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# REVIEW COMMENTARY

# CONCERNING THE DEVELOPMENT OF SCALES OF SOLVENT IONIZING POWER BASED ON SOLVOLYSES OF BENZYLIC SUBSTRATES

DENNIS N. KEVILL* AND MALCOLM J. D'SOUZA
*Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.*

**Based on analysis of recently reported measurements, it is suggested that, provided a sufficiently large set of specific rate measurements in a wide variety of solvent types is available, the negligible to moderate improvements in the correlations of other types of benzylic chlorides, which are gained by use of a benzylic chloride (in place of 1-adamantyl chloride) as the standard substrate, do not justify the development of new specialized scales of solvent ionizing power. A similar conclusion is reached concerning solvent ionizing power scales developed for use with benzylic *p*-nitrobenzoates. However, such scales could be helpful when specific rates of solvolysis in only a limited variety of solvents are available, e.g. when a change in mechanism severely limits the range of operation of one of the pathways. Contrary to a previous claim, variations in ion-pair return could be the cause of deviations from Grunwald–Winstein plots for solvolyses of benzhydryl chloride in fluorinated alcohol solvents; such effects could be coupled, at least in part, with variations in aromatic ring solvation.**

## INTRODUCTION

Recently, a new $Y$ scale for benzylic chlorides ($Y_{\mathrm{BnCl}}$) has been introduced,[1,2] based on the solvolysis of 2-chloro-2-(3′-chlorophenyl)adamantane (**2d**). This solvent ionizing power scale was developed for use within the Grunwald–Winstein equation:[3]

$$\log(k/k_0) = mY + c \qquad (1)$$

when the solvolyses under investigation involve a benzylic chloride. In equation (1), $k$ and $k_0$ are the specific rates of solvolysis of the substrate in a given solvent and in 80% ethanol, $m$ is the sensitivity of the solvolysis of the substrate to changes in solvent ionizing power ($Y$) and $c$ is the intercept.

Dispersion effects (separate plots for different binary solvent mixtures) has been observed previously[4–7] when solvolyses of α-aryl-substituted substrates were correlated against solvent ionizing power scales based on solvolyses of *tert*-butyl chloride or, more recently, an appropriate adamantyl substrate. Differences in solvation effects at the incipient carbocation, associated with more efficient charge delocalization, have been proposed as the major source of these dispersions.[1,2,7,8] Accordingly, for treatment of $S_N2$ solvolyses of benzylic substrates (no carbocation intermediate), it has been argued[9] that the $Y$ scales based on solvolyses of adamantyl derivatives are appropriate for use within the extended (two-term) Grunwald–Winstein equation:

$$\log(k/k_0) = lN + mY + c \qquad (2)$$

which is equation (1) with addition of an $lN$ term, where $l$ is the sensitivity of the solvolysis to changes in solvent nucleophilicity ($N$).

It is a well recognized aspect of linear free energy relationships that the closer in structure the standard substrate is to the one under investigation, the more confidence one can place in the correlation. The $Y_{\mathrm{BnCl}}$ scale should, therefore, usually give better correlations for benzylic chlorides than the $Y_{\mathrm{Cl}}$ scale (based on 1-adamantyl chloride solvolysis). However, especially in view of the recent proliferation of $Y_{\mathrm{X}}$ scales,[10] one should be reluctant to undertake the development of further scales, unless a truly significant improvement in correlations can be achieved. Recently, the establishment of $Y_{\mathrm{R}}$ scales for solvolysis of RX has been discussed[11] and, also, a $Y_{\mathrm{BnOPNB}}$ scale for use in the correlation of benzylic *p*-nitrobenzoates has been presented.[12]

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[*] Author for correspondence.

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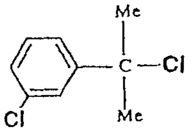
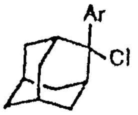
## SPECIFIC RATES OF SOLVOLYSIS

In Table 1, we present analyses of the specific rates of solvolysis of **2d**,[1,2] 2-chloro-2-phenyladamantane (**2c**),[1] 2-chloro-2,3,3-trimethylbutane (**3**),[1] 2-chloro-2-(3′-chlorophenyl)propane (**1b**)[1] and 2-chloro-3,3-dimethyl-2-phenylbutane (**4**)[1] against $Y_{\mathrm{BnCl}}$[1,2] [$\log(k/k_0)$ for 2-chloro-2-(3′-chlorophenyl)adamantane (**2d**)] or $Y_{\mathrm{Cl}}$[10] scales. We have also included analyses of data reported by Bentley *et al.*[8] for solvolyses of *p*-methoxybenzyl chloride (**5**). To assist in cross-referencing, the previously used[1] numbering of compounds **1**–**4** is retained.

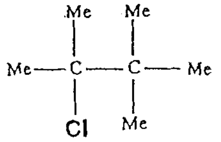


**1 b**

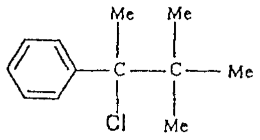


**2**

**c**, Ar = phenyl
**d**, Ar = 3′-chlorophenyl



**3**



**4**

Although it was claimed[1] both that the $Y_{\mathrm{Cl}}$ scale failed to correlate the solvolysis rates of several tertiary benzylic chlorides and that the $Y_{\mathrm{BnCl}}$ scale was superior for this type of substrate, very little numerical analysis was presented. In particular, there was no report concerning the interrelationship between the $Y_{\mathrm{BnCl}}$ and $Y_{\mathrm{Cl}}$ scales. The first entry in Table 1 (and also Figure 1) presents such a correlation. The three specific rate measurements in 2,2,2-trifluoroethanol (TFE)–ethanol mixtures are combined with recently determined[13] $Y_{\mathrm{Cl}}$ values for this binary mixture. The correlation can be seen to be of average quality, with a slope (*m* value) of essentially unity. This indicates that, with a good mix of solvent types in the solvolysis of a given substrate, essentially identical *m* values would be obtained irrespective of whether $Y_{\mathrm{BnCl}}$ or $Y_{\mathrm{Cl}}$ was chosen as the reference scale.

