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SHORT COMMUNICATION

NUCLEOPHILIC PARTICIPATION IN THE SOLVOLYSES OF 2-ARYL-2-HALOPROPANES AND THE PREVIOUSLY CLAIMED ADVANTAGE OF USING Y_{BnX} SCALES

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Contrary to a recent report, the specific rates of solvolyses of five 2-aryl-2-chloropropanes give only marginally (not significantly) better correlations with use of the Y_{BnCl} scale rather than the Y_{Cl} scale. With the use of the extended (two-term) Grunwald–Winstein equation, some evidence for a weak nucleophilic solvation is obtained, but at a low confidence level. The specific rates of 2-bromo-2(*p*-trifluoromethylphenyl)propane solvolysis are significantly better correlated using Y_{Br} (rather than Y_{BnBr}) values and, indeed, the use of N_{T} values in conjunction with Y_{Br} values leads to an *l* value of 0·17 ± 0·06 and evidence for a weak nucleophilic participation at a 98·7% confidence level.

Recently, we demonstrated[1] that, provided a sufficiently large set of specific rates measurements in a wide variety of solvent types was available, only modest improvements result from use of the Y_{BnCl} scale[2,3] [based on solvolysis of 2-chloro–2-(3′-chlorophenyl)adamantane] rather than the Y_{Cl} scale[4–6] (based on solvolysis of 1-chloroadamantane) within the Grunwald–Winstein equation:[6,7]

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

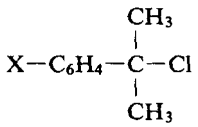
where k and k_0 are the specific rates of solvolysis of the substrate in a given solvent and in 80% ethanol, m is the sensitivity of the solvolysis of the substrate to changes in solvent ionizing power (Y) and c is the intercept. Indeed, for 20 solvents, it was found[1] that the Y_{BnCl} scale correlates reasonably well with the Y_{Cl} scale: $m = 1{\cdot}01 \pm 0{\cdot}07$, $c = 0{\cdot}22 \pm 0{\cdot}52$ and correlation coefficient $(r) = 0{\cdot}956$. Accordingly, we were very surprised to see, in a recent short communication,[8] a claim of considerably better correlations for a series of 2-aryl-2-chloropropanes (*tert*-cumyl chlorides) using Y_{BnCl} values rather than Y_{Cl} values in equation (1).

Also, since we had demonstrated[1] good correlations using the two-term (extended) Grunwald–Winstein equation:

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

for the solvolysis of *tert*-cumyl *p*-nitrobenzoate, using N_{T} values[5,9] in conjunction with either Y_{OTs}[6] or Y_{BnOPNB}[10] values, we were unable at first sight to understand the extremely poor correlations using equation (2) (with N_{T} and Y_{Cl} values).[8] In equation (2), the additional term involves the sensitivity (l) of the solvolysis to changes in solvent nucleophilicity (N).

Inspection of the solvents used to study[8] the solvolyses of $XC_6H_4C(CH_3)_2Cl$ compounds:



$$X{-}C_6H_4{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}Cl$$

1a: $X{=}4'{-}CH_3$
1b: $X{=}4'{-}F$
1c: $X{=}H$
1d: $X{=}3'{-}Cl$
1e: $X{=}4'{-}CF_3$

showed them to be small in number (6–11 used in the overall correlations) and not particularly well chosen as regards variation in solvent type. Indeed, the fluctuations described as 'random' can, at least in part, be related to different solvents being used in the correlation for different substrates. Nonetheless, to account

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for the considerably better correlations with Y_{BnCl} than with Y_{Cl}, a particularly ill-chosen set of solvents (outliers on the $Y_{\mathrm{BnCl}}-Y_{\mathrm{Cl}}$ correlation) would have had to be selected. In attempting to duplicate the reported correlations, we find we can accurately reproduce the correlations against Y_{BnCl} (Table 2 in Ref. 8) but not the correlations when Y_{Cl} is incorporated into either equation (1) or (2), as presented in Table 3 in Ref. 8. In the latter case we obtain higher (more positive) values for both *l* and *m* and considerably larger correlation coefficients. For example, where the correlation using equation (1) with Y_{Cl} is reported[8] as poor ($r = 0{\cdot}83 - 0{\cdot}91$), we obtain *r* values in the range 0·91 – 0·97 for the five correlations. We find that we can come very close to duplicating all of the data reported in Table 3 in Ref. 8 if a Y_{Cl} value of −0·08 (rather than the accepted[4,6] value of −0·8) is used for 80% acetone.

