald–Winstein plots and, in particular, the aqueous 2,2,2-trifluoroethanol (TFE) solvents were above the correlation line, inconsistent with nucleophilic assistance and suggesting an effect due to the conjugation of π electrons with the developing positive charge.[18] A new equation [eqn. (5)] was proposed,[24]

$$\log (k/k_0)_{\mathbf{ROTs}} = m_{\mathbf{c}} Y_{\mathbf{OTs}} + m_{\Delta} Y_{\Delta} \tag{5}$$

involving a linear combination of terms governed by the ionizing power scale for an unassisted solvolysis ($Y_{\mathbf{OTs}}$) and by the ionizing power scale for an anchimerically assisted solvolysis (Y_{Δ}, based on the solvolyses of p-methoxyneophyl tosylate[23,26]), with the sensitivity to changes in the values for these scales being represented by $m_{\mathbf{c}}$ and m_{Δ}, respectively. Further, it was shown[27] that use of eqn. (5) significantly improved, over use of eqn. (1), the correlations of the rates of those solvolyses of benzylic tosylates which lay mechanistically towards the S_N1 extreme of the S_N1–S_N2 spectrum of behaviour.[28]

It was pointed out[27] that the mechanism of charge delocalization by an aryl group is independent of whether the aryl group is initially attached to the α-carbon or is in the process of migration from a β-carbon. Just as eqn. (5) can be used to correlate solvolyses of α-aryl-substituted tosylates solvolysing without anchimeric assistance, the inverse should also hold, such that eqn. (3) can be used to correlate those solvolyses of β-arylalkyl tosylates which proceed with anchimeric assistance.

In this paper, it is shown that, in addition to its previous successful applications, the hI term can be used within eqn. (3), in conjuction with an $mY_{\mathbf{OTs}}$ term, to give very good to excellent correlations of the solvolyses of several β-arylalkyl tosylates. The advantages of using eqn. (3) rather than eqn. (5) are presented and discussed.

Results and discussion

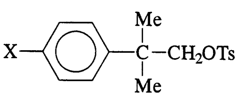
For each of the substrates for which the specific rates of solvolysis, at 25.0 or 45.0 °C, have been analysed in terms of eqns. (1)–(4), the ABSTAT statistical package (Anderson–Bell, Arvada, Colorado, USA) has been applied. The 'goodness of fit' is considered in terms of the overall correlation coefficient, the F-test values, the probabilities that each individual term is statistically insignificant (reported if greater than 0.005), the standard error of the estimate (reported associated with the c value) and the standard errors associated with the calculated l, m and h values. Also, if multicolinearity is a problem, a warning is issued to the effect that 'the results may be spurious due to a high degree of multicolinearity'.

Solvolyses of 2-(*p*-methoxyphenyl)-2-methylpropyl toluene-*p*-sulfonate (*p*-methoxyneophyl tosylate, 1A) and the parent compound (neophyl tosylate, 1H)

Solvolysis of **1A** was taken as the standard for establishment of the Y_{Δ} scale [eqn. (6)]. In terms of eqn. (5), it is assumed that

$$\log (k/k_0)_{\mathbf{1A}} = Y_{\Delta} \tag{6}$$

$m_{\mathbf{c}}$ is zero and m_{Δ} is unity. For 49 solvents, a correlation, using specific rates at 45.0 °C, against $Y_{\mathbf{OTs}}$ values [eqn. (1)] led[24] to an m value of 0.50 and a correlation coefficient (r) of 0.953. Our results for correlations, using eqns. (1)–(4), in 38 solvents for which $N_{\mathbf{T}}$, $Y_{\mathbf{OTs}}$ and I values are all available, are presented in Table 1. The 38 solvents are those listed[24] for Y_{Δ} values, but excluding acetic and formic acids and their mixtures and the aqueous acetonitrile solvents, and adding a value for 10% acetone.[23] The negative l value observed when eqn. (2) is applied is a direct result of the neglect of the hI term and when eqn. (4) is applied the l value is essentially zero (0.03 ± 0.03), with a very high probability (0.32) that the lN term is statistically insignificant. Use of eqn. (1) leads to m and r values identical to those for the full 49 solvents.



1A: X = p-MeO
1H: X = H

By far the most interesting of the four correlations for **1A** is that in terms of eqn. (3). It is found that this gives the best correlation with a rather modest h value of 0.59 ± 0.05, consistent with the β-aryl group having only partially migrated to the α-carbon at the transition state, and a correlation coefficient of 0.9891. The F-test value of 791 is considerably higher than for any of the other three correlations.