### 2-Chloro-2-phenyladamantane (2c)

Compound **2c** differs from the standard **2d** only in the removal of the 3′-chloro substituent. As one would expect, an outstanding correlation of the specific rates

Table 1. Correlation of specific rates of solvolysis of compounds **1**–**6** against solvent ionizing power using the Grunwald–Winstein equation

| Correlation[a] | $n$[b] | $m$[c] | $c$[c] | $r$[d] |
|---|---|---|---|---|
| **2d**[e], $Y_{\mathrm{Cl}}$ | 20[f] | 1·01 ± 0·07 | 0·22 ± 0·52 | 0·956 |
| **2c**, $Y_{\mathrm{Cl}}$ | 15 | 0·95 ± 0·08 | 0·01 ± 0·48 | 0·959 |
| **2c**, $Y_{\mathrm{BnCl}}$ | 15 | 1·00 ± 0·02 | −0·18 ± 0·13 | 0·997 |
| **3**, $Y_{\mathrm{Cl}}$ | 10 | 0·75 ± 0·03 | 0·13 ± 0·14 | 0·993 |
| **3**, $Y_{\mathrm{BnCl}}$ | 10[g] | 0·63 ± 0·08 | 0·11 ± 0·40 | 0·933 |
| **1b**, $Y_{\mathrm{Cl}}$ | 10 | 0·68 ± 0·06 | −0·11 ± 0·27 | 0·975 |
| **1b**, $Y_{\mathrm{BnCl}}$ | 10 | 0·70 ± 0·06 | −0·21 ± 0·29 | 0·970 |
| **4**, $Y_{\mathrm{Cl}}$ | 12 | 0·79 ± 0·06 | −0·05 ± 0·28 | 0·969 |
| **4**, $Y_{\mathrm{BnCl}}$ | 12[g,h] | 0·65 ± 0·05 | 0·11 ± 0·24 | 0·976 |
| **5**, $Y_{\mathrm{Cl}}$ | 31 | 0·79 ± 0·03 | −0·16 ± 0·27 | 0·985 |
| **5**, $Y_{\mathrm{BnCl}}$ | 16 | 0·83 ± 0·04 | −0·31 ± 0·28 | 0·981 |
| **6**, $Y_{\mathrm{Cl}}$ | 21[i] | 0·85 ± 0·06 | −0·14 ± 0·52 | 0·954 |
| **6**, $Y_{\mathrm{BnCl}}$ | 18[j] | 0·90 ± 0·03 | −0·25 ± 0·26 | 0·986 |

[a] Correlation of $\log(k/k_0)$ for solvolysis of the indicated substrate against the indicated solvent ionizing power scale.

[b] Number of solvents; identical solvents for correlation with $Y_{\mathrm{Cl}}$ or $Y_{\mathrm{BnCl}}$ for substrates **1b**, **2c**, **3** and **4**.

[c] From equation (1), and with associated standard error.

[d] Correlation coefficient.

[e] $Y_{\mathrm{BnCl}}$ is defined as $\log(k/k_0)$ for **2d**.

[f] Using the solvents of Table 1 in Ref. 2, but omitting (no $Y_{\mathrm{Cl}}$ value available) 95% EtOH, *i*-PrOH and formamide.

[g] Using an extrapolated $Y_{\mathrm{BnCl}}$ value of 2.21 for 40% acetone.

[h] Using an extrapolated $Y_{\mathrm{BnCl}}$ value of 3.63 for 50% TFE.

[i] The 22 solvents indicated in text, but excluding 40% $CH_3CN$ (no $Y_{\mathrm{Cl}}$ value).

[j] The 22 solvents indicated in text, but excluding 40, 30 and 20% $CH_3CN$ and 50% EtOH (no $Y_{\mathrm{BnCl}}$ values).

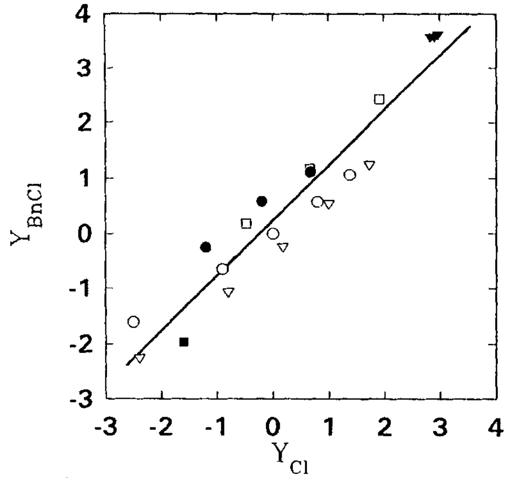


Figure 1. Plot of $Y_{\mathrm{BnCl}}$ against $Y_{\mathrm{Cl}}$. Solvent systems: (▽) acetone–water; (▼) TFE–$H_2O$; (○) EtOH–$H_2O$; (●) MeOH–$H_2O$; (□) TFE–EtOH; (■) acetic acid

of solvolysis of **2c** with $Y_{\mathrm{BnCl}}$ and a correlation against $Y_{\mathrm{Cl}}$ paralleling that for solvolysis of **2d** are observed (Table 1).

