Considerably improved Grunwald–Winstein correlations for solvolyses of several secondary and tertiary benzylic derivatives upon inclusion of a term governed by the aromatic ring parameter (*I*)

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In almost all cases, Grunwald–Winstein treatments of the specific rates of solvolysis of a series of secondary and tertiary benzylic toluene-*p*-sulfonates, *p*-nitrobenzoates, chlorides and bromides exhibit a considerably improved correlation coefficient and a higher *F*-test value on incorporation of an *hI* term, where *h* is the sensitivity towards changes in the recently developed aromatic ring parameter (*I*). The *h* values increase on introduction of a second aromatic ring at the α-carbon, on introduction of an electron-withdrawing α-trifluoromethyl group, and on introduction of an electron-supplying aromatic-ring substituent.

Dispersion into separate lines in the correlation of the specific rates of solvolysis of a substrate in a variety of binary solvent mixtures was documented[1–3] in early treatments using the Grunwald-Winstein equation [eqn. (1)]. In eqn. (1), k and k_o

$$\log(k/k_o) = mY + c \qquad (1)$$

are the specific rates of solvolysis of a substrate in a given solvent, of solvent ionizing power Y, and in 80% ethanol respectively, m is the sensitivity to changes in Y value, and c is a residual (constant) term.

For substrates subject to bimolecular attack by the solvent, it was recognized[2] that appreciable dispersion is to be expected because of the need also to incorporate a consideration of solvent nucleophilicity.[4–8] Indeed, the magnitude of the separation has been used as a measure of the extent of nucleophilic assistance provided by the solvent, as in the evaluation of the ratio of the specific rates of solvolysis in acetic or formic acid and the aqueous ethanol mixture of identical Y value (but higher solvent nucleophilicity value).[2,9] More recently the Raber–Harris probe has been developed,[10] involving a comparison of Grunwald-Winstein plots for solvolysis in ethanol–water and (lower nucleophilicity for a given Y value) 2,2,2-trifluoroethanol (TFE)–water mixtures. The preferred treatment when data is available for a reasonably wide range of solvent type is in terms of the extended Grunwald-Winstein equation [eqn. (2)].[2,4] Eqn. (2) is similar to eqn. (1),

$$\log(k/k_o) = lN + mY + c \qquad (2)$$

except for the incorporation of an additional term lN where N is the solvent nucleophilicity value and l is a measure of the sensitivity of the specific rate of solvolysis to changes in N value. The solvent nucleophilicity scales most frequently employed are based on methyl toluene-*p*-sulfonate (tosylate) solvolysis[4] (N_{OTs} values) or on the solvolysis of the *S*-methyldibenzothiophenium ion[8] (N_T values).

Another cause of dispersion in Grunwald–Winstein plots using eqn. (1) is when the leaving group in the solvolysis of a given substrate differs from the leaving group present in the standard substrate used to establish the Y scale being used in the correlation.[11] From the similarity model approach, ideally the standard substrate and the substrate under study should have the same leaving group or, failing that, they should be as similar as possible. The development of a series of Y_x scales for correlation of the solvolyses of an RX substrate has recently been reviewed.[12] These scales are based on the solvolyses of 1- or 2-adamantyl derivatives, where rearside nucleophilic assistance from the solvent is impossible or is strongly impeded.[13,14]

Treatments using the extended Grunwald–Winstein equation have revealed that nucleophilic assistance to solvolyses is more widespread than originally thought and it is frequently observed for solvolyses of secondary[4] and tertiary[15–17] derivatives in the absence of carbocation stabilization by electron-supplying substituents and/or appreciable steric hindrance to rearside attack at the α-carbon. Indeed, even the original standard solvolysis for establishing a Y scale, that of *tert*-butyl chloride, has been found to have an appreciable l value when correlation is against a combination of N_T (or N_{OTs}) and Y_{Cl} values.[16,18] This assistance is believed to differ in character from that observed in the classical S_N2 process and it has been described in terms of an S_N2 (intermediate) mechanism[16,19] or in terms of nucleophilic solvation within an S_N1 process.[7,18] In the present communication, we consider Grunwald-Winstein type correlations for the solvolyses of secondary and tertiary benzylic derivatives which are of a type where nucleophilic assistance from the solvent is expected to be only weak, or possibly absent, due not only to the resonance stabilization within benzylic carbocations but also due to appreciable crowding in the vicinity of the reaction centre.[20]

Even when the leaving group is identical with that of the standard substrate and nucleophilic assistance from the solvent is believed to be absent, many examples of dispersion in plots according to eqn. (1) are known. The majority of these cases involve solvolyses of substrates containing π-electron systems which are conjugated with the developing positive charge on the α-carbon. These systems are most frequently benzylic,[21–23] but occasionally allylic or propargylic.[24] The magnitude of the dispersion appears to be related to the number of adjacent π electrons[24] and it was observed in early studies that solvolysis of benzhydryl chloride (two α-phenyl groups) exhibits larger dispersions than the solvolysis of α-phenylethyl chloride.[22] Also, other factors being essentially identical, the dispersions observed are in the order of benzylic > propargylic > allylic.[24]