The observation that the specific rates of solvolysis of **1A**, the standard system for the Y_{Δ} scale incorporated into eqn. (5), are

Table 2 Correlation of the specific rates of solvolysis of *threo*-2-aryl-1-methylpropyl toluene-*p*-sulfonates using the Grunwald–Winstein approach and various combinations of $Y_{\mathbf{OTs}}$, $N_{\mathbf{T}}$ and I parameters; including indirectly determined [*via* eqn. (5)] values for m and h (designated as m' and h')[a]

Compound[b] m' h' (n')	n[b]	l[c]	m[c]	h[c]	c[d]	r[e]	F[f]
2A	30		0.62 ± 0.03		−0.03 ± 0.24	0.9613	341
0.63 0.62			0.62 ± 0.02	0.63 ± 0.06	−0.08 ± 0.11	0.9920	834
(37)		−0.16 ± 0.04	0.51 ± 0.04		−0.08 ± 0.19	0.9765	277
		0.02 ± 0.03 (0.48)	0.64 ± 0.03	0.68 ± 0.09	−0.08 ± 0.11	0.9922	546
2AC	28		0.59 ± 0.03		−0.05 ± 0.21	0.9656	358
0.60 0.50			0.60 ± 0.02	0.55 ± 0.06	−0.09 ± 0.11	0.9912	701
(31)		−0.12 ± 0.04	0.50 ± 0.04		−0.09 ± 0.18	0.9767	259
		0.04 ± 0.03 (0.23)	0.63 ± 0.03	0.64 ± 0.10	−0.09 ± 0.11	0.9917	477
2M	30		0.75 ± 0.03		−0.01 ± 0.24	0.9732	501
0.75 0.58			0.75 ± 0.01	0.65 ± 0.05	−0.06 ± 0.09	0.9960	1696
(33)		−0.17 ± 0.04	0.63 ± 0.04		−0.07 ± 0.18	0.9857	460
		0.01 ± 0.03 (0.85)	0.76 ± 0.02	0.66 ± 0.08	−0.06 ± 0.09	0.9961	1090
2H	30		0.73 ± 0.02		−0.04 ± 0.17	0.9843	870
0.73 0.34			0.73 ± 0.02	0.35 ± 0.07	−0.07 ± 0.13	0.9919	823
(35)		−0.07 ± 0.03 (0.05)	0.68 ± 0.03		−0.07 ± 0.16	0.9863	484
		0.07 ± 0.04 (0.08)	0.78 ± 0.03	0.48 ± 0.10	−0.06 ± 0.12	0.9928	595
2B	22		0.48 ± 0.06		−0.14 ± 0.27	0.8666	60
0.50 −0.35			0.42 ± 0.06	−0.53 ± 0.17 (0.01)	−0.03 ± 0.22	0.9148	49
(23)		0.21 ± 0.05	0.60 ± 0.05		−0.07 ± 0.20	0.9327	64
		0.18 ± 0.08 (0.04)	0.57 ± 0.09	−0.11 ± 0.24 (0.65)	−0.06 ± 0.20	0.9335	41

[a] Specific rates at 45.0 °C (except those for **2A** are at 25.0 °C), from ref. 24; values in parentheses are the probabilities that the associated term is not statistically significant (reported if greater then 0.005). [b–f] See corresponding footnotes to Table 1.

very well correlated by eqn. (3) leads to direct relationships between the sensitivities calculated within each of the two types of correlation.

Using the relevant values from Table 1, we can write: $Y_\Delta = 0.52Y_{\mathbf{OTs}} + 0.59I$ and, substituting within eqn. (5) and rearranging, we get: log $(k/k_0)_{\mathbf{ROTs}} = (m_\mathbf{c} + 0.52m_\Delta)Y_{\mathbf{OTs}} + 0.59m_\Delta I$ such that sensitivities for eqn. (3) can be expressed as in eqns. (7) and (8). However, the overall correlation is not quite as

$$m = m_\mathbf{c} + 0.52m_\Delta \quad (7)$$

$$h = 0.59m_\Delta \quad (8)$$

good as for the solvolyses of the unsubstituted **1H** and a slightly modified proportionality constant of 0.65, expressed in eqn. (9), is recommended. Accordingly, in addition to a direct

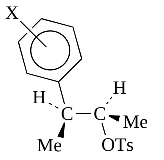
$$h = 0.65m_\Delta \quad (9)$$

determination by use of eqn. (3), the m and h values can be obtained indirectly by application of eqn. (5), followed by application of eqns. (7) and (9). In Table 1, and subsequent tables, the indirect values, obtained by conversion from the $m_\mathbf{c}$ and m_Δ values reported[24,25] by Fujio, Tsuno and co-workers, are designated as m' and h'.

The unsubstituted neophyl tosylate (**1H**) was found[24] to correlate very well using eqn. (5), with a small $m_\mathbf{c}$ value and an m_Δ value slightly below unity. It also correlates very well, for 37 solvents at 45.0 °C, against a combination of $Y_{\mathbf{OTs}}$ and I parameters (Table 1), with a correlation coefficient of 0.9916. Use of eqn. (4) again indicates a negligible contribution from solvent nucleophilicity ($l = 0.02 \pm 0.03$). The solvents used were identical to those for **1A**,[23] except no specific rate was available in 10% acetone.

Solvolyses of *threo*-2-aryl-1-methylpropyl toluene-*p*-sulfonates

The specific rates of solvolysis of the unsubstituted *threo*-1-methyl-2-phenylpropyl tosylate **2H** and four derivatives, with one or two substituents within the phenyl group, have been determined in a wide range of solvents.[24] With the exception of the carboxylic acids and their mixtures and the aqueous acetonitrile mixtures, I values (and also $N_\mathbf{T}$ and $Y_{\mathbf{OTs}}$ values) are available for the solvents used in the original study and now incorporated into the Grunwald–Winstein-type analysis reported in Table 2.