### 2-Chloro-2,3,3-trimethylbutane (3)

The solvolysis of **3** correlates much better with $Y_{\mathrm{Cl}}$ than with $Y_{\mathrm{BnCl}}$ (Table 1). However, the number of rate measurements is small and it is possible that the differences would be reduced with an extended series of solvents. The low $m$ value (0·75 when $Y_{\mathrm{Cl}}$ is used) does not appear to be due to any appreciable nucleophilic assistance; multiple regression analysis against both $N_{\mathrm{T}}$ values[14] and $Y_{\mathrm{Cl}}$ values[10] leads to values of 0·10 ± 0·04 for $l$, 0·82 ± 0·04 for $m$ and 0·13 ± 0·11 for the intercept ($r = 0{\cdot}996$; $n = 10$). For comparison, *tert*-butyl chloride (with the α-*tert*-butyl group of **3** replaced with a methyl group) gives corresponding values of 0·37 ± 0·04, 0·89 ± 0·04 and 0·03 ± 0·11 ($r = 0{\cdot}995$; $n = 10$) in the same solvents; the appreciable dependence of the specific rates of *tert*-butyl chloride solvolysis on solvent nucleophilicity has been discussed previously.[15,16]

### 2-Chloro-2-(3′-chlorophenyl)propane (1b) and 2-chloro-3,3-dimethyl-2-phenylbutane (4)

A better comparison of the relative efficiencies of $Y_{\mathrm{Cl}}$ and $Y_{\mathrm{BnCl}}$ in correlating the solvolyses of substrates containing α-aryl substituents is afforded by the solvolyses of **1b** and **4**, which do not closely resemble either of the standard substrates. Liu *et al.*[1] suggested that a more pronounced conjugation at the transition state within the incipient carbocation formed from **1b** leads to the $Y_{\mathrm{BnCl}}$ scale being preferable for correlation of **1b** and the $Y_{\mathrm{Cl}}$ scale for correlation of **4**. Our analyses (Table 1) do not support either of these assignments. We find virtually identical $m$ values and correlation coefficients for each of the four correlations involving either **1b** or **4** with either $Y_{\mathrm{Cl}}$ or $Y_{\mathrm{BnCl}}$. In the earlier report,[1] $m$ and $r$ values of 0·908 and 0·988 were reported for correlation of **4** with $Y_{\mathrm{Cl}}$. These values can be reproduced if the correlation is restricted to the seven solvent systems common to the studies of both **3** and **4**.

### *p*-Methoxybenzyl chloride (5)

Bentley *et al.*[8] have developed a scale based on the solvolysis of **5**. In 31 solvents for which values for both this scale and the $Y_{\mathrm{Cl}}$ scale are available ($Y_{\mathrm{Cl}}$ values for 20% and 30% aqueous acetonitrile and aqueous dioxane from a recent report[17]), we find (Table 1 and Figure 2) a good correlation ($r = 0{\cdot}985$). It follows that solvolyses which correlate with one scale will also correlate reasonably well with the other and, provided that a sufficiently large assembly of solvents of varying character is employed, there will be a little advantage in using a scale based on **5** rather than the $Y_{\mathrm{Cl}}$ scale.

Although one might expect an improved correlation of the specific rates of solvolysis of **5** using $Y_{\mathrm{BnCl}}$ values, this is not observed in an analysis involving the 16 solvent systems for which $Y_{\mathrm{BnCl}}$ values are available; a slightly lower correlation coefficient (0·981) is observed. Use of the two-term Grunwald–Winstein equation to correlate $\log(k/k_0)$ for **5** with both $N_{\mathrm{T}}$[14,18] and $Y_{\mathrm{Cl}}$[10,17] values leads to values of 0·10 ± 0·10 for $l$, 0·81 ± 0·04 for $m$ and −0·13 ± 0·27 for the intercept ($r = 0{\cdot}986$; $n = 31$), supporting the concept[8] of little or no nucleophilic assistance to the ionization process. A corresponding correlation with $N_{\mathrm{T}}$ and $Y_{\mathrm{BnCl}}$ leads to

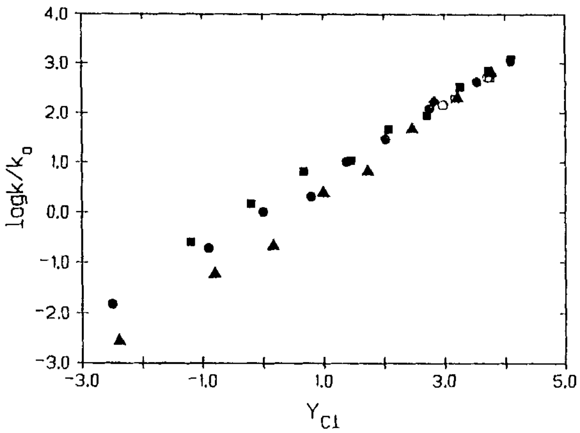


Figure 2. Plot of $\log(k/k_0)$ for **5** against $Y_{\mathrm{Cl}}$. Solvent systems: (▲) acetone–water; (●) EtOH–$H_2O$; (■) MeOH–$H_2O$; (◆) 97% TFE–$H_2O$; (○) $CH_3CN$–$H_2O$; (□) dioxane–water