For the solvolyses of a benzylic derivative, taking the Grunwald–Winstein plot for the solvolysis in aqueous ethanol as a reference correlation, it has been recognized[20,25] that the ordering of the deviations for solvolyses in other pure and binary solvents do not parallel the differences in solvent nucleophilicities. Indeed, the positioning of data points for aqueous–TFE mixtures above or below the reference line can be taken as a qualitative indication of the dominance of effects due to the presence of α-phenyl groups or of effects due to solvent nucleophilicity, respectively. We recently suggested[26] that, since the dispersions seem to follow a consistent pattern, it should be possible to develop an aromatic ring parameter (*I*), which, as qualified by the appropriate sensitivity (*h*), can be added to eqns. (1) or (2) to give eqns. (3) or (4), respectively.

$$\log(k/k_o) = mY + hI + c \qquad (3)$$

$$\log(k/k_o) = lN + mY + hI + c \qquad (4)$$

A scale of *I* values was developed[26] based on differences in the nature of the variations of the specific rates of solvolysis of the *p*-methoxybenzyldimethylsulfonium ion and of the 1-adamantyldimethylsulfonium ion[17b] (no aromatic ring) as the solvent composition was altered [eqn. (5)]. Six examples of the application of the I scale were given[26] and considerably improved correlations were observed for the solvolyses of 2-chloro-2-(*m*-chlorophenyl)adamantane,[20] 2-chloro-2-phenyladamantane,[20] α-(*tert*-butyl)benzyl tosylate,[27] α-*tert*-butyl-α-methylbenzyl chloride,[25] *p*-methoxybenzyl chloride[23] and benzhydryl chloride.[22,28]

$$I = \log(k/k_o)_{p\text{-MeOC}_6\text{H}_4\text{CH}_2\overset{+}{\text{S}}\text{Me}_2} - 1.3\log(k/k_o)_{1\text{-Ad}\overset{+}{\text{S}}\text{Me}_2} \qquad (5)$$

We are fortunate in that, in probing the applicability of similarity models developed for use as *Y* scales (Y_{BnX} values), Liu and co-workers have presented[20,25,29–35] specific rates of solvolysis in a variety of solvents for several secondary and tertiary benzylic derivatives. The majority of these studies are sufficiently comprehensive for use in a consideration of the utility of the aromatic ring parameter (*I*) within Grunwald–Winstein correlations.

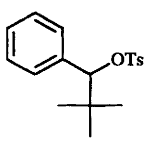
Results and discussion

For each of the substrates for which correlations have been performed, all of the available specific rates of solvolysis at 25.0 °C have been analysed in terms of eqns. (1)–(4) using the ABSTAT statistical package (Anderson-Bell, Arvada, Colorado, USA). 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.

Solvolyses of benzylic tosylates

The five solvolyses analysed are using specific rates of solvolysis abstracted from a publication by Liu and co-workers.[32] The substrates involved are α-*tert*-butylbenzyl tosylate **1**, α-*tert*-butyl-*m*-chlorobenzyl tosylate **2**, α-trifluoromethyl-*p*-methylbenzyl tosylate **3**, α-methyl-α-trifluoromethylbenzyl tosylate **4** and α-(3,5-dichlorophenyl)-α-trifluoromethylbenzyl tosylate **5**. The analyses (Table 1) were performed using N_T values,[8] *I* values[26] and Y_{OTs} values,[12] with those Y_{OTs} values based on 1-adamantyl (rather than 2-adamantyl) tosylate solvolysis adjusted[36] in the manner recommended by Allard and Casadevall.[37]

In the initial examples[26] chosen to illustrate the use of the *I* parameter, specific rates of solvolysis of **1** presented by Tsuno and co-workers[27] were analysed. Virtually simultaneous to the appearance of the Tsuno paper, a parallel study carried out independently by Liu and co-workers appeared;[32] we present an analysis of this data in Table 1. The solvent systems were similar to those for the study we analysed earlier, with the main difference being the inclusion of three TFE–ethanol mixtures in the Liu study. The trends observed are very similar to those from analysis of the Tsuno study and, in particular, the negative *l* value obtained from use of eqn. (2) again becomes a very small positive value when the *hI* term is also included in the analysis [eqn. (4)]. This is nicely consistent with the conclusion from a study of substituent effects[38] that the solvolysis is unimolecular, without nucleophilic assistance or neighbouring methyl participation. Liu chose the solvolyses of **1** as a similarity model for other benzylic tosylate solvolyses (Y_{BnOTs} values). This choice was dictated in part by the belief that a tertiary 2-aryl-2-adamantyl tosylate, paralleling the substrates for Y_{BnX} scales with X = Cl, Br, OPNB (*p*-nitrobenzoate), would be too reactive for convenient measurement. The choice is a fortunate one because the Y_{BnOTs} scale (unlike the other Y_{BnX} scales) is based on a solvolysis which has a typical *h*/*m* value for solvolyses of those benzylic derivatives which have only one α-aryl group.[26]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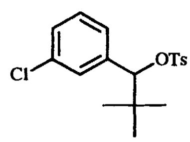
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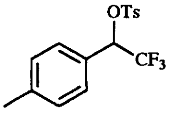
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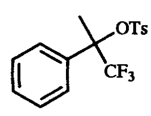
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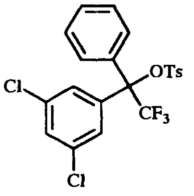
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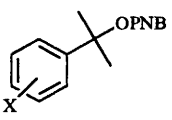
For all five of the benzylic tosylates analysed, a substantial improvement in the value for the correlation coefficient is observed on going from the application of eqn. (1) to the application of eqn. (3) and, in contrast, only very small increases in correlation coefficient are observed on going instead to the use of eqn. (2). Clearly, if a two-term correlation is considered, incorporation of the *hI* term is to be strongly preferred over incorporation of the *lN* term. For each of the benzylic tosylate substrates, application of eqn. (2) leads to negative *l* values, which are now understood[26] to reflect a very approximate negative relationship between the *I* and *N* scales. Using the full eqn. (4) leads to the *l* value becoming essentially zero for solvolysis of **5** and small positive values being observed for solvolyses of **1**–**4**. These observations are also reflected in the pattern for *F*-test values. In all cases, the *F*-test value rises in going from use of eqn. (1) to use of eqn. (3) and falls in going from use of eqn. (1) to use of eqn. (2). Considering all four types of analysis [eqns. (1)–(4)], for each of the five systems, the largest *F*-test value is always the one associated with the application of eqn. (3).