2A: X = *p*-MeO
2AC: X = 4-MeO, 3-Cl
2M: X = *p*-Me
2H: X = H
2B: X = *m*-Br

Consistent with previous observations for benzylic systems,[9,15,18] the h values are slightly higher when the substituent X is electron-supplying. When eqn. (3) is used, values in the range of 0.55–0.65 for **2A**, **2AC** and **2M** fall to 0.35 for **2H**. Use of the full eqn. (4) leads to l values in the range of 0.01–0.04 for **2A**, **2AC** and **2M**, with very high (>0.22) probabilities that the lN term is statistically insignificant. The l value rises to 0.07 ± 0.04 for **2H**, but still with a fairly high (0.08) probability that the lN term is statistically insignificant. The m values [eqn. (3) or (4)] in the range of 0.60–0.78 for these four substrates are consistent with the proposal of an ionization which is anchimerically assisted, such that the values fall towards those observed for an S_N2 process (for example, a value of 0.55 is observed for solvolyses of methyl toluene-*p*-sulfonate[12,13]).

For **2A**, **2AC** and **2M**, the F-test value is highest with use of eqn. (3) and, for **2H**, the lower h value leads to use of eqn. (1) having a marginally higher F-test value than use of eqn. (3). The h/m ratios are close to unity for the first three compounds

(1.01, 0.92 and 0.87, respectively), with a sharp fall-off to a value of 0.48 for **2H**. This is consistent with the previously expressed[24] belief that the k_Δ pathway is still the exclusive pathway for solvolyses of **2H**, but with a reduced extent of anchimeric assistance. The three values of around unity for the ratio are of the same order of magnitude as for most solvolyses of benzylic substrates when there is only one aromatic ring conjugated with the developing positive charge,[9,15,18] reflecting the reductions in both h and m values.

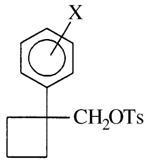
The correlation of the solvolyses of **2B** is much more problematic. Rather unsatisfactory correlations are obtained for correlations using eqns. (1)–(4), consistent with previous observations[24] when eqn. (5) was used. Using eqn. (5), a negative m_Δ value was obtained with an overall correlation coefficient of only 0.951 (much less than the >0.995 for the other correlations).[24] In the present analyses (Table 2), the F-test values are all low and similar in value, with the highest value being from use of eqn. (2), a correlation which had the lowest F-test value for each of the other four substrates. Using eqn. (2), an l value of 0.21 ± 0.05 is observed, identical to that previously obtained using N_{OTs} and Y_{OTs} values,[24] with a correlation coefficient of 0.9327 (lower than the 0.977 of the previous study because we have not excluded the solvolyses in methanol and 80% methanol). It is highly unlikely that this low l value reflects a concerted S_N2 mechanism, as was previously suggested;[24] the value is considerably lower than the l value of 0.38 for the solvolyses of *tert*-butyl chloride,[29,30] a value believed[13] to reflect nucleophilic solvation of the developing cation in a unimolecular (S_N1 + E1) process. Also, incorporating the hI term [eqn. (4)] leads to an h value of -0.11 ± 0.24 (probability that the hI term is statistically insignificant of 0.65) and the correlation coefficient rises only by 0.0008. The observation of a negative h value is consistent [eqn. (9)] with the negative m_Δ value of the previous study.

We have repeated all of the analyses of the solvolyses of compounds **1** and **2** using eqn. (5) and it is noteworthy that in only one instance, for the poorly correlated solvolyses of **2B**, does our statistical package not issue a warning that the results may be spurious due to multicolinearity. The multicolinearity is certainly to be expected because, for 38 solvents, Y_Δ correlates with Y_{OTs} with a correlation [eqn. (1)] of 0.952 (previously reported[24] as 0.955 for 37 solvents). That the correlations in terms of eqn. (5) do work, despite the multicolinearity, is due to the earlier observation [eqns. (7) and (8)] that the $m_\Delta Y_\Delta$ term is divisible into two components: of the two components, one can be incorporated into the $m_c Y_{OTs}$ term and the remaining component is equivalent to the aromatic ring parameter term (hI).

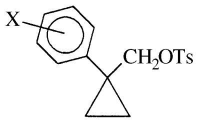
A probable explanation for the poor correlation of the solvolyses of **2B** is that the dominant mechanism is a k_c process with accompanying nucleophilic solvation. One can then argue that the l value is rather low for such a process and the correlation poor because an anchimerically assisted k_Δ process (l *ca.* 0) makes a moderate contribution in the poorly nucleophilic and highly ionizing fluoroalcohol-containing solvents, such that the data points for these solvents do not lie as far below the correlation line in the plot against Y_{OTs}[24] as they would for operation of only the k_c process with nucleophilic solvation. This leads directly to a lack of precision and a reduction in the apparent (averaged) l value from eqn. (2). The h value for the k_Δ process would, presumably, be lower than the 0.35 ± 0.07 for solvolyses of **2H** and a non-dominant component in only a minority of the solvents would not be expected to lead to any significant overall hI component to eqn. (4), as is observed. In a Hammett-type study of substituent effects using *p*-bromobenzenesulfonates in acetic acid and 80% ethanol,[31a] for the acetolysis, the points for the *p*-MeO and *p*-Me derivatives were on the k_Δ correlation line, the points for the unsubstituted compound just a little above and the point for the *m*-Br derivative was considerably above, indicating an appreciable contribution from a second mechanism. This second mechanism was described as a k_s pathway with, on the basis of a ρ_s value of close to unity as opposed to *ca.* 0.2 for a corresponding study of 2-arylethyl toluene-*p*-sulfonates, appreciable carbocationic character. This carbocationic character could very reasonably be considered to be sufficiently developed for an alternative description, as a k_c process with nucleophilic solvation, to be more appropriate. However, the pathway without anchimeric assistance usually leads to inversion of configuration,[31b] suggesting that any k_c process must involve a tight rearside solvation.