values of 0·20 ± 0·11 for $l$, 0·90 ± 0·06 for $m$ and −0·25 ± 0·26 for the intercept ($r = 0{\cdot}984$; $n = 16$). However, illustrating the advantages of a good mix of solvents, the correlation coefficients for the analyses involving $Y_{\mathrm{Cl}}$ fall when the correlations are limited to the same 16 solvents as used in the analysis involving $Y_{\mathrm{BnCl}}$; for correlation against $Y_{\mathrm{Cl}}$, $m = 0{\cdot}78 \pm 0{\cdot}06$, $c = -0{\cdot}17 \pm 0{\cdot}38$ ($r = 0{\cdot}963$; $n = 16$), and for correlation against $N_{\mathrm{T}}$ and $Y_{\mathrm{Cl}}$, $l = 0{\cdot}09 \pm 0{\cdot}16$, $m = 0{\cdot}81 \pm 0{\cdot}08$, $c = -0{\cdot}14 \pm 0{\cdot}39$ ($r = 0{\cdot}963$; $n = 16$). Although, for the same solvents, use of the $Y_{\mathrm{BnCl}}$ scale leads to a better correlation, a more important factor is to carry out the study with a well chosen series of solvents, such that use of $Y_{\mathrm{Cl}}$ in 31 solvents is preferable to the use of $Y_{\mathrm{BnCl}}$ in only 16 solvents.

Scales such as the $Y_{\mathrm{BnCl}}$ scale or, especially, the scale based on solvolysis of **5** could possibly be preferable to $Y_{\mathrm{Cl}}$ in situations where only a limited number of specific rates of solvolysis of an $\alpha$-aryl-substituted substrate are available; for example, a solvent-induced change in mechanism[8] might lead to a carbocation-forming pathway dominating for only a very restricted range of solvents.

## Benzhydryl chloride (b)

Benzhydryl chloride has played a major role in the study of $S_{\mathrm{N}}1$ reactions. The mechanism for nucleophilic substitution of **6** was established very early as being unimolecular[19] and it afforded an early example of common-ion rate depression, indicative of product formation from free carbocations.[20] In considerations of Grunwald–Winstein plots, the solvolyses of benzhydryl chloride are a prime example of reactions believed to be $S_{\mathrm{N}}1$ but showing appreciable dispersion for different mixed solvent systems in linear free energy plots of specific rates of solvolysis against specific rates of solvolysis of the original standard (*tert*-butyl chloride) substrate.[21] Use of $\alpha$-phenylethyl chloride as the standard substrate reduced, but did not eliminate, the dispersion;[21] the remaining dispersion could be a consequence of two aryl groups in the substate but only one in the standard. However, parallel correlation against the specific rates of solvolysis of *p*-methoxybenzyl chloride (**5**) demonstrates a considerably reduced dispersion.[8]

We have made use of previously reported specific rates of solvolysis of benzhydryl choride in 22 solvents.[7,21] [in Ref. 7, the data presented in Table 1 contain several typographic errors. Comparison with the corresponding $\log(k/k_0)$ values of Figure 1 indicates that the specific rates reported as being for 50% acetone and 60% ethanol are actually for 40% acetone and 50% ethanol, respectively. A specific rate of $177 \times 10^{-3}\,\mathrm{s}^{-1}$ has been measured recently for the solvolysis in 60% ethanol[22]]. These solvents are 100, 90, 80, 70, 60, 50 and 40% (v/v) ethanol–water, 100, 90 and 60% (v/v) methanol–water, 90, 80, 70, 60, 50 and 40% (v/v) acetone–water, 97 and 70% (w/w) 2,2,2-trifluoroethanol (TFE)–water, 40, 30 and 20% (v/v) acetonitrile–water [by interpolation within data reported for % (w/w) solvents] and acetic acid.

Correlations against $Y_{\mathrm{BnCl}}$ or $Y_{\mathrm{Cl}}$ (Table 1) lead to $m$ values of 0·90 or 0·85, with $Y_{\mathrm{BnCl}}$ giving the better correlation ($r$ value of 0·986 as opposed to 0·954). The best correlation is, however, against $\log(k/k_0)$ for *p*-methoxybenzyl chloride (**5**) solvolysis (no values for 70% TFE and acetic acid). Values for $m$ of 1·01 ± 0·03 and for $c$ of 0·10 ± 0·18 ($r = 0{\cdot}993$; $n = 20$) are obtained.

Use of the extended Grunwald–Winstein equation, incorporating $N_{\mathrm{T}}$ and $Y_{\mathrm{Cl}}$ values, did not significantly improve the correlation over that using $Y_{\mathrm{Cl}}$ alone: $l = 0{\cdot}11 \pm 0{\cdot}17$, $m = 0{\cdot}87 \pm 0{\cdot}07$, $c = -0{\cdot}09 \pm 0{\cdot}53$ ($r = 0{\cdot}955$; $n = 21$). Similarly, only a modest improvement was achieved with use of $N_{\mathrm{T}}$ and $Y_{\mathrm{BnCl}}$ rather than $Y_{\mathrm{BnCl}}$ alone: $l = 0{\cdot}19 \pm 0{\cdot}07$, $m = 0{\cdot}95 \pm 0{\cdot}03$, $c = -0{\cdot}16 \pm 0{\cdot}22$ ($r = 0{\cdot}992$; $n = 18$).

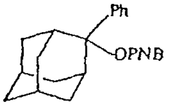
The scales based on aryl-substituted standards do give better correlations than $Y_{\mathrm{Cl}}$ but the $l$ and $m$ values obtained are very similar and correlations using the $Y_{\mathrm{Cl}}$ scale are adequate for assignment of mechanism. Indeed, the most surprising feature of the correlations is the indication of a modest nucleophilic assistance when $N_{\mathrm{T}}$ and $Y_{\mathrm{BnCl}}$ values are used within the extended (two-term) equation.