The *h* values, obtained from application of either eqn. (3) or (4), are a little below unity for **1** and they fall slightly on incorporation of an *m*-Cl electron-withdrawing substituent

Table 1 Correlation of the specific rates of solvolysis of benzylic tosylates using the Grunwald–Winstein approach and various combinations of Y_{OTs}, N_T and I parameters[a]

Compound[b]	n[b]	l[c]	m[c]	h[c]	c[d]	r[e]	F[f]
1	25		0.99 ± 0.04		0.13 ± 0.26	0.9821	625
			0.93 ± 0.02	0.76 ± 0.08	0.06 ± 0.12	0.9965	1573
		−0.10 ± 0.06 (0.09)	0.90 ± 0.06		0.08 ± 0.25	0.9843	343
		0.09 ± 0.03 (0.01)	0.99 ± 0.03	0.91 ± 0.09	0.10 ± 0.10	0.9975	1395
2	13		0.98 ± 0.06		0.08 ± 0.23	0.9817	293
			0.91 ± 0.03	0.59 ± 0.11	0.10 ± 0.13	0.9950	501
		−0.10 ± 0.06 (0.15)	0.86 ± 0.09		0.10 ± 0.22	0.9853	166
		0.10 ± 0.05 (0.07)	1.00 ± 0.05	0.81 ± 0.15	0.09 ± 0.11	0.9966	440
3	12		0.97 ± 0.08		−0.11 ± 0.40	0.9653	137
			0.80 ± 0.07	1.10 ± 0.27	−0.14 ± 0.25	0.9881	186
		−0.08 ± 0.16 (0.64)	0.89 ± 0.19		−0.15 ± 0.42	0.9662	63
		0.17 ± 0.10 (0.12)	0.95 ± 0.11	1.37 ± 0.28	−0.06 ± 0.22	0.9915	155
4	13		0.94 ± 0.06		−0.02 ± 0.31	0.9788	251
			0.85 ± 0.04	0.86 ± 0.19	−0.07 ± 0.19	0.9929	350
		−0.03 ± 0.10 (0.75)	0.91 ± 0.12		−0.04 ± 0.32	0.9790	115
		0.12 ± 0.06 (0.08)	0.96 ± 0.06	1.04 ± 0.19	0.01 ± 0.16	0.9951	303
5	10		1.08 ± 0.12		0.36 ± 0.41	0.9526	78
			0.88 ± 0.06	1.46 ± 0.24	0.20 ± 0.17	0.9928	239
		−0.18 ± 0.20 (0.40)	0.94 ± 0.20		0.23 ± 0.41	0.9576	39
		−0.01 ± 0.09 (0.90)	0.87 ± 0.09	1.45 ± 0.27	0.19 ± 0.19	0.9928	137

[a] Specific rates, at 25.0 °C, from ref. 32; values in parentheses are the probabilities that the lN term is not statistically significant (corresponding probabilities for mY and hI terms were in all instances less than 0.003). [b] For designation, see the text; n is the number of solvents studied. [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.



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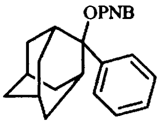
a X = *p*-MeS
b X = *p*-Me
c X = *o*-Me
d X = H



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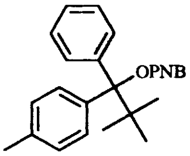

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(compound **2**). The compounds **3**–**5** all incorporate an α-trifluoromethyl group. This electron-withdrawing group has been shown to decelerate both S_N1 and S_N2 reactions.[39] It has been suggested that the positive charge delocalized into the aromatic ring of an α-trifluoromethyl-substituted benzylic cation is maximized, such that the greatest effect of the aryl substituent is realized and large Hammett ρ values are observed.[40] If the hI contribution arises to a large degree because the solvation effects in the presence of α-aryl substituents differ in character from those observed with α-alkyl groups (no π electrons conjugated with the reaction centre),[20,23,24] it is reasonable to suppose that the sensitivity towards the I parameter, in the presence of an α-trifluoromethyl group, will be magnified.