Solvolyses of (1-arylcycloalkyl)methyl toluene-*p*-sulfonates

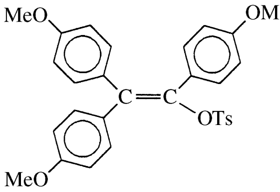
Fujio, Tsuno and co-workers have determined the specific rates of solvolysis for eight (1-arylcyclobutyl)methyl and two (1-arylcyclopropyl)methyl toluene-*p*-sulfonates in a wide range of solvents.[25] For acetolysis at 55 °C of the corresponding *p*-bromobenzenesulfonate esters, substituent effect studies have indicated[32] that, for the cyclobutyl derivatives **3**, the β-aryl-assisted pathway is dominant only for substrates containing strongly electron-supplying substituents and this pathway does not appear to occur at all for the two cyclopropyl derivatives **4**. It was predicted[24] that these differences in the response to substituent variations would also influence the responses to solvent variation.



3A: X = *p*-MeO
3MM′: X = 3,4-diMe
3M: X = *p*-Me
3M′: X = *m*-Me
3AB′: X = 3-Br, 4-MeO
3H: X = H
3C: X = *p*-Cl
3B′: X = *m*-Br



4A: X = *p*-MeO
4H: X = H



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The solvolyses of the indicated compounds of types **3** and **4** were studied in a series of solvents very similar to those used for studies of compounds of types **1** and **2**. Again, N_T, Y_{OTs} and I values were available for all except the carboxylic acids and their mixtures and the aqueous acetonitrile mixtures. The usual correlations against various combinations of these parameters are reported in Table 3, together with m' and h' values obtained by taking the m_c and m_Δ values [previously calculated[25] using eqn. (5)] and converting them to m' and h' values by using eqns. (7) and (9). There is again good agreement between the values obtained directly from eqn. (3) and those estimated from the reported m_c and m_Δ values.

For solvolyses of **3A** and **3MM′**, the h values and h/m ratio are essentially identical to those for **1A**, **1H**, **2A**, **2AC** and **2M** solvolyses, where the k_Δ mechanism is believed to be sufficiently dominant that it can be considered as the only pathway operating. The h values and the h/m ratios then fall off as one progresses to substrates with more electron-withdrawing substituents, becoming essentially zero for solvolyses of **3C** and **3B′**. The concept[25] of a continuous spectrum of aryl-assisted solvolyses with varying degrees of nucleophilic assistance is supported by these analyses. The neopentyl-like structure will severely limit the involvement of nucleophilic solvation as an aid towards a k_c process and, under these conditions, a weak anchimeric assistance can be observed under conditions where

Table 3 Correlation of the specific rates of solvolysis of (1-arylcycloalkyl)methyl toluene-*p*-sulfonates **3** and **4** and of 1,2,2-tris(*p*-methoxyphenyl)vinyl toluene-*p*-sulfonate **5** using the Grunwald–Winstein approach and various combinations of Y_{OTs}, N_{T} and I parameters; including indirectly determined [*via* eqn. (5)] values for m and h (designated as m' and h')[a]