## Tertiary *p*-nitrobenzoate esters

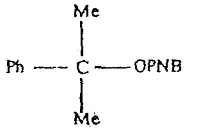
Despite an approximately $10^9$ difference in leaving-group ability,[23] the $Y_{\mathrm{OTs}}$ solvent ionizing power scale, based on solvolysis of 2-adamantyl *p*-toluenesulfonate,[24] has been used to give an excellent correlation of the specific rates of solvolysis of diarylmethyl *p*-nitrobenzoates[25] and a very good correlation of the specific rates of solvolysis of 1-(1-methyl-2-pyrrolyl)-2,2,2-trifluoroethyl *p*-nitrobenzoate.[26] The use of $Y_{\mathrm{OTs}}$ for correlation of *p*-nitrobenzoate ester solvolyses is consistent with the claim of a low sensitivity for the *p*-toluenesulfonate/*p*-nitrobenzoate solvolysis rate ratio towards solvent and structural effects.[23]

Recently, Liu *et al.*[12] have considered whether the $Y_{\mathrm{OTs}}$ scale is also suitable for the correlation of the specific rates of solvolyses of four tertiary (as opposed to secondary) *p*-nitrobenzoate esters (**7**–**10**). They concluded that it is desirable to set up a $Y_{\mathrm{BnOPNB}}$ scale, similar to the $Y_{\mathrm{BnCl}}$ scale, for use in correlations involving solvolyses (with alkyl—oxygen bond fission) of benzylic *p*-nitrobenzoates.

In our analyses, comparing the use of $Y_{\mathrm{OTs}}$ and $Y_{\mathrm{BnOPNB}}$, we have adjusted those $\log(k/k_0)$ values which are for solvolyses of the bridgehead adamantyl ester to



**7**



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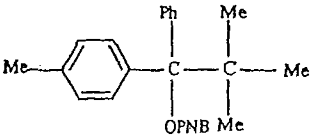

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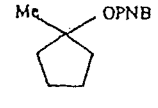

**10**

obtain $Y_{\mathrm{OTs}}$ values, in the manner suggested by Allard and Casadevall.[28] However, use of non-adjusted values as $Y_{\mathrm{OTs}}$ led to only very small differences in the calculated sensitivities, intercepts and correlation coefficients. The $m$ and $c$ values [equation [1]) plus the correlation coefficient for correlations of 2-phenyl-2-adamantyl *p*-nitrobenzoate (**7**) against $Y_{\mathrm{OTs}}$ and for correlations of *tert*-cumyl *p*-nitrobenzoate (**8**), 2,2-dimethyl-1-(4′-methylphenyl)-1-phenyl-1-propyl *p*-nitrobenzoate (**9**) and 1-methyl-1-cyclopentyl *p*-nitrobenzoate (**10**) against either $Y_{\mathrm{OTs}}$ or $Y_{\mathrm{BnOPNB}}$ [$\log(k/k_0)$ for **7**] are presented in Table 2.

Compound **7** correlates rather poorly with $Y_{\mathrm{OTs}}$, but **8**, **9** and **10** all give reasonable correlations. Surprisingly, only **9** gives a good correlation with $Y_{\mathrm{BnOPNB}}$ and

Table 2. Correlation of specific rates of solvolysis of compounds **7**–**10** against solvent ionizing power[a] using the Grunwald–Winstein equation

| Correlation[b] | $n$[c] | $m$[d] | $c$[d] | $r$[e] |
|---|---|---|---|---|
| **7**[f], $Y_{\mathrm{OTs}}$ | 13[g] | 1·09 ± 0·12 | 0·18 ± 0·39 | 0·935 |
| **8**, $Y_{\mathrm{OTs}}$ | 13 | 0·81 ± 0·06 | −0·09 ± 0·18 | 0·973 |
| **8**, $Y_{\mathrm{BnOPNB}}$ | 13 | 0·67 ± 0·07 | −0·21 ± 0·27 | 0·940 |
| **9**, $Y_{\mathrm{OTs}}$ | 8 | 1·18 ± 0·14 | −0·05 ± 0·31 | 0·961 |
| **9**, $Y_{\mathrm{BnOPNB}}$ | 8 | 0·84 ± 0·03 | −0·06 ± 0·11 | 0·995 |
| **10**, $Y_{\mathrm{OTs}}$ | 12 | 0·72 ± 0·04 | −0·05 ± 0·12 | 0·987 |
| **10**, $Y_{\mathrm{BnOPNB}}$ | 12 | 0·57 ± 0·08 | −0·13 ± 0·28 | 0·919 |

[a] The $Y_{\mathrm{OTs}}$ scale is using adjusted values (Refs 27 and 28) for those values determined experimentally using 1-adamantyl *p*-toluenesulfonate.
[b] Correlation of $\log(k/k_0)$ for solvolysis of the indicated substrate against the indicated solvent ionizing power scale.
[c] Number of solvents, specific rates from Table 1 in Ref. 12.
[d] From equation (1), and with associated standard error.
[e] Correlation coefficient; values are consistent with those reported in Ref. 12.
[f] $Y_{\mathrm{BnOPNB}}$ is defined as $\log(k/k_0)$ for **7**.
[g] The first thirteen solvents of Table 1 in Ref. 12.