Compound **3** shows a considerably increased h value but it is not possible to partition the increase between components due to replacing the α-*tert*-butyl group by the α-trifluoromethyl group and due to introduction of the electron-supplying *p*-methyl group. Compound **4** corresponds to cumyl tosylate but with the three hydrogens of one of the two methyl groups replaced by fluorine. The corresponding cumyl tosylate would be too reactive for convenient study but analysis of data for cumyl chloride (Table 2) gives h values of 0.58 and 0.68 with use of eqn. (3) or (4), lower, as predicted, than the corresponding values of 0.86 and 1.04 for **4**. Compound **5** contains, in addition to an α-trifluoromethyl group, two phenyl groups, one of which contains two *meta*-chloro substituents. As one would expect with two α-aryl groups, a relatively high h value [1.46 from eqn. (3) and 1.45 from eqn. (4)] is obtained. As regards the other substituents, one would predict that the two *meta*-chloro substituents would tend to decrease and the α-trifluoromethyl group would tend to increase the h value.

The observed h values for solvolyses of **1**–**5** are consistent with the structures of the substrates and the inclusion of the hI term [eqns. (3) and (4)] considerably improves the correlations, as judged in terms of appreciable increases in both correlation coefficient and F-test values.

Solvolyses of benzylic *p*-nitrobenzoates

Specific rate values are available for the solvolyses of four cumyl *p*-nitrobenzoates (**6a**–**6d**),[30,31] of 2-phenyl-2-adamantyl-*p*-nitrobenzoate (**7**)[30] and of α-*tert*-butyl-α-phenyl-*p*-methylbenzyl *p*-nitrobenzoate (**8**).[30] The data for **7** have been used to establish a Y_{BnOPNB} scale.[30]

Table 2 Correlation of the specific rates of solvolysis of cumyl chloride and derivatives [$XC_6H_4CR(CH_3)Cl$] using the Grunwald–Winstein approach and various combinations of Y_{Cl}, N_T and I parameters[a]

X[b]	R[b]	n[b]	l[c]	m[c]	h[c]	c[d]	r[e]	F[f]
o-Me	Me	11[g]		0.73 ± 0.06		0.10 ± 0.27	0.9674	131
				0.68 ± 0.03	0.78 ± 0.12	−0.03 ± 0.11	0.9953	421
			0.00 ± 0.22 (0.99)	0.73 ± 0.10		0.10 ± 0.28	0.9674	58
			0.13 ± 0.08 (0.12)	0.72 ± 0.03	0.83 ± 0.11	0.03 ± 0.10	0.9967	354
H	Me	11[g]		0.75 ± 0.06		−0.03 ± 0.24	0.9736	164
				0.71 ± 0.04	0.58 ± 0.28 (0.01)	−0.13 ± 0.17	0.9885	171
			0.21 ± 0.19 (0.28)	0.82 ± 0.08		0.07 ± 0.24	0.9774	86
			0.33 ± 0.08	0.81 ± 0.03	0.68 ± 0.11	0.01 ± 0.10	0.9968	362
m-Cl	Me	12[h]		0.68 ± 0.05		−0.13 ± 0.25	0.9774	214
				0.66 ± 0.05	0.36 ± 0.23 (0.15)	−0.17 ± 0.23	0.9824	124
			0.07 ± 0.10 (0.49)	0.72 ± 0.08		−0.08 ± 0.25	0.9786	102
			0.12 ± 0.09 (0.23)	0.72 ± 0.07	0.45 ± 0.23 (0.09)	−0.09 ± 0.22	0.9855	90
p-CF_3	Me	10[i]		0.65 ± 0.06		−0.28 ± 0.31	0.9673	116
				0.61 ± 0.06	0.50 ± 0.34 (0.18)	−0.36 ± 0.29	0.9751	68
			0.12 ± 0.15 (0.46)	0.73 ± 0.12		−0.17 ± 0.32	0.9700	56
			0.12 ± 0.14 (0.42)	0.68 ± 0.11	0.50 ± 0.34 (0.19)	−0.26 ± 0.29	0.9779	44
H	Et	11[j]		0.81 ± 0.05		0.10 ± 0.23	0.9801	219
				0.75 ± 0.04	0.70 ± 0.18	−0.05 ± 0.14	0.9934	298
			0.10 ± 0.17 (0.58)	0.84 ± 0.08		0.14 ± 0.24	0.9809	102
			0.22 ± 0.08 (0.02)	0.81 ± 0.03	0.80 ± 0.13	0.03 ± 0.10	0.9969	380
H	$\mathrm{Pr^i}$	11[g]		0.80 ± 0.07		0.11 ± 0.31	0.9644	120
				0.74 ± 0.02	0.94 ± 0.09	−0.04 ± 0.09	0.9975	790
			−0.11 ± 0.25 (0.67)	0.77 ± 0.11		0.06 ± 0.32	0.9653	55
			0.05 ± 0.07 (0.51)	0.75 ± 0.03	0.96 ± 0.10	−0.02 ± 0.09	0.9976	493
m-Cl	$\mathrm{Pr^i}$	11[j]		0.73 ± 0.07		0.13 ± 0.35	0.9561	96
				0.71 ± 0.04	0.85 ± 0.20	0.06 ± 0.21	0.9869	150
			−0.26 ± 0.13 (0.08)	0.57 ± 0.10		0.01 ± 0.31	0.9708	66
			−0.10 ± 0.10 (0.34)	0.65 ± 0.07	0.74 ± 0.22 (0.01)	0.02 ± 0.20	0.9887	101
H	$\mathrm{Bu^t}$	15[g,k]		0.84 ± 0.06		−0.04 ± 0.31	0.9691	201
				0.79 ± 0.03	0.80 ± 0.15	−0.07 ± 0.17	0.9912	337
			−0.23 ± 0.09 (0.02)	0.68 ± 0.08		−0.10 ± 0.26	0.9803	148
			−0.08 ± 0.07 (0.34)	0.75 ± 0.06	0.70 ± 0.18	−0.09 ± 0.17	0.9920	225
m-CH_3	$\mathrm{Bu^t}$	12[g]		0.83 ± 0.11		0.19 ± 0.42	0.9283	62
				0.86 ± 0.04	1.11 ± 0.14	0.04 ± 0.15	0.9916	265
			−0.47 ± 0.11	0.48 ± 0.11		0.07 ± 0.26	0.9756	89
			−0.18 ± 0.07 (0.03)	0.72 ± 0.06	0.86 ± 0.15	0.03 ± 0.12	0.9954	288
3,4-di-Me	$\mathrm{Bu^t}$	11[g]		0.69 ± 0.14		0.24 ± 0.47	0.8489	23
				0.82 ± 0.03	1.33 ± 0.09	0.07 ± 0.10	0.9946	365
			−1.00 ± 0.26	0.29 ± 0.14 (0.07)		−0.02 ± 0.30	0.9497	37
			−0.08 ± 0.15 (0.60)	0.78 ± 0.08	1.26 ± 0.16	0.06 ± 0.10	0.9948	222