Compound[b] m' h' (n')	n[b]	l[c]	m[c]	h[c]	c[d]	r[e]	F[f]
3A	29		0.51 ± 0.03		0.00 ± 0.22	0.9503	252
0.52 0.58			0.52 ± 0.02	0.58 ± 0.06	−0.05 ± 0.11	0.9887	567
(35)		−0.15 ± 0.04	0.41 ± 0.04		−0.06 ± 0.13	0.9693	202
		0.02 ± 0.03 (0.51)	0.53 ± 0.03	0.62 ± 0.09	−0.05 ± 0.11	0.9889	370
3MM′	29		0.62 ± 0.04		0.02 ± 0.25	0.9578	300
0.62 0.59			0.62 ± 0.01	0.66 ± 0.06	−0.04 ± 0.10	0.9933	957
(33)		−0.19 ± 0.04	0.48 ± 0.04		−0.05 ± 0.17	0.9801	317
		−0.02 ± 0.03 (0.47)	0.60 ± 0.03	0.61 ± 0.09	−0.04 ± 0.10	0.9934	627
3M	29		0.61 ± 0.03		0.01 ± 0.18	0.9760	543
0.62 0.44			0.62 ± 0.01	0.48 ± 0.06	−0.03 ± 0.09	0.9937	1030
(32)		−0.12 ± 0.03	0.53 ± 0.03		−0.03 ± 0.14	0.9855	438
		0.01 ± 0.03 (0.81)	0.63 ± 0.03	0.49 ± 0.09	−0.03 ± 0.10	0.9938	662
3M′	28		0.60 ± 0.02		0.03 ± 0.13	0.9871	992
0.60 0.27			0.61 ± 0.01	0.27 ± 0.06	0.00 ± 0.09	0.9935	957
(31)		−0.07 ± 0.02	0.55 ± 0.02		0.01 ± 0.11	0.9911	689
		0.00 ± 0.03 (0.91)	0.61 ± 0.03	0.28 ± 0.09 (0.01)	0.00 ± 0.09	0.9935	613
3AB′	28		0.52 ± 0.02		0.03 ± 0.14	0.9799	628
0.52 0.29			0.53 ± 0.01	0.31 ± 0.06	−0.01 ± 0.09	0.9908	668
(31)		−0.07 ± 0.03 (0.01)	0.47 ± 0.03		0.00 ± 0.12	0.9847	399
		0.04 ± 0.03 (0.23)	0.56 ± 0.03	0.40 ± 0.09	−0.01 ± 0.09	0.9913	454
3H	26		0.62 ± 0.02		−0.05 ± 0.10	0.9904	1231
0.61 0.14 (30)			0.62 ± 0.02	0.12 ± 0.05 (0.05)	−0.05 ± 0.09	0.9920	707
		−0.02 ± 0.02 (0.41)	0.61 ± 0.02		−0.05 ± 0.10	0.9907	609
		0.04 ± 0.03 (0.20)	0.65 ± 0.03	0.21 ± 0.09 (0.03)	−0.05 ± 0.09	0.9926	488
3C	22		0.59 ± 0.03		−0.11 ± 0.12	0.9777	434
0.57 −0.02 (24)			0.60 ± 0.03	−0.10 ± 0.08 (0.21)	−0.12 ± 0.12	0.9796	225
		0.05 ± 0.02 (0.03)	0.64 ± 0.03		−0.12 ± 0.11	0.9827	267
		0.08 ± 0.04 (0.06)	0.66 ± 0.04	0.09 ± 0.12 (0.45)	−0.11 ± 0.11	0.9832	174
3B′[g]	10		0.56 ± 0.04		−1.04 ± 0.10	0.9786	181
0.57 −0.04 (11)			0.60 ± 0.05	−0.13 ± 0.10 (0.26)	−1.10 ± 0.09	0.9825	98
		0.03 ± 0.03 (0.36)	0.60 ± 0.06		−1.07 ± 0.10	0.9812	90
		−0.02 ± 0.07 (0.82)	0.59 ± 0.06	−0.19 ± 0.26 (0.50)	−1.12 ± 0.10	0.9827	56
4A	28		0.66 ± 0.02		−0.11 ± 0.11	0.9909	1416
0.64 0.05 (31)			0.65 ± 0.02	−0.02 ± 0.07 (0.82)	−0.11 ± 0.11	0.9910	682
		0.06 ± 0.02 −(0.02)	0.69 ± 0.02		−0.08 ± 0.10	0.9929	866
		0.10 ± 0.03	0.72 ± 0.02	0.16 ± 0.08 (0.06)	−0.08 ± 0.09	0.9939	646
4H	24		0.69 ± 0.02		−0.11 ± 0.12	0.9893	1010
0.68 0.07 (26)			0.69 ± 0.02	0.03 ± 0.09 (0.76)	−0.11 ± 0.12	0.9893	484
		0.06 ± 0.03 (0.07)	0.73 ± 0.03		−0.08 ± 0.12	0.9908	565
		0.10 ± 0.04 (0.01)	0.76 ± 0.03	0.18 ± 0.10 (0.07)	−0.08 ± 0.11	0.9922	424
5	24		0.70 ± 0.07		−0.18 ± 0.43	0.9077	103
0.65 1.24			0.66 ± 0.02	1.29 ± 0.08	−0.14 ± 0.13	0.9928	721
(26)		−0.30 ± 0.07	0.51 ± 0.07		−0.26 ± 0.32	0.9550	103
		0.06 ± 0.05 (0.19)	0.70 ± 0.04	1.42 ± 0.13	−0.13 ± 0.12	0.9934	500

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[a] Specific rates for compounds **3** and **4** from ref. 25 (at 45.0 °C for **3** and 25.0 °C for **4**) and for compound **5** from ref. 39 (at 45.0 °C); values in parentheses are the probabilities that the associated term is not statistically significant (reported if greater than 0.005). [b–f] See corresponding footnotes to Table 1. [g] No specific rate value (k_0) for 80% ethanol and (5 + log k) is plotted in place of log (k/k_0).

nucleophilic solvation within a k_c process would otherwise be the favoured pathway.