Table 3. Correlation of specific rates of solvolysis of compounds **7**–**10** against a combination of $N_{\mathrm{T}}$ solvent nucleophilicity values and solvent ionizing power[a] using the extended (two-term) Grunwald–Winstein equation

| Correlation[b,c] | $l$[d] | $m$[d] | $c$[d] | $r$[e] |
|---|---|---|---|---|
| **7**[f], $Y_{\mathrm{OTs}}$ | −0·27 ± 0·14 | 0·83 ± 0·18 | 0·04 ± 0·35 | 0·953 |
| **8**, $Y_{\mathrm{OTs}}$ | 0·10 ± 0·07 | 0·91 ± 0·09 | −0·03 ± 0·18 | 0·977 |
| **8**, $Y_{\mathrm{BnOPNB}}$ | 0·22 ± 0·11 | 0·87 ± 0·12 | −0·13 ± 0·24 | 0·958 |
| **9**, $Y_{\mathrm{OTs}}$ | −0·02 ± 0·16 | 1·14 ± 0·27 | −0·06 ± 0·33 | 0·961 |
| **9**, $Y_{\mathrm{BnOPNB}}$ | 0·08 ± 0·05 | 0·92 ± 0·05 | −0·03 ± 0·10 | 0·997 |
| **10**, $Y_{\mathrm{OTs}}$ | 0·05 ± 0·05 | 0·77 ± 0·06 | −0·02 ± 0·12 | 0·988 |
| **10**, $Y_{\mathrm{BnOPNB}}$ | 0·08 ± 0·14 | 0·64 ± 0·15 | −0·10 ± 0·29 | 0·922 |

[a] The $Y_{\mathrm{OTs}}$ scale is using adjusted values (Refs 27 and 28) for those values based on 1-adamantyl *p*-toluenesulfonate solvolysis.
[b] Correlation of $\log(k/k_0)$ for solvolysis of the indicated substrate against a combination of $N_{\mathrm{T}}$ values and the values from the indicated solvent ionizing power scale.
[c] The solvents are identical with those for the corresponding analyses in Table 2.
[d] Using $\log(k/k_0) = lN_{\mathrm{T}} + mY + c$; with associated standard errors.
[e] Correlation coefficient.
[f] $Y_{\mathrm{BnOPNB}}$ is defined as $\log(k/k_0)$ for **7**.

**8** and **10** correlate much better with $Y_{\mathrm{OTs}}$. One can rationalize that solvolysis of the non-benzylic **10** should correlate better with the non-benzylic $Y_{\mathrm{OTs}}$ scale than with a benzylic $Y_{\mathrm{BnOPNB}}$ scale, but the value (0·919) for the correlation coefficient against $Y_{\mathrm{BnOPNB}}$ is considerably lower than one would probably anticipate. The dispersion observed in the plot of **8** against $Y_{\mathrm{BnOPNB}}$ was suggested to arise from nucleophilic solvent assistance. Assignments of this nature without detailed analyses are dangerous and can lead to erroneous conclusions. The dangers in assigning dispersion effects to *nucleophilic assistance* have been discussed, with an example,[29] earlier.[30]

To examine quantitatively for possible nucleophilic participation in the solvolyses of **7**–**10**, we have analyzed (Table 3) in terms of the extended Grunwald–Winstein equation [equation (2)]. In all but two instances, the low $l$ value and only marginal improvement in the correlation coefficient (over that obtained in correlation against the $Y$ scale alone) indicates little or no nucleophilic assistance.

When solvolysis of **7** ($Y_{\mathrm{BnOPNB}}$) is correlated with $N_{\mathrm{T}}$ and $Y_{\mathrm{OTs}}$, a negative value for $l$ of $-0{\cdot}27 \pm 0{\cdot}11$ suggests that increases in solvent nucleophilicity tend to reduce the rate of solvolysis. It is difficult to see how such an effect could operate in the solvolysis of **7**. When solvolysis of **8** is correlated against $N_{\mathrm{T}}$ and $Y_{\mathrm{BnOPNB}}$, the $l$ value of $0{\cdot}22 \pm 0{\cdot}11$ does indeed give support for the claim[12] of modest nucleophilic participation by the solvent. However, a parallel correlation with $Y_{\mathrm{OTs}}$ substituted for $Y_{\mathrm{BnOPNB}}$ leads to both a better correlation and a much reduced $l$ value ($0{\cdot}10 \pm 0{\cdot}07$).

## POSSIBLE NUCLEOPHILIC ASSISTANCE IN SOLVOLYSES OF CUMYL DERIVATIVES

Liu and co-workers claimed that the analysis in terms of the simple Grunwald–Winstein equation of the specific rates of solvolysis of both **1b**[1,2] and **8**[12] shows evidence for a nucleophilic solvent assistance. However, Liu *et al.* themselves[31] and also Allen *et al.*[32] have demonstrated convincingly that solvolyses of 1-aryl-1-(trifluoromethyl)ethyl *p*-toluenesulfonates have characteristics which 'indicate a rate-limiting ionization process without intervention of solvent participation.'[31] It seems very unlikely that replacement of the trifluoromethyl group of these compounds by a methyl group would cause a shift in the direction of increased nucleophilic solvent participation. It is of interest that an important contribution to the study by Liu *et al.* involves linear Grunwald–Winstein plots with slopes of close to unity in correlations of the specific rates of solvolysis of the benzylic substrates against the non-benzylic $Y_{\mathrm{OTs}}$ scale.