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[a] Values in parentheses are the probabilities that the term is not statistically significant (recorded if greater than 0.005). [b] The substituents within the general formula given in the table heading; n is the number of solvents studied. [c–f] See corresponding footnotes to Table 3. [g] Specific rates, at 25.0 °C, from ref. 33. [h] Specific rates, at 25.0 °C, from refs. 25 and 34. [i] Specific rates, at 25.0 °C, from ref. 34. [j] Specific rates, at 25.0 °C, from ref. 35. [k] One value, 80% acetone, from ref. 45.

Table 3 Correlation of the specific rates of solvolysis of benzylic *p*-nitrobenzoates using the Grunwald–Winstein approach and various combinations of Y_{OTs}, N_{T} and I parameters[a]

Compound[b]	n[b]	l[c]	m[c]	h[c]	c[d]	r[e]	F[f]
6a[g]	14		0.84 ± 0.06		0.17 ± 0.24	0.9740	221
			0.79 ± 0.02	0.82 ± 0.07	0.04 ± 0.07	0.9980	1405
		−0.12 ± 0.09 (0.19)	0.72 ± 0.10		0.09 ± 0.23	0.9779	120
		0.00 ± 0.03 (0.95)	0.79 ± 0.03	0.81 ± 0.08	0.04 ± 0.07	0.9980	852
6b[g]	15		0.92 ± 0.05		0.03 ± 0.24	0.9782	288
			0.87 ± 0.02	0.81 ± 0.09	−0.09 ± 0.09	0.9970	1000
		−0.08 ± 0.09 (0.39)	0.84 ± 0.10		−0.01 ± 0.24	0.9796	142
		0.04 ± 0.04 (0.25)	0.91 ± 0.04	0.86 ± 0.10	−0.07 ± 0.09	0.9974	694
6c[g]	14		0.89 ± 0.07		0.01 ± 0.22	0.9689	184
			0.82 ± 0.03	0.74 ± 0.09	−0.07 ± 0.08	0.9961	704
		−0.13 ± 0.09 (0.16)	0.74 ± 0.12		−0.04 ± 0.21	0.9742	103
		−0.02 ± 0.04 (0.62)	0.80 ± 0.05	0.72 ± 0.10	−0.08 ± 0.09	0.9962	438
6d[g]	15		0.81 ± 0.05		−0.09 ± 0.18	0.9802	319
			0.80 ± 0.05	0.23 ± 0.18 (0.22)	−0.12 ± 0.18	0.9827	169
		0.10 ± 0.06 (0.16)	0.91 ± 0.08		−0.04 ± 0.17	0.9834	176
		0.16 ± 0.06 (0.02)	0.95 ± 0.07	0.42 ± 0.16 (0.02)	−0.06 ± 0.14	0.9899	180
7[h]	16		1.10 ± 0.08		0.19 ± 0.37	0.9614	171
			1.03 ± 0.03	1.32 ± 0.11	0.02 ± 0.11	0.9969	1060
		−0.27 ± 0.11 (0.03)	0.85 ± 0.13		0.05 ± 0.32	0.9732	116
		−0.08 ± 0.04 (0.06)	0.96 ± 0.04	1.22 ± 0.11	−0.01 ± 0.10	0.9978	886
8[i]	8		1.19 ± 0.13		−0.06 ± 0.29	0.9643	80
			0.88 ± 0.06	1.34 ± 0.17	−0.06 ± 0.09	0.9973	462
		−0.01 ± 0.16 (0.93)	1.17 ± 0.26		−0.07 ± 0.32	0.9644	33
		0.02 ± 0.05 (0.77)	0.90 ± 0.09	1.34 ± 0.19	−0.05 ± 0.10	0.9974	253

[a] Values in parentheses are the probabilities that the term is not statistically significant (recorded if greater than 0.005). [b] For designation, see the text; n is the number of solvents studied. [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] Specific rates, at 25.0 °C, from ref. 31. [h] Specific rates, at 25.0 °C, from refs. 30 and 31. [i] Specific rates, at 25.0 °C, from ref. 30.