The behaviour of compounds **4** is consistent with the prediction[25] based on the observation of only phenylcyclobutyl derivatives as products.[33,34] This indicates that, for these atypical substrates, alkyl migration is favoured over aryl migration. Also, the *h* values of very close to zero suggest that very little charge has developed adjacent to the aromatic ring in the transition state. This is more consistent with ionization followed by ring-expansion than with the concerted, one-step process to give a resonance-stabilized carbocation. Similarly, the *l* value of 0.31 for cyclopropylmethyl tosylate solvolysis,[25] indicating an appreciable nucleophilic solvation of the developing carbocation,[35] can also be considered to be more consistent with a simple ionization, rather than a concerted ionization–rearrangement process leading to a resonance-stabilized carbocation. An even higher *l* value of 0.46 has previously been reported for solvolyses of the corresponding bromide.[36] The suggestion[25] that the *l* value arises because of diversion in the product-forming stage away from a very unreactive cyclobutyl tosylate does not appear to be valid. If, as the experimental section states,[25] the specific rates are based on experimental infinity readings then the determined specific rates will be for the *sum* of solvolysis plus cyclobutyl tosylate formation.

The solvolyses of **4A** and **4H** correlate best with Y_{OTs}, with a rather low *m* value (0.66–0.69) due to the alkyl-migration anchimeric assistance. Use of eqn. (2) indicates a low *l* value and use of eqn. (3) indicates a low *h* value, values which are confirmed by use of the full eqn. (4).

Additional considerations

In two recent publications,[25,27] the m_c and m_Δ parameters, obtained by using Y_{OTs} and Y_Δ scales within eqn. (5), have been converted into alternative parameters. It can be shown that these new parameters are either identical to or closely related to those of eqn. (3). Further, a new scale, termed the charge delocalization effect ($Y_\Delta - Y_{\mathrm{OTs}}$), has been suggested, where $Y_\Delta = Y_\Delta/0.51$. These values are to be expected to be proportional to the aromatic ring parameter (*I*) values. However, it must be emphasized that the arguments[12,13,17,37] in favour of developing *N* scales using RX$^+$-type (rather than RX-type) substrates apply even more forcibly for the development of a scale of *I* values. Indeed, the ($Y_\Delta - Y_{\mathrm{OTs}}$) value often represents a small difference between two large numbers; for example, the value of 0.48 for 97% 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) is the difference between 4.09 and 3.61. Under these conditions, it is essential that the normalization factor of 0.51 that is being applied to the Y_Δ scale be of a high accuracy. The difficulty in arriving at a value for this factor parallels exactly that of arriving at the needed *m* value for methyl tosylate solvolysis in establishment of the N_{OTs} scale. However, contrary to what (constant solvent nucleophilicities) is presented as the argument favouring use of aqueous acetone data,[25] what is required is the choice of a series of solvents with essentially constant *I* values, such that the *hI* term within eqn. (3) is a constant, and aqueous acetone solvents show only slight variation.[9] If constant solvent nucleophilicity was indeed the required factor, the obvious choice would have been those alcohol and aqueous alcohol solvents which were assumed to have equal solvent nucleophilicities in the establishment of the scale of N_{OTs} values.[38] Presumably, these solvents were found to be unsuitable, as one would predict on the basis of quite large variations in their *I* values.[9] The 0.51 obtained in this way should be identical to the *m* value from treatment of the solvolyses of **1A** using eqn. (3) and, indeed, the calculated value of 0.52 from a consideration of 38 solvolyses (Table 1) is essentially identical to the value obtained by neglecting the *hI* term (almost constant *I* values) in aqueous-acetone solvents.

One of the two new types of coefficients developed from the calculated m_c and m_Δ values is termed 'the conventional measure *m* of the response to the solvent polarity', defined as in eqn. (10). This equation is identical to eqn. (7) and *m* is best

$$m = m_c + 0.51m_\Delta \qquad (10)$$

considered as being the *m* of the mY_{X} term of eqn. (3). The other new coefficient was defined as M_Δ, representing the 'degree of aryl-assistance' and defined as in eqn. (11). Substituting from eqns. (7) and (9), it follows that M_Δ is equal to 0.78*h/m*,

$$M_\Delta = \frac{0.51m_\Delta}{(m_c + 0.51m_\Delta)} \qquad (11)$$

proportional to the *h/m* ratio that we make extensive use of in our analyses. Just as we have suggested[9] that the *h/m* ratio is useful for correlating the magnitude of perturbations introduced by conjugated π electrons, so also have Fujio, Tsuno and co-workers proposed the use of M_Δ for this purpose.[27]

An interesting compound, whose specific rates of solvolysis were previously determined,[39] is 1,2,2-tris(*p*-methoxyphenyl)vinyl toluene-*p*-sulfonate **5**. The analyses in terms of eqns. (1)–(4) are presented in Table 3. Analysis in terms of eqn. (5) led[25] to the values for m_c of −0.34 and for m_Δ of 1.90, leading, in turn, to values for *m* of 0.63 and for M_Δ of 1.54. Negative values, such as the one obtained here for m_c, often indicate that an inappropriate form of the Grunwald–Winstein equation is being used. For example, a negative *l* value using eqn. (2) may indicate that eqn. (3) should be used and a negative *h* value using eqn. (3) that eqn. (2) should be used. These negative values usually disappear when the full eqn. (4) is employed. The negative value here arises from a different source, it is a result of using eqn. (5) rigidly parameterized for an aryl-migration-driven anchimeric assistance for other types of solvolysis, in which the participation of the aromatic ring is more direct and, hence, more intense. Indeed, by combining eqns. (7) and (9), it can be shown that a negative m_c value will result whenever the *h/m* ratio is greater than 1.25. It then follows, as can also be seen from eqn. (11), that a negative m_c will be accompanied by the recently defined M_Δ having a value of above unity.