Richard *et al.*[33] have investigated the reactions of both cumyl chlorides and cumyl *p*-nitrobenzoates in 50% aqueous TFE. They found no evidence for nucleophilic assistance, even in the presence of powerful nucleophiles, such as azide ion or propanethiol. Their demonstration of the absence of nucleophilic solvent participation in the solvolysis reaction in 50% TFE is convincing for this high ionizing power[10] and low nucleophilicity[14] solvent. Although the absence of bimolecular reaction with powerful nucleophiles would argue against it, it is not impossible that a change in mechanism could occur, introducing a dependence on solvent nucleophilicity, for solvolyses in solvents of lower ionizing power and higher nucleophilicity. However, when the conclusions of this study are combined with those of Liu *et al.*[31] and of Allen *et al.*[32] nucleophilic assistance from solvent towards the solvolyses of *tert*-cumyl derivatives appears unlikely.

We have already demonstrated, in the previous subsection, that analysis in terms of the extended (two-term) Grunwald–Winstein equation using $N_{\mathrm{T}}$ and $Y_{\mathrm{BnOPNB}}$ values does give support to the claim of nucleophilic solvent participation in solvolysis of **8**, but the calculated $l$ value ($0{\cdot}22 \pm 0{\cdot}11$) is considerably reduced when $Y_{\mathrm{OTs}}$ values are substituted for $Y_{\mathrm{BnOPNB}}$ values ($0{\cdot}10 \pm 0{\cdot}07$). Similarly, correlation of the solvolyses of **1b** against $N_{\mathrm{T}}$ and $Y_{\mathrm{BnCl}}$ leads to values of $0{\cdot}30 \pm 0{\cdot}09$ for $l$, of $0{\cdot}90 \pm 0{\cdot}07$ for $m$ and of $-0{\cdot}03 \pm 0{\cdot}20$ for $c$ ($r = 0{\cdot}988$; $n = 10$). Again, the $l$ value is considerably reduced when $Y_{\mathrm{Cl}}$ values are substituted for the $Y_{\mathrm{BnCl}}$ values: $l = 0{\cdot}07 \pm 0{\cdot}11$, $m = 0{\cdot}73 \pm 0{\cdot}09$, $c = 0{\cdot}06 \pm 0{\cdot}27$ ($r = 0{\cdot}976$; $n = 10$).

Since different sensitivities to changes in solvent nucleophilicity are indicated for solvolyses of **1b** and **8** when either $Y_{\mathrm{BnX}}$ (X = Cl or OPNB) or $Y_{\mathrm{X}}$ (X = Cl or OTs) scales are used within the extended (two-term) Grunwald–Winstein equation, we have also considered the incorporation of the solvent ionizing power scale developed, for use with benzylic substrates, by Bentley *et al.*[8] Unfortunately, there is somewhat of a mismatch between the solvents used in the study of **1b** and **8** and those used in the study of **5** (the Bentley standard). We can analyze only for a series of aqueous ethanol, aqueous methanol and aqueous acetone solvents plus 100% TFE (actually, **5** was studied in 97% TFE but all previous scales for which accurate $Y_{\mathrm{X}}$ values are available have shown essentially identical values for 100 and 97% TFE[10]); an analysis using these solvents places heavy weight on the 100% TFE data.

Correlation of the specific rates of solvolysis of **1b** against a combinaton of $N_{\mathrm{T}}$ values and $\log(k/k_0)$ values for **5** (as the $Y$ scale) leads to values for $l$ of $0{\cdot}07 \pm 0{\cdot}08$, for $m$ of $0{\cdot}87 \pm 0{\cdot}06$ and for $c$ of $0{\cdot}12 \pm 0{\cdot}16$ ($r = 0{\cdot}992$; $n = 10$). Corresponding correlation of the specific rates of solvolysis of **8** leads to values of $0{\cdot}13 \pm 0{\cdot}06$ for $l$, $0{\cdot}80 \pm 0{\cdot}06$ for $m$ and $0{\cdot}02 \pm 0{\cdot}14$ for $c$ ($r = 0{\cdot}986$; $n = 11$). A somewhat lower correlation coefficient is to be anticipated for the correlation of the specific rates of solvolysis of **8**, since we are using a scale established with a chloride ion leaving group for correlation of the solvolysis of a *p*-nitrobenzoate ester. The $l$ values obtained in these analyses are very similar to those obtained when values from the $Y_{Cl}$ or $Y_{OTs}$ scales were used, and they are noticeably lower than when the $Y_{BnCl}$ or $Y_{BnOPNB}$ scales were employed.

The indications of nucleophilic solvent participation in solvolyses of **1b** and **8** when $Y_{BnCl}$ or $Y_{BnOPNB}$ scales are incorporated appear to carry over to other analyses. Both *p*-methoxybenzyl chloride (**5**)[8] and benzhydryl chloride (**6**)[7] are considered to solvolyze without nucleophilic solvent participation. This view is given indirect support by the observation of only a very low dependence of the specific rates of solvolysis of both *p*-methoxybenzyldimethylsulfonium ion and benzhydryldimethylsulfonium ion on solvent composition, with the small variations in specific rate being unrelated to solvent nucleophilicity changes.[34] It has been reported above that correlation of the specific rates of solvolysis of **5** and **6** with $N_T$ and $Y_{BnCl}$ values leads to $l$ values of $0{\cdot}20 \pm 0{\cdot}11$ and $0{\cdot}19 \pm 0{\cdot}07$, respectively.

