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SHORT COMMUNICATION

NUCLEOPHILIC SOLVENT INTERVENTION IN THE SOLVOLYSIS OF 2-ARYL-2-CHLOROPROPANES. AN EXAMPLE TO DEMONSTRATE THE ADVANTAGE OF USING THE Y_{BnCl} SCALE IN CORRELATION ANALYSIS

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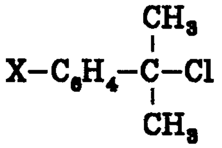
The advantage of using the Y_{BnCl} scale over the Y_{Cl} scale in Grunwald–Winstein-type correlation analysis was demonstrated by the kinetic evidence of a significant nucleophilic solvent intervention in the solvolysis of 2-aryl-2-chloropropanes. A depression of log k values measured in ethanol–trifluoroethanol mixtures and a positive azide salt effect were observed.

Correlation analyses with the Grunwald–Winstein equation (1)[1] or (2)[2] are generally employed to the study of solvolytic mechanisms, and in which the solvent ionizing power Y is the empirical solvent polarity scale[3] for measuring solvent effects. New Y_{BnX} scales have been found to be superior to Y_{X} scales[4] for benzylic bromides,[5] chlorides,[6] *p*-nitrobenzoates[7] and tosylates.[8]

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

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

The deviation of log k values measured in isodielectric[9,10] ethanol–trifluoroethanol mixtures from linear plots had been observed for several *tert*-cumyl derivatives,[5,6a,7] and nucleophilic assistance by solvents was thus considered to be involved. A recent paper by Kevill and D'Souza[11] suggesting the general preference of Y_{X} scales prompted us to present our definite evidence which could demonstrate the advantage of using the new Y_{BnX} scales. In this paper, the kinetic evidence for the nucleophilic solvent intervention in the solvolysis of 2-aryl-2-chloropropanes (*tert*-cumyl chlorides; Scheme 1) is reported.



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

1a : X = 4′−CH$_3$
1b : X = 4′−F
1c : X = H
1d : X = 3′−Cl
1e : X = 4′−CF$_3$

Scheme 1

Solvolytic rates for a series of 2-aryl-2-chloropropanes, **1a–e**, were monitored conductimetrically or titrimetrically. Good agreement of rate constants with literature data[12] or between those obtained by different methods were observed. Pertinent rate constants are listed in Table 1. Correlation analyses were carried out using equation (1) with Y_{BnCl} values[6b] and with Y_{Cl} values,[4,13] and using equation (2) with Y_{Cl} and N_{T} values.[14] The results are given in Tables 2 and 3. The log k versus Y_{BnCl} plots for **1a**, **c** and **d** are shown in Figure 1.

Comparison of Tables 2 and 3 clearly indicates that the correlation with Y_{Cl} is poor[15] ($R = 0{\cdot}83$–$0{\cdot}91$) and random for all five substrates, whereas the variations of both m and R are in reasonable agreement from the correlation with Y_{BnCl}. The excellent linear correlation[15] ($R = 0{\cdot}995$) with $m(Y_{\mathrm{BnCl}})$ of 0·907 observed in the case of the *p*-methyl derivative **1a** suggests that a limiting S_N1 process is involved in the solvolysis. The m value decreases and the correlation changes to satisfactory ($R = 0{\cdot}98$) and less satisfactory ($R = 0{\cdot}97$) as the substituent becomes less electron-donating (**1b**) or more electron-withdrawing (**1d** and **1e**). Moreover, the depression of the data points

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Table 1. Solvolytic rate constants for chlorides **1a**–**e**[a]