It is frequently instructive to see how an equation deals with a situation where it should not apply. The study of compounds **2** was accompanied by the determination of the specific rates of solvolysis of 1-(1-adamantyl)ethyl toluene-*p*-sulfonate in 41 solvents.[24] Use of eqn. (1), with Y_{OTs}, gave an excellent correlation and an *m* value of 0.90 (correlation coefficient of 0.996). Since there are no π electrons in the substrate, one would predict that eqn. (5) would lead to an unchanged m_c value and an m_Δ value of zero. This is not the case, and the m_c value falls to 0.72 with an m_Δ value of 0.36 (correlation coefficient of 0.998), suggesting a degree of aryl-assistance (M_Δ) of 0.20. This illustrates very well the potential for spurious results due to multicollinearity when eqn. (5) is employed.

Conclusions

Of the three commonly used techniques for the treatment of dispersion in Grunwald–Winstein plots, when the dispersion is associated with π electrons being conjugated in the transition state with the developing positive charge, the most restricted is the similarity model approach. This approach requires not only an identical (or, at least, very similar) leaving group in both the standard and the substrate but also a 'similarity' in the aryl-substituted R group of the RX-substrate. We have shown previously[9] that a structural similarity within R is only a secondary consideration and the prime consideration is similarity in the *h/m* ratio [from eqn. (3)] for solvolyses of the standard and the substrate. This makes choice of a suitable standard difficult, unless eqn. (3) has already been applied, in which case (in almost all instances) application of the similarity model approach would be superfluous. It is now well recognized[11,14] that any significant difference in the number of π electrons entering into conjugation will require a new model to be found and, even for a constant leaving group, there is a need for a multiplicity of similarity models.

The approach of Fujio, Tsuno and co-workers using eqn. (5) is somewhat more versatile and, although examples of such application are not yet available, it should be capable of dealing with multiple aromatic rings without the need for a multiplicity of Y_Δ scales. However, with multiple aromatic rings entering into conjugation with the developing positive charge, the *h/m* ratio will usually be greater than 1.25, which means that negative m_c values will frequently be observed. The intercorrelation between $Y_{\mathbf{OTs}}$ and Y_Δ (correlation coefficient of 0.952) leads to statistical analyses in terms of eqn. (5) almost invariably being accompanied by a multicollinearity warning. However, the correlation does work, because the $m_\Delta Y_\Delta$ term can be divided into two components, one of which can be incorporated into the $m_c Y_{\mathbf{OTs}}$ term and the other of which is equivalent to the hI term of eqn. (3). Unfortunately, the $Y_{\mathbf{OTs}}$ plus Y_Δ approach does retain one of the major inflexibilities of the similarity model approach in that the Y_Δ scale applies only for a toluene-*p*-sulfonate leaving group and, for eqn. (5) to be applicable, for each new leaving group present in RX, a new $Y_{\Delta X}$ scale would have to be established, to accompany the $Y_{\mathbf{X}}$ scale.

The most versatile treatment is in terms of eqn. (3) or, if solvent nucleophilicity is also a factor, eqn. (4). Here one uses the appropriate $Y_{\mathbf{X}}$ scale, values already tabulated for the more commonly used leaving groups,[7] in conjunction with the aromatic ring parameter (I),[9] which can be used irrespective of leaving group and even for both $R{-}X^+$- and RX-type substrates. These equations have been successfully applied previously to the specific rates of solvolysis of a wide variety of benzylic, naphthylmethyl, anthranylmethyl and benzhydryl derivatives, with h values (sensitivities to changes in the I parameter) and the associated *h/m* ratios varying in a logical manner. It is now shown that eqn. (3) can very well be used to treat those solvolyses of β-arylalkyl toluene-*p*-sulfonates which proceed with an anchimeric assistance involving migration of the aryl group to the α-carbon. Further, it is shown that the m_c and m_Δ values obtained whenever eqn. (5) is employed can be readily converted, using eqns. (7) and (9), into the corresponding m and h values of eqn. (3), such that the $Y_{\mathbf{OTs}}$ plus Y_Δ approach can be considered as one special case (for a toluene-*p*-sulfonate leaving group) of the application of $Y_{\mathbf{X}}$ plus I within eqn. (3).