Table 1. Correlation of the specific rates of solvolysis of compounds **1a–e** against solvent ionizing power values using the Grunwald–Winstein equation (1)

Correlation[a]	*n*[b]	*m*[c]	*c*[c]	*r*[d]
1a, Y_{Cl}	9	0·95 ± 0·08	0·57 ± 0·39	0·973
1a, Y_{BnCl}	9	0·92 ± 0·03	0·16 ± 0·12	0·997
1b, Y_{Cl}	11	0·80 ± 0·06	−0·06 ± 0·30	0·974
1b, Y_{BnCl}	11	0·80 ± 0·05	−0·27 ± 0·23	0·985
1c, Y_{Cl}	12	0·77 ± 0·05	−0·01 ± 0·24	0·983
1c, Y_{BnCl}	12	0·74 ± 0·04	−0·24 ± 0·22	0·985
1d, Y_{Cl}	12	0·68 ± 0·05	−0·13 ± 0·25	0·977
1d, Y_{BnCl}	12	0·66 ± 0·06	−0·27 ± 0·30	0·966
1e, Y_{Cl}	10	0·65 ± 0·06	−0·28 ± 0·31	0·967
1e, Y_{BnCl}	10	0·62 ± 0·05	0·49 ± 0·28	0·972

[a] Correlation of $\log(k/k_0)$ for solvolysis of the indicated substrate against Y_{Cl} (Refs 4–6) or Y_{BnCl} (Refs 2 and 3) solvent ionizing power scales.

[b] Number of solvents, identical solvents for correlations with Y_{Cl} or Y_{BnCl} and from Table 1 in Ref. 8, but omitting (no Y_{Cl} value available) propan-2-ol and adding 100% TFE for **1a–c** and 70% ethanol for **1c** and **d** (see text).

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

[d] Correlation coefficient.

We choose not to report our corrected values corresponding to the previous analyses but, instead, we report, in Tables 1 and 2, the correlations obtained using equations (1) and (2), respectively, and incorporating either Y_{BnCl} or Y_{Cl} after maximizing the number of solvents. For **1c**[11] and **1d**,[2] specific rates available in 70% ethanol are incorporated and for **1a–c** specific rates in 100% 2,2,2-trifluoroethanol (TFE) were obtained by extrapolation of the excellent Grunwald–Winstein plots for TFE–ethanol mixtures against Y_{BnCl} values[8] ($\log k/k_0$ values of 3·50 for **1a**, 2·38 for **1b** and 2·30 for **1c**). For **1d**, the original specific rate[2] in 80% ethanol was used and the more recently reported value[8] (claimed to correspond to the original) was assumed to be erroneous. A listing of errata has recently been published.[12] Values replacing those originally in Table 3 in Ref. 8 are now consistent with those which we had previously calculated using the identical solvents. However, within the listing of errata, no changes were made to the conclusions reached in Ref. 8, and our comments concerning major problems introduced by a not particularly well chosen set of solvents remain valid. For example, as regards the change made to p. 125 of Ref. 8 (last of the errata), we must point out that the new negative *l* value −0·37, which is quoted for solvolysis of **1a**, is associated with a standard error of ±0·89 and a probability that the *lN* term is not statistically significant of 0·71! Indeed, even

Table 2. Correlation of the specific rates of solvolysis of compounds **1a–e** against a combination of solvent nucleophilicity values and solvent ionizing power using the extended (two-term) Grunwald–Winstein equation (2)

Correlation[a]	*l*[b,c]	*m*[b]	*c*[b]	*r*[d]
1a, Y_{Cl}	−0·17 ± 0·20 (0·44)	0·84 ± 0·17	0·41 ± 0·40	0·976
1a, Y_{BnCl}	−0·10 ± 0·05 (0·12)	0·86 ± 0·04	0·09 ± 0·11	0·998
1b, Y_{Cl}	−0·03 ± 0·14 (0·86)	0·78 ± 0·11	−0·08 ± 0·32	0·974
1b, Y_{BnCl}	0·14 ± 0·11 (0·22)	0·89 ± 0·08	−0·19 ± 0·22	0·987
1c, Y_{Cl}	0·01 ± 0·01 (0·96)	0·77 ± 0·08	0·00 ± 0·25	0·983
1c, Y_{BnCl}	0·13 ± 0·10 (0·24)	0·82 ± 0·07	−0·17 ± 0·22	0·987
1d, Y_{Cl}	0·08 ± 0·10 (0·47)	0·72 ± 0·08	−0·08 ± 0·25	0·979
1d, Y_{BnCl}	0·24 ± 0·12 (0·08)	0·80 ± 0·09	−0·14 ± 0·27	0·976
1e, Y_{Cl}	0·12 ± 0·15 (0·44)	0·73 ± 0·11	−0·17 ± 0·31	0·970
1e, Y_{BnCl}	0·19 ± 0·14 (0·20)	0·73 ± 0·10	−0·36 ± 0·27	0·978

[a] Correlation of $\log(k/k_0)$ for solvolysis of the indicated substrate against N_{T} and either Y_{Cl} or Y_{BnCl} values, in the same solvents as used in Table 1 (see footnote b to Table 1).