Solvent[b]	**1a**	**1b**	k(s^{-1})[c] **1c**[d]	**1d**[e]	**1e**
100E	$1{\cdot}06\times10^{-2}$	$7{\cdot}89\times10^{-4}$	$3{\cdot}80\times10^{-4}$	$6{\cdot}68\times10^{-6}$	$6{\cdot}50\times10^{-7}$[g]
90E	0·108	$8{\cdot}42\times10^{-3}$	$3{\cdot}91\times10^{-3}$	$6{\cdot}38\times10^{-5}$	$6{\cdot}76\times10^{-6}$[f]
80E	0·245[f]	$4{\cdot}09\times10^{-2}$	$1{\cdot}73\times10^{-2}$	$1{\cdot}09\times10^{-3}$	$3{\cdot}08\times10^{-5}$
100M	0·128	$1{\cdot}04\times10^{-2}$	$5{\cdot}22\times10^{-3}$	$8{\cdot}00\times10^{-5}$	$7{\cdot}33\times10^{-6}$[f]
90A	$3{\cdot}22\times10^{-3}$	$2{\cdot}05\times10^{-4}$	$1{\cdot}24\times10^{-4}$	$1{\cdot}94\times10^{-6}$[f]	$1{\cdot}67\times10^{-7}$[f]
80A	$4{\cdot}72\times10^{-2}$	$2{\cdot}86\times10^{-3}$	$1{\cdot}79\times10^{-3}$	$2{\cdot}52\times10^{-5}$	$2{\cdot}15\times10^{-6}$
70A		$2{\cdot}63\times10^{-2}$	$1{\cdot}19\times10^{-2}$	$1{\cdot}60\times10^{-4}$	$1{\cdot}39\times10^{-5}$
60A		0·130		$8{\cdot}64\times10^{-4}$	
i-PrOH	$9{\cdot}99\times10^{-4}$	$1{\cdot}03\times10^{-4}$	$5{\cdot}14\times10^{-5}$[g]		
100T				$1{\cdot}82\times10^{-2}$	$1{\cdot}38\times10^{-3}$
80T–20E			0·451[f]	$3{\cdot}08\times10^{-3}$[h]	$1{\cdot}81\times10^{-4}$
60T–40E	4·32[f]	0·135	$5{\cdot}49\times10^{-2}$	$4{\cdot}18\times10^{-4}$[h]	$3{\cdot}68\times10^{-5}$
40T–60E	0·575[f]	$1{\cdot}89\times10^{-2}$	$8{\cdot}60\times10^{-3}$		

[a] ±3%.

[b] Abbreviations of solvents: A = acetone; E = ethanol; i-PrOH=2-propanol; M = methanol; T = 2,2,2-trifluoroethanol. The numbers denote the volume percent of the specific solvent in the solvent mixture.

[c] At 25 °C unless stated otherwise.

[d] Literature data, Ref. 20.

[e] Literature data, Ref. 6a, unless stated otherwise.

[f] Calculated from data obtained at other temperature.

[g] Literature data, Ref. 12.

[h] This work.

Table 2. Correlation analyses for **1a**–**e** against Y_{BnCl}

Substrate	m(all)[a,b]	m(NU)[b,c]	m(TE)[d,e]
1a	0·907	0·893	0·939
	($R = 0{\cdot}995$, $n = 9$)	($R = 0{\cdot}992$, $n = 7$)	($R = 1{\cdot}000$, $n = 3$)
1b	0·872	0·967	0·797
	($R = 0{\cdot}982$, $n = 11$)	($R = 0{\cdot}993$, $n = 9$)	($R = 1{\cdot}000$, $n = 3$)
1c	0·772	0·943	0·766
	($R = 0{\cdot}986$, $n = 11$)	($R = 0{\cdot}997$, $n = 8$)	($R = 1{\cdot}000$, $n = 4$)
1d	0·649	0·935	0·665
	($R = 0{\cdot}972$, $n = 11$)	($R = 0{\cdot}993$, $n = 8$)	($R = 1{\cdot}000$, $n = 4$)
1e	0·616	0·941	0·635
	($R = 0{\cdot}972$, $n = 10$)	($R = 0{\cdot}988$, $n = 7$)	($R = 0{\cdot}999$, $n = 4$)

[a] All solvents.

[b] SD = 0·03–0·06.

[c] Nucleophilic solvents, including aqueous acetone, ethanol, 2-propanol and methanol.

[d] TFE–EtOH.