A scale of Y_{OPNB} values, based on the solvolysis of an adamantyl *p*-nitrobenzoate, is not available. We have previously used the observation of a low sensitivity for the tosylate/*p*-nitrobenzoate solvolysis rate ratio to changes in solvent and structural effects[41] to justify the use of the Y_{OTs} scale as a similarity model for the non-existent Y_{OPNB} scale.[42,43] Details of the analyses of the solvolyses of compounds **6**, **7** and **8** involving use of Y_{OTs} or Y_{BnOPNB} either alone [eqn. (1)] or in combination with N_{T} values [eqn. (2)] have been reported previously.[42,43] These analyses are repeated in Table 3 with, in the case of **7**, additional data points and with inclusion of standard error of the estimate and F-test values. These analyses are required for a comparison with those obtained upon incorporation of the hI term [eqns. (3) and (4)]. For compounds **6**, the solvents are those reported previously[32] and similarly[31] for **7** and **8**, except that, for **7**, Y_{BnOPNB} values [equivalent to $\log(k/k_0)$ for solvolysis of **7**] for 97, 70, and 58% (by weight) TFE were extracted from a figure presented in the similarity model analysis of the specific rates of solvolysis of cumyl *p*-nitrobenzoates.[32]

The solvolyses of cumyl *p*-nitrobenzoates with electron-supplying substituents, **6a–c**, and of **7** and **8** show characteristics essentially identical with those observed for the solvolyses of the benzylic tosylates (**1–5**) in that considerable improvements in correlation coefficient occur on going from the linear regression against Y_{OTs} to a multiple regression against Y_{OTs} and I but only extremely modest improvements occur on going from Y_{OTs} to Y_{OTs} plus N_{T}. In terms of the F-test values, the values increase in going from the eqn. (1) treatment to the eqn. (3) treatment but decrease on going from the eqn. (1) treatment to the eqn. (2) treatment. As with tosylates **1–5**, the highest F-test values are associated with the treatments in terms of eqn. (3). The negative l values observed in the treatments in terms of eqn. (2) all become very close to zero when treatment is in terms of the full eqn. (4): compound **7** exhibits an l value of -0.08 ± 0.04 and **6a–c** and **8** have values within the range of ± 0.04. The h values are consistent with predictions: in the range of 0.72–0.86 for **6a–c**, and somewhat higher for the 2-aryl-2-adamantyl derivative **7** and the benzhydryl derivative **8**. The higher values observed for **7** and **8** are consistent with the higher h values previously reported for structurally similar chlorides.[26]

Based on previous studies of the solvolysis of **6d**, it has been suggested that nucleophilic solvation of the developing carbocation makes an appreciable contribution to the linear free energy relationship.[30,31] Comparison of the log (k/k_o) values for solvolyses of **6a–d** shows that they are close to being independent of the substrate involved, except for the five TFE-containing solvents,[31] where for each of the solvents the value is about 0.4 units lower for solvolyses of **6d** than for the similar values for the three derivatives. It has previously been pointed out[31] that the data points for these five solvents lie below the correlation line in a Grunwald–Winstein plot of log k for **6d** against Y_{BnOPNB}; this behaviour was considered to 'prove' the existence of nucleophilic intervention in the solvolyses of cumyl *p*-nitrobenzoates.

All three of the multiple regression correlations of the specific rates of solvolysis of **6d** are surprisingly unsatisfactory. The correlation coefficient of 0.980 for linear regression against Y_{OTs} [eqn. (1)] increases only slightly, reaching a value of 0.990 for the full eqn. (4). The *F*-test value is at a maximum with use of eqn. (1) and approximately constant at only a little over 50% of this value when eqns. (2)–(4) are employed. The l values of 0.10 ± 0.06 and 0.16 ± 0.06 with use of eqns. (2) and (4), respectively, do suggest a rather modest nucleophilic assistance but the h values of only 0.23 ± 0.18 with use of eqn. (3) and 0.42 ± 0.16 with use of eqn. (4) are unusually low for solvolyses of this type of benzylic derivative. In view of the normal behaviour for the solvolyses of **6a–c**, the unusual behaviour for the solvolysis of **6d** is puzzling.

Solvolyses of benzylic chlorides

Liu and co-workers have reported[20,25,33–35] specific rates of solvolysis at 25.0 °C for a variety of compounds of the general type $XC_6H_4CMeRCl$, where R is methyl or one of its α-methylated derivatives (ethyl, isopropyl or *tert*-butyl). In many instances X is hydrogen and in others it is *ortho*- or *meta*-methyl, *para*-trifluoromethyl or *meta*-chloro; in one instance the aromatic ring is disubstituted as a 3,4-dimethyl derivative.

Imposing the requirement that an adequate representation of fluoroalcohol-containing solvents is required, the solvolyses of the two derivatives of the parent cumyl chloride ($R = CH_3$) with *p*-methyl- and *p*-fluoro-substituents[34] have been omitted from the analysis. For these solvolyses only two TFE–ethanol mixtures, relatively low in TFE content, were included as fluoroalcohol-containing solvents. Analysis of the solvolyses of the ten remaining substrates, using N_{T},[8] I[26] and Y_{Cl}[12,16a] values, are presented in Table 2, with incorporation of all of the available specific rates of solvolysis. It is unfortunate that, with one exception, the number of solvents in which each substrate was studied is rather low ($\leqslant 12$) and, again with the one exception, only TFE–ethanol mixtures represent fluoroalcohol-containing solvents, and none of the important TFE–water mixtures were included. As we have pointed out previously for several of these solvolyses,[44] deficiencies in the type and number of solvents lead to many of the multiple regression analyses being less than completely satisfactory.