[b] From equation (2) and with associated standard error.

[c] Values in parentheses represent the probability that the *lN* term is not statistically significant.

[d] Correlation coefficient.

the accompanying Y_{Cl} value of 0·61 is associated with a standard error of ±0·39. Obviously, these values cannot be considered to indicate anything clearly, other than that the choice of five similar solvents (EtOH, 80% EtOH, MeOH, 80% acetone and 60% TFE–40% EtOH) is totally inadequate for carrying out an extended Grunwald–Winstein treatment. For the corresponding analyses (six solvents) of the solvolyses of **1c** and **1e**, our multiple linear regression program (ABSTAT; Anderson–Bell, Arvada, CO, U.S.A.) issued a warning: 'Results may be spurious due to a high degree of multicollinearity.'

In Table 1, the values for **1d** in 12 solvents are very similar to those reported previously[1] for this compound in 10 solvents, indicating the data to be reasonably robust. For **1d**, the correlation coefficient is slightly higher when Y_{Cl} values are used but the reverse is the situation for the other four substrates. With the marginal exception of **1a**, no considerable improvement results from use of Y_{BnCl} rather than Y_{Cl} values, in contrast to the claim[8] of 'definite evidence which could demonstrate the advantage of using the new Y_{BnX} scales' (average correlation coefficients for the correlations of the five substrates of 0·975 ± 0·006 with use of Y_{Cl} and of 0·981 ± 0·012 with use of Y_{BnCl}, range of values of 0·969 – 0·983 with use of Y_{Cl} and of 0·966 – 0·997 with use of Y_{BnCl}).

The improvements in the correlation coefficient on incorporating the lN term [in equation (2)] are extremely small and, coupled with relatively high probabilities that the lN term is not statistically significant (Table 2), one can conclude that, if present at all, the nucleophilic solvation of the developing carbocation must be weak. Further, as pointed out previously,[1] dispersion effects are frequently observed in one-term [equation (1)] treatments, and care must be taken not to misassign them as effects due to nucleophilic participation by the solvent. The best evidence favoring a weak nucleophilic solvation is the trend for an increased sensitivity towards changes in solvent nucleophilicity as one goes from substituents which internally stabilize the incipient carbocation to those which will destabilize it; the trends are, however, only just outside the ranges accommodated by the associated standard errors.

Recently, a Y_{BnBr} scale has been developed[13] and compared with Y_{Br} values[4,6] (including additional values[13] for TFE–ethanol mixtures). Although specific rates for the solvolysis of *p*-trifluoromethylcumyl bromide (**1e** with bromine replacing chlorine) were reported and correlated graphically with Y_{Br} and Y_{BnBr} values, no numerical analyses were reported. We find considerably better correlations with the use of Y_{Br} than with the use of Y_{BnBr} for the 12 solvents (90–60% ethanol–water, 80–50% acetone–water, 100–40% TFE–ethanol). Using equation (1), with Y_{Br}, values of $m = 0{\cdot}63 \pm 0{\cdot}05$ and $c = -0{\cdot}20 \pm 0{\cdot}19$ ($r = 0{\cdot}965$) and, with Y_{BnBr}, values of $m = 0{\cdot}59 \pm 0{\cdot}11$ and $c = -0{\cdot}09 \pm 0{\cdot}35$ ($r = 0{\cdot}870$) are obtained. Using equation (2), with N_T and Y_{Br}, values of $l = 0{\cdot}17 \pm 0{\cdot}06$, $m = 0{\cdot}76 \pm 0{\cdot}06$ and $c = -0{\cdot}15 \pm 0{\cdot}14$ ($r = 0{\cdot}983$) and, with N_T and Y_{BnBr}, values of $l = 0{\cdot}21 \pm 0{\cdot}15$, $m = 0{\cdot}78 \pm 0{\cdot}17$, $c = -0{\cdot}01 \pm 0{\cdot}33$ ($r = 0{\cdot}894$) are obtained. The reasons for the much better correlations with Y_{Br} than with Y_{BnBr} are not clear, but this observation is certainly contrary to the claim[8] that benzylic substrates are better correlated using Y_{BnX} scales. The l value obtained using Y_{Br} and N_T values is associated with a 98·7% confidence level that the lN term is statistically significant; when Y_{BnBr} values are substituted, this value falls to 80%.

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