[e] SD = 0·01–0·02.

measured in iso-dielectric and low nucleophilic solvents could be estimated from the difference in slopes (m value) of the lines defined by those measured in nucleophilic solvents (m_{NU}) and in ethanol–trifluoroethanol (EtOH–TFE) (m_{TE}). Essentially no deviation ($\Delta m < 0{\cdot}10$) could be observed for **1a**, and the deviation increases from **1b** ($\Delta m = 0{\cdot}17$) to **1e** ($\Delta m = 0{\cdot}31$). The different extent of the deviation can also be seen in Figure 1. These results could be interpreted by the nucleophilic solvent intervention, and the significance of acceleration diminishes as the cationic transition state becomes more stable. This is in agreement with what has been observed for 2-aryl-2-propyl *p*-nitrobenzoates.[16]

In addition, Table 4 indicates a positive azide salt effect[17] in 90% acetone. The difference between these and the results obtained by Richard *et al.*[18] is probably due to the solvent employed, as has been shown for *p*-methoxybenzyl derivatives.[19] The disagreement between the amount of the azide product observed and that calculated from an $S_{\mathrm{N}}2$ process[17a] suggests the solvent intervention is not of purely $S_{\mathrm{N}}2$ type. The

Table 3. Correlation analyses for **1a–e** against Y_{Cl} and N_T

	Y_{Cl}		Y_{Cl} and N_T	
Substrate	m(all)[a]	m(NU)[b]	m	l
1a	0·652	0·402	0·387	−0·742
	(R = 0·829, n = 6)	(R = 0·763, n = 5)	(R = 0·854, n = 5)	
1b	0·565	0·517	0·640	0·138
	(R = 0·865, n = 8)	(R = 0·857, n = 7)	(R = 0·874, n = 6)	
1c	0·624	0·430	0·587	−0·140
	(R = 0·894, n = 8)	(R = 0·761, n = 6)	(R = 0·911, n = 6)	
1d	0·552	0·482	0·586	−0·031
	(R = 0·914, n = 9)	(R = 0·860, n = 7)	(R = 0·925, n = 7)	
1e	0·502	0·406	0·654	0·252
	(R = 0·882, n = 8)	(R = 0·744, n = 6)	(R = 0·901, n = 6)	

[a] All solvents; SD = 0·10–0·22.

[b] Nucleophilic solvents, including aqueous acetone, ethanol and methanol; SD = 0·13–0·20.

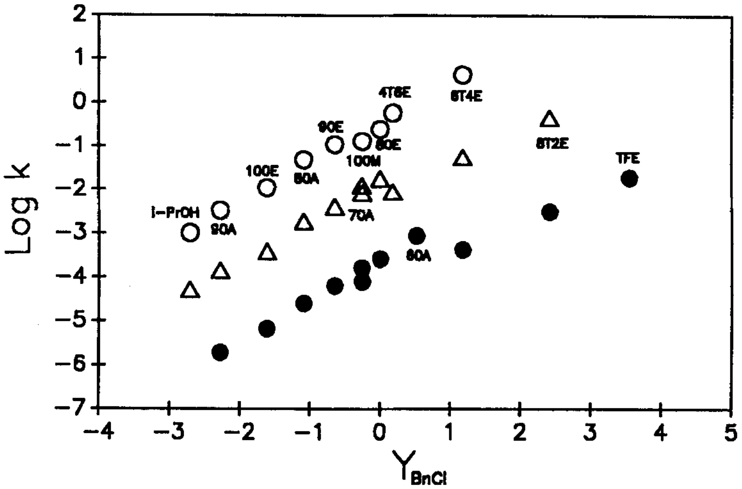

Figure 1. Correlations of logarithms of rate constants for (○) **1a**, (△) **1c** and (●) **1d** against Y_{BnCl}

Table 4. Azide salt effect in the solvolysis of **1c** in 90% acetone[a]

Salt concentration (M)	$k(NaN_3)$ (s^{-1})	$k(NaClO_4)$ (s^{-1})	%RN_3(GC)[b]	%RN_3(t)[c]	%$RN_3(S_N2)$[d]
0·00	$1{\cdot}24 \times 10^{-4}$	$1{\cdot}24 \times 10^{-4}$			
0·04	$1{\cdot}79 \times 10^{-4}$	$1{\cdot}35 \times 10^{-4}$	14·8	13·9	24·6
0·08	$1{\cdot}90 \times 10^{-4}$	$1{\cdot}39 \times 10^{-4}$	26·6	26·9	32·1

[a] At 25 °C.