The most extensively studied compound, α-*tert*-butylbenzyl chloride (X = H, R = Bu^t; the chloride equivalent of tosylate ester **1**) was originally studied in 14 solvents,[33] including two TFE–water mixtures, and an additional specific rate value (for 80% acetone) has since become available.[45] The usual pattern of a considerable increase in correlation coefficient on incorporating the hI term, only modest increase in correlation coefficient on incorporating the lN term (with an appreciably negative l value), and highest *F*-test value associated with the use of eqn. (3) is present. With use of the full eqn. (4), the l value becomes negligible (−0.08 ± 0.07). The h values of 0.80 ± 0.15 and 0.70 ± 0.18 obtained with use of eqn. (3) and eqn. (4), respectively, are very similar to the corresponding values of 0.76 ± 0.08 and 0.91 ± 0.09 for the solvolyses of **1**.

Of the other nine solvolyses reported in Table 2, three (X = *o*-Me, R = Me;[33] X = H, R = Pr^i,[33] X = *m*-Cl, R = Pr^i)[35] show the standard characteristics of considerable increase in correlation coefficient on incorporating the hI term and the highest *F*-test value being associated with the correlation in terms of eqn. (3). The h values observed are within the range of 0.74–0.96 and the l values from use of eqn. (4) are low: 0.13 ± 0.08, 0.05 ± 0.07 and −0.10 ± 0.10, respectively. The solvolysis of the substrate with X = *m*-CH_3 and R = Bu^t is close to standard in its characteristics, except that the *F*-test value using eqn. (4) is slightly higher than that using eqn. (3), with the use of eqn. (4) involving an unusually large negative l value of −0.18 ± 0.07. The other substrate with R = Bu^t contains two methyl substituents (in *meta* and *para* positions) and it shows the usual behaviour except that the h values [1.33 ± 0.09 with use of eqn. (3) and 1.26 ± 0.16 with use of eqn. (4)] are the largest entries in the table, a situation which can be considered to reflect the presence of two electron-supplying substituents; maintaining R = Bu^t, the h values can be compared to values of 1.11 ± 0.14 and 0.86 ± 0.15 for the *m*-methyl derivative and 0.80 ± 0.15 and 0.70 ± 0.18 for the unsubstituted (X = H) derivative.

The entry in Table 2 with X = H and R = Et also shows only slight deviation from the normal pattern of behaviour. The h values of 0.70 ± 0.18 and 0.80 ± 0.13 with use of eqn. (3) or eqn. (4) are within the normal range of values, with the correlations considerably improved on incorporating the hI term. The *F*-test value is, however, highest with use of eqn. (4), accompanied by an appreciable l value (0.22 ± 0.08) and modest nucleophilic assistance from the solvent at a 98% confidence level is indicated. This behaviour is amplified for the parent cumyl chloride (X = H, R = Me) with not only the *F*-test value at its highest with the use of eqn. (4) but with the correlation coefficient showing an unusually large improvement in going from eqn. (3) to eqn. (4); the l value of 0.33 ± 0.08 indicates a fairly weak, but statistically significant, nucleophilic assistance from the solvent.

Consistent with the increases in h value on introduction of aromatic-ring methyl substituents mentioned above, the introduction of electron-withdrawing substituents into cumyl chloride (X = *m*-Cl, R = Me; X = *m*-CF_3, R = Me) leads to reduced h values. Also, the multiple regression correlations in the presence of these substituents [eqns. (2)–(4)] are rather unsatisfactory, with the largest *F*-test value being in terms of eqn. (1), correlation against only Y_{Cl}, and with the *F*-test value for eqn. (3) correlation being only slightly higher than for eqn. (2) or eqn. (4) correlation. In the full eqn. (4) correlations for solvolyses of these substrates, both the lN and hI terms have high probabilities (>0.09) of being statistically insignificant.

We wish to re-emphasize what we pointed out at the beginning of this section: for the solvolyses of all but one of the benzylic chlorides reported in Table 2, the number of solvents and the variation in type of solvent is only marginally sufficient for a correlation against two parameters[44] [eqns. (2) and (3)] and it is very risky to attempt a correlation against three solvent parameters [eqn. (4)]. Nonetheless, we have reported in Table 2 the analyses using both eqns. (3) and (4) because, although the l and h values may change significantly upon addition of further solvents (especially recommended are TFE–water solvents), the trends observed do give strong support to the concept of improved Grunwald–Winstein type correlations upon incorporation of the hI term.