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References

1 K.-T. Liu, H.-C. Sheu, H.-I Chen, P.-F. Chiu and C.-R. Hu, *Tetrahedron Lett.*, 1990, **31**, 3611.
2 K.-T. Liu and H.-C. Sheu, *J. Org. Chem.*, 1991, **56**, 3021.
3 K.-T. Liu, H.-I. Chen and C.-P. Chin, *J. Phys. Org. Chem.*, 1991, **4**, 463.
4 K.-T. Liu and H.-C. Sheu, *J. Chin. Chem. Soc. (Taipei)*, 1991, **38**, 29.
5 K.-T. Liu, J.-S. Yang, S.-M. Chang, Y.-S. Lin, H.-C. Sheu and M.-L. Tsao, *J. Org. Chem.*, 1992, **57**, 3041.
6 E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 1948, **70**, 846.
7 T. W. Bentley and G. Llewellyn, *Prog. Phys. Org. Chem.*, 1990, **17**, 121.
8 T. W. Bentley, I. S. Koo and S. J. Norman, *J. Org. Chem.*, 1991, **56**, 1604.
9 D. N. Kevill, N. HJ Ismail and M. J. D'Souza, *J. Org. Chem.*, 1994, **59**, 6303.
10 D. N. Kevill and M. J. D'Souza, *J. Phys. Org. Chem.*, 1992, **5**, 287.
11 D. N. Kevill and M. J. D'Souza, *Org. React. (Tartu)*, 1995, **29**, 55.
12 D. N. Kevill and S. W. Anderson, *J. Org. Chem.*, 1991, **56**, 1845.
13 D. N. Kevill, in *Advances in Quantitative Structure-Property Relationships*, vol. 1, ed. M. Charton, Jai Press, Greenwich, Connecticut, 1996, pp. 81–115.
14 K.-T. Liu, *J. Chin. Chem. Soc. (Taipei)*, 1995, **42**, 607.
15 D. N. Kevill and M. J. D'Souza, *J. Chem. Res.* (*S*), 1996, 286; (*M*) 1996, 1649.
16 D. N. Kevill and S. W. Anderson, *J. Am. Chem. Soc.*, 1986, **108**, 1579.
17 D. N. Kevill and G. M. L. Lin, *J. Am. Chem. Soc.*, 1979, **101**, 3916.
18 D. N. Kevill and M. J. D'Souza, *J. Chem. Soc., Perkin Trans. 2*, 1995, 973.
19 D. N. Kevill, S. W. Anderson and N. HJ Ismail, *J. Org. Chem.*, 1996, **61**, 7256.
20 T. W. Bentley, J.-P. Dau-Schmidt, G. Llewellyn and H. Mayr, *J. Org. Chem.*, 1992, **57**, 2387.
21 I. Lee, H. J. Koh and B. D. Chang, *Bull. Korean Chem. Soc.*, 1995, **16**, 1104; H. K. Oh, Y. B. Kown, H. J. Koh and I. Lee, *New J. Chem.*, 1996, **20**, 579.
22 K.-T. Liu, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 327.
23 M. Fujio, M. Goto, K. Funatsu, T. Yoshino, Y. Saeki, K. Yatsugi and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 46.
24 M. Fujio, Y. Saeki, K. Nakamoto, K. Yatsugi, N. Goto, S. H. Kim, Y. Tsuji, Z. Rappoport and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2603.
25 M. Fujio, Y. Saeki, K. Nakamoto, S. H. Kim, Z. Rappoport and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 751.
26 M. Fujio, T. Susuki, M. Goto, K. Yatsugi, Y. Tsuji, Y. Saeki, S. H. Kim and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2233.
27 M. Fujio, T. Susuki, K. Yatsugi, Y. Saeki, M. Goto, S. H. Kim, Y. Tsuji, Z. Rappoport and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2619.
28 D. N. Kevill and H. Ren, *J. Org. Chem.*, 1989, **54**, 5654.
29 T. W. Bentley and G. E. Carter, *J. Am. Chem. Soc.*, 1982, **104**, 5741.
30 D. N. Kevill and M. J. D'Souza, *J. Chem. Res. (S)*, 1993, 174.
31 (*a*) M. Fujio, N. Goto, T. Dairokuno, M. Goto, Y. Saeki, Y. Okusako and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 3072; (*b*) F. L. Schadt III, C. J. Lancelot and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1978, **100**, 228.
32 Y. Saeki, PhD Thesis, Kyushu University, November 1994, quoted (with figure) in ref. 25.
33 J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, 1962, **27**, 3430.
34 D. D. Roberts and T. M. Watson, *J. Org. Chem.*, 1970, **35**, 978 and references therein.
35 D. N. Kevill, A. J. Oldfield and M. J. D'Souza, *J. Chem. Res. (S)*, 1996, 122.
36 M. H. Abduljaber, PhD Dissertation, Northern Illinois University, June 1992, quoted in ref. 35.
37 D. N. Kevill, S. W. Anderson and E. K. Fujimoto, in *Nucleophilicity*, eds. J. M. Harris and S. P. McManus, Adv. Chem. Ser., No. 215, Am. Chem. Soc., Washington, DC, 1987, pp. 269–283; D. N. Kevill, S. W. Anderson, N. HJ Ismail and E. K. Fujimoto, *Studies Org. Chem.*, 1987, **31**, 311.
38 T. W. Bentley, in *Nucleophilicity*, eds. J. M. Harris and S. P. McManus, Adv. Chem. Ser., No. 215, Am. Chem. Soc., Washington, DC, 1987, pp. 255–268.
39 M. Fujio, M. Goto, Y. Tsuno, S. Kobayashi and H. Taniguchi, *Tetrahedron Lett.* 1990, **31**, 7039.

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