[b] By GC analysis on Carbowax 20M.

[c] By titration.

[d] Calculated.[17a]

solvation of cationic transition states by nucleophilic solvents is likely to be significant.[20] Further studies are in progress.

On the other hand, the multiple regression analysis [equation (2)] of log k against Y_{Cl} and N_T values[14] could not improve the correlation (Table 3). Moreover, the observed irregular trend from **1a** to **e** and the negative l values found for **1a** and **c** clearly indicate that the use of equation (2) with the N_T[11,14] scale will not be a suitable choice for correlating the solvolytic reactivities of **1a–e**. Despite the statement that 'one should be reluctant to undertake the development of further scales,'[11] it is obvious that in line with the recently proposed 'similarity model'[21] a better understanding of the solvolytic mechanism for *tert*-cumyl chlorides can only be achieved by using the newly developed Y_{BnCl} scale[6] and not the Y_{Cl} scale.

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REFERENCES

1. E. Grunwald and S. Winstein, *J. Am. Chem. Soc.* **70**, 846 (1948).
2. S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.* **73**, 2700 (1951).
3. For a review, see C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd edn, Chapt. 7. VCH, Weinheim (1988).
4. For the latest review, see T. W. Bentley and G. Llewellyn, *Prog. Phys. Org. Chem.* **17**, 1211 (1990).
5. K.-T. Liu and H.-C. Sheu, *J. Chin. Chem. Soc.* **38**, 29 (1991).
6. (a) K.-T. Liu, H.-C. Sheu, H.-I. Chen, P.-F. Chiu and C.-R. Hu, *Tetrahedron Lett.* **25**, 3611 (1990); (b) K.-T. Liu and H.-C. Sheu, *J. Org. Chem.* **56**, 3021 (1991).
7. K.-T. Liu, H.-I Chen and C.-P. Chin, *J. Phys. Org. Chem.* **4**, 463 (1991).
8. K.-T. Liu, J.-S. Yang, S.-M. Chang, Y.-S. Lin, H.-C. Sheu and M.-L. Tsao, *J. Org. Chem.* **57**, 3041 (1992).
9. D. A. de Roza, L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.* **95**, 7003 (1973).
10. J. Kaspi and Z. Rappoport, *J. Am. Chem. Soc.* **102**, 3829 (1980).
11. D. N. Kevill and M. J. D'Souza, *J. Phys. Org. Chem.* **5**, 287 (1992).
12. Y. Okamoto, T. Inukai and H. C. Brown, *J. Am. Chem. Soc.* **80**, 4972 (1958).
13. D. N. Kevill and J. B. Kyong, *J. Org. Chem.* **57**, 258 (1992).
14. D. N. Kevill and S. W. Anderson, *J. Org. Chem.* **56**, 1845 (1991).
15. H. H. Jaffe, *Chem. Rev.* **53**, 191 (1953).
16. K.-T. Liu, L.-W. Chang and P.-S. Chen, *J. Org. Chem.* **57**, 4791 (1992).
17. For examples of pioneering work, see (a) D. J. Raber, J. M. Harris, R. E. Hall and P. v. R. Schleyer, *J. Am. Chem. Soc.* **93**, 4821 (1971); (b) R. A. Sneen, *Acc. Chem. Res.* **6**, 46 (1973).
18. J. P. Richard, T. L. Amyes and T. Vontor, *J. Am. Chem. Soc.* **113**, 5871 (1991).
19. T. L. Amyes and J. P. Richard, *J. Am. Chem. Soc.* **112**, 9507 (1990).
20. K.-T. Liu, P.-S. Chen, P.-F. Chiu and M.-L. Tsao, *Tetrahedron Lett.* **33**, 6499 (1992).
21. T. W. Bentley, J. Dau-Schmidt, G. Llewellyn and H. Mayr, *J. Org Chem.* **57**, 2387 (1992).