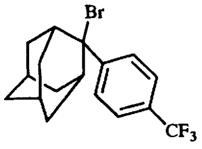
Solvolyses of 2-bromo-2-(*p*-trifluoromethylphenyl)-adamantane (9)

The solvolyses of **9** have been used previously to establish a Y_{BnBr} scale.[29] The values for the specific rates of solvolysis in 16 solvents, the reported values with exclusion of propan-2-ol

Table 4 Correlation of the specific rates of solvolysis of **9** in 16 solvents, using the Grunwald–Winstein approach and various combinations of Y_{Br}, N_T and I parameters[a,b]

l[c]	m[c]	h[c]	c[d]	r[e]	F[f]
	0.77 ± 0.08		0.06 ± 0.37	0.9352	98
	0.81 ± 0.03	1.09 ± 0.13	−0.06 ± 0.15	0.9907	344
−0.22 ± 0.12 (0.10)	0.64 ± 0.11		−0.03 ± 0.35	0.9483	58
0.03 ± 0.07 (0.65)	0.83 ± 0.05	1.13 ± 0.15	−0.06 ± 0.15	0.9908	216

[a] Values in parentheses are the probabilities that the lN term is not statistically significant. [b] Specific rates, at 25.0 °C, from ref. 29. [c-f] See corresponding footnotes to Table 3.



9

(no I value available) and 90% acetone (no Y_{Br} value), have been correlated against N_T,[8] I[26] and Y_{Br}[12,16a] values. The results for analyses using eqns. (1)–(4) are reported in Table 4. The correlation coefficient increases markedly on incorporating the hI term and only modestly on incorporating the lN term. Using the full eqn. (4), the l value is (as expected) negligible (0.03 ± 0.07). The h values of 1.09 ± 0.13, using eqn. (3), and 1.13 ± 0.15, using eqn. (4), are above unity but somewhat less than the corresponding values of 1.75 ± 0.24 and 1.83 ± 0.28 for the chloride[26] (with an *m*-chloro rather than the *p*-CF_3 substituent) and of 1.32 ± 0.11 and 1.22 ± 0.11 for the *p*-nitrobenzoate **7** (without the *p*-CF_3 substituent; Table 3). Owing to lower m values, the h/m ratios, important in a consideration of suitable similarity models,[26] of 1.34 and 1.36 are essentially identical with those for **7** (1.28 and 1.27) but still considerably lower than the values observed[26] for the chloride used to establish the Y_{BnCl} scale[20] (1.79 and 1.83).

Conclusions

The recently developed aromatic ring parameter (I) has previously been shown to give considerable improvement when added as an hI term to typical Grunwald–Winstein correlations of the solvolyses of five benzylic chlorides and one benzylic tosylate.[26]

Using specific rates of solvolysis reported by Liu and co-workers[20,25,29-35] we now show that the hI term can be very usefully applied not only to the analyses of the solvolyses of additional benzylic chlorides and tosylates but also to the analyses of several solvolyses of benzylic *p*-nitrobenzoates and bromides.

Incorporation of the aromatic ring parameter (I) gives a very marked improvement in the correlations of the solvolyses of five benzylic tosylates (Table 1); the correlation coefficients for correlation against mY [eqn. (1)] are only marginally increased on adding the lN term [eqn. (2)] but show a large increase on adding the hI term (the range of 0.953–0.982 becoming 0.988–0.997). With consideration of eqns. (1)–(3) plus the full eqn. (4), the F-test value is in all instances at its highest with use of eqn. (3).

Parallel results are obtained for five of six tertiary benzylic *p*-nitrobenzoates studied (Table 3), with the correlation coefficients of 0.961–0.978 increasing to 0.996–0.998 on incorporation of the hI term. Obviously, only very minor further increases are possible on inclusion also of the lN term [eqn. (4)]. Since Y_{OPNB} values are not available, Y_{OTs} values were used as a similarity model.[41] The one tertiary benzylic *p*-nitrobenzoate which behaved in an unusual manner was the parent cumyl *p*-nitrobenzoate **6d**. We observe that the log (k/k_o) values for solvolysis of this substrate in fluoroalcohol-containing solvents are all about 0.4 units lower than the very similar values for **6a–c** and this is reflected in an apparent modest dependence on solvent nucleophilicity (l value) and unusually low h values. Even with use of the full eqn. (4) the correlation coefficient has increased only to 0.990 from the value of 0.980 for use of eqn. (1) and, accordingly, the F-test value is highest with use of eqn. (1).

Unfortunately, in the kinetic studies (Table 2) of the solvolyses of a series of tertiary benzylic chlorides (XC_6H_4-CMeRCl), in only one instance are the important TFE–H_2O mixtures included. The analyses, especially using the full eqn. (4), are less reliable but do in the majority of cases show all or most of the characteristics, outlined above, which support the incorporation of the hI term. The three solvolyses which showed the most atypical behaviour were all with R = Me within the substrate. When X = H, the behaviour was fairly normal except that a high l value is observed, 0.33 ± 0.08 with use of eqn. (4), and, as a consequence, the highest F-test value accompanied the use of eqn. (4). When X was the electron-withdrawing *m*-Cl or *p*-CF_3, the h value was reduced and it was associated with a rather large standard error. In both of these cases, the largest F-test value was with use of eqn. (1).

The solvolysis of the benzylic bromide **9** (Table 4) has been used[29] to establish a Y_{BnBr} scale. The correlation coefficient increases from 0.935 to 0.991 on incorporation of the hI term and this value is essentially unchanged on going to the full eqn. (4); the highest F-test value is with use of eqn. (3).

Acknowledgements

D. N. K. thanks the NATO Collaborative Research Grant Program (Grant 921261) for financial support and T. W. Bentley (University of Wales, Swansea) for helpful discussions. M. J. D. thanks the University of Wisconsin Center's Grant Program for financial support.

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Paper 4/06944G
Received 14*th November* 1994
Accepted 23*rd January* 1995