The apparently anomalous $l$ values for certain substrates associated with incorporation of $Y_{BnCl}$ or $Y_{BnOPNB}$ within equation (2) may be related to the negative $l$ values obtained when $Y_{BnOPNB}$ values (based on specific rates of solvolysis of **7**) are correlated against $N_T$ and $Y_{OTs}$ values; a similar negative value is obtained in correlations of $Y_{BnCl}$ values with $N_T$ and $Y_{Cl}$ values: $l = -0{\cdot}15 \pm 0{\cdot}11$, $m = 0{\cdot}92 \pm 0{\cdot}10$, $c = 0{\cdot}12 \pm 0{\cdot}51$ ($r = 0{\cdot}960$; $n = 20$).

## CAUSES OF DISPERSION IN GRUNWALD–WINSTEIN PLOTS FOR SOLVOLYSES OF α-ARYLALKYL DERIVATIVES

Bentley *et al.*[8] have recently tabulated and referenced various suggestions for the origin of dispersions in Grunwald–Winstein plots: solvation effects, ion-pair return, nucleophilic solvent assistance, anchimeric assistance and general-base catalysis. For unimolecular solvolyses of benzylic subtrates, dispersions have usually been explained in terms of solvation effects and/or ion-pair return. The authors favored solvation effects, involving the differences in solvation between aromatic rings and alkyl groups, as the cause of dispersions frequently observed when the specific rates of solvolyses of benzylic substrates were correlated with $Y$ scales based on *tert*-butyl chloride or an appropriate adamantyl derivative. For reactions of tertiary benzylic substrates proceeding without nucleophilic solvent assistance, Liu and co-workers[2,12] also favored solvation effects as a cause of dispersion, and emphasized the need to be able to delocalize the developing positive charge into the aromatic rings.[2,12]

Fainberg and Winstein[35] recognized the importance of differential solvation as a cause of the observed dispersions, but Winstein *et al.*[21] also emphasized the probability that ion-pair return effects are important. They pointed out that, in the acetolysis of benzhydryl chloride, the true ionization rate is at least ten times the titrimetric rate and, therefore, a situation is to be expected where the extent of ion-pair return diminishes as acetic acid–water mixtures become more aqueous. This can rationalize very well the higher slope obtained for Grunwald–Winstein plots of solvolyses in this mixed solvent system relative to solvolyses in other binary aqueous mixtures. In terms of evaluating ion-pair return, it is unfortunate that acetic acid–water mixtures have been neglected in subsequent Grunwald–Winstein treatments. Ion-pair return has also been favored by McManus *et al.*[36] as the prime cause of dispersions observed in Grunwald–Winstein plots of the solvolyses (with anchimeric assistance) of mustard chlorohydrins and related compounds.

Bunton *et al.*[7] extended the earlier[21] studies of benzhydryl chloride solvolysis and, in particular, they studied solvolyses in fluorinated solvents such as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and 97% and 70% aqueous TFE. The specific rates of solvolysis in fluorinated solvents were higher than would be predicted from a Grunwald–Winstein plot based on other binary aqueous mixtures. They argued against ion-pair return on the grounds that attack by these low-nucleophilicity solvents on intermediate ion pairs would be disfavored and one would predict negative not positive deviations from the Grunwald–Winstein plot. Although the arguments are sound for nucleophilic attack on ion-pair intermediates, they represent a misreading of the situation for benzhydryl chloride solvolysis, where nucleophilic attack is believed to be primarily (consistent with common-ion rate depression) at the free ion stage. For such a situation, the competition would be between ion-pair return and ion-pair separation, leading towards free ions. The separation process will be favored by high ionizing power (as in the fluorinated solvents) and will be essentially independent of solvent nucleophilicity. With this view of the overall mechanism of solvolysis, positive deviations in fluorinated solvents are consistent with, and could very well arise from, ion-pair return effects.

Even extensive ion-pair return would not necessarily lead to deviations from Grunwald–Winstein plots. It is possible that, for a given substrate, the percentage of ion-pair return following ionization might over a range of hydroxylic solvents be fairly constant. The 1-Ad$^+$Cl$^-$ ion pairs formed during solvolysis–decomposition of 1-adamantyl chloroformate[37] show fairly constant solvolysis/collapse ratios. What is needed, in order to obtain dispersions in Grunwald–Winstein plots, are appreciable variations in the extent of ion-pair return, relative to the return to the standard substrate, as the solvent is varied. To take an extreme example, as outlined above, if for one substrate attack is at the ion-pair stage then the collapse/solvolysis ratio will have a high dependence on solvent nucleophilicity, and it would vary with solvent in a different way to a situation for which capture by solvent is after progression to free ions, where the collapse/solvolysis ratio would have a high dependence on solvent ionizing power. The adamantyl substrates, recommended as standards, represent an intermediate situation, with attack believed to be at the solvent-separated ion-pair stage,[38] and, again, such a situation would be expected to show a different pattern of solvent-induced variations is the extent of ion-pair return[39] relative to, for example, solvolyses of *p*-methoxybenzyl or benzhydryl derivatives, where products are formed after further separation of the ions. Accordingly, differences in ion-pair return patterns could very well lead to dispersions in Grunwald–Winstein plots of unimolecular solvolyses of benzylic derivatives against $Y_X$ scales based on solvolyses of adamantyl derivatives.

Variations 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, are not necessarily totally independent processes. In the solvolyses of benzylic substrates, products tend to be produced at a later stage in the Winstein ion-pair scheme,[38] owing to the carbocation-stabilizing influences of the dispersal of positive charge from the $\alpha$-carbon into the aromatic rings. Solvation at the rings can disperse the positive charge further (into the solvent) and influence any dispersions in Grunwald–Winstein plots associated with ion-pair return.

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