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SHORT COMMUNICATION

THE GRUNWALD–WINSTEIN TYPE CORRELATION FOR 2-CHLORO-2,4,4-TRIMETHYLPENTANE: A SIMPLE TERTIARY ALKYL CHLORIDE THAT SHOWS ESSENTIALLY LIMITING BEHAVIOUR IN SOLVOLYSIS

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Evaluation of the rates of solvolysis of 2-chloro-2,4,4-trimethylpentane (4) in 17 solvents on the basis of the Grunwald–Winstein type equation $[\log(k/k_0) = lN_T + mY_{Cl} + c]$ gives an excellent correlation with $l = -0·01 \pm 0·02$ and $m = 0·74 \pm 0·01$. The neopentyl group in 4 more effectively shields the rear side of the reaction center than the *tert*-butyl group in 2-chloro-2,3,3-trimethylbutane. The rate ratio between 4 and 2-chloro-2-methylpropane (3) at 25 °C is 275 in trifluoroethanol and predicted to increase to 950 in trifluoroacetic acid. The previous 4:3 rate ratio of 22 in 80% ethanol evidently underestimated the B-strain effect on the solvolysis rate of 4 by a factor of at least 40.

The major solvent intervention in solvolytic reactions has been evaluated by the extended Grunwald–Winstein equation:[1]

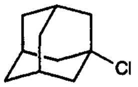
$$\log(k/k_0) = lN + mY + c \qquad (1)$$

The equation includes the nucleophilic (N) and electrophilic (Y) parameters of solvents, where k_0 and k refer to the specific rates of solvolysis in 80% aqueous ethanol and a given solvent, respectively, and c is the intercept.[1] The N parameter is based on the solvolyses of methyl tosylate[1b] (N_{OTs}) or S-methyldibenzothiophenium ion[2] (N_T). As the Y parameter for alkyl chloride solvolyses it has been recommended to use Y_{Cl}, which is based on 1-chloroadamantane (1) as a standard substrate ($l = 0·000$, $m = 1·000$).[3] Recently, Kevill and D'Souza[1c] applied equation (2) to the solvolysis rates of 2-chloro-2,3,3-trimethylbutane (2) that had been reported by Liu *et al.*,[4] and showed the l and m values to be $0·10 \pm 0·04$ and $0·82 \pm 0·04$, respectively. Although the number of rate data was limited ($n = 10$), the relatively small l value suggested a marked decrease in nucleophilic solvent intervention compared with 2-chloro-2-methylpropane (3) ($l = 0·37 \pm 0·04$, $m = 0·89 \pm 0·04$)[1c] in the same solvents.

$$\log(k/k_0) = lN_T + mY_{Cl} + c \qquad (2)$$

We now report that 2-chloro-2,4,4-trimethylpentane (4) is an open-chain tertiary alkyl substrate that undergoes essentially limiting S_N1 solvolysis. Actually, 4 was used more than four decades ago as the first model compound for examination of the back strain (B-strain) effect in solvolysis.[5] However, the greater rear-side shielding effect of the neopentyl group in 4 toward nucleophilic solvent intervention than the *tert*-butyl group in 2 has never been noticed.

The rates of solvolysis of 4 were determined in various solvents by a titrimetric or a conductimetric method in the presence of 0·025 or 0·0002 M of 2,6-lutidine, respectively.[6] The rates of 4 in trifluoroacetic acid (TFA),



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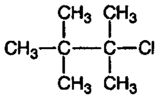
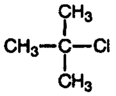


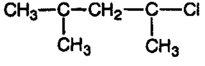
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-Cl$

2



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

3



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl$

4

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formic acid and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) were expected to be too fast to be measured; therefore, these solvents were not included. The low solubilities of **4** and solvolysis products in aqueous solvents hampered the rate studies in 40% acetone, 50% methanol and 50% ethanol and their more aqueous mixtures. The specific rates are summarized in Table 1 and the plot of log *k* values against Y_{Cl} is shown in Figure 1. For comparisons similar plots are also shown for **2**[4] and **3**[7–9] by using selected reported data. The products of solvolysis of **4** were examined in methanolysis and acetolysis at 50 °C under buffered conditions. The major products were the expected alkenes, 2,4,4-trimethylpent-1- and -2-enes; a single substitution product was formed in 35% and 9% yields in methanolysis and acetolysis, respectively.

Table 1. Specific rates for the solvolysis of **4** at 25·0 °C

Solvent[a]	10^5k (s^{-1})[b]	Solvent[a]	10^5k (s^{-1})[b]
100E	0·373[c]	90A	0·454
90E	4·19	80A	4·61
80E	20·3	70A	24·5
70E	65·9	60A	129[d]
60E	205[d]	50A	521[d]
100M	3·54[e]	AcOH	1·61[f]
80M	79·4	100T	2860[d]
60M	1040[d]	70T	3590[d]
		50T	5790[d]

[a] E, M, A, and T denote ethanol, methanol, acetone and 2,2,2-trifluoroethanol, respectively, and the preceding for E, M and A indicate volume % of the organic components in aqueous mixtures at 25 °C and those for T denote weight % of T.

[b] Determined titrimetrically in the presence of 0.025 M 2,6-lutidine within an experimental error of ±2% unless noted otherwise.

[c] $k = 9{\cdot}70 \times 10^{-5}$ s^{-1} at 50·0 °C; $\Delta H^\ddagger = 24{\cdot}4$ kcal mol^{-1}; $\Delta S^\ddagger = -1{\cdot}7$ cal K^{-1} mol^{-1} (1 kcal = 4·184 kJ).

[d] Determined conductimetrically in the presence of 2×10^{-4} M 2,6-lutidine within an experimental error of ±1%.

[e] $k = 7{\cdot}30 \times 10^{-4}$ s^{-1} at 50·0 °C; $\Delta H^\ddagger = 22{\cdot}6$ kcal mol^{-1}; $\Delta S^\ddagger = -3{\cdot}2$ cal K^{-1} mol^{-1}.

[f] $k = 2{\cdot}89 \times 10^{-4}$ s^{-1} at 50·0 °C; $\Delta H^\ddagger = 21{\cdot}5$ kcal mol^{-1}; $\Delta S^\ddagger = -8{\cdot}3$ cal K^{-1} mol^{-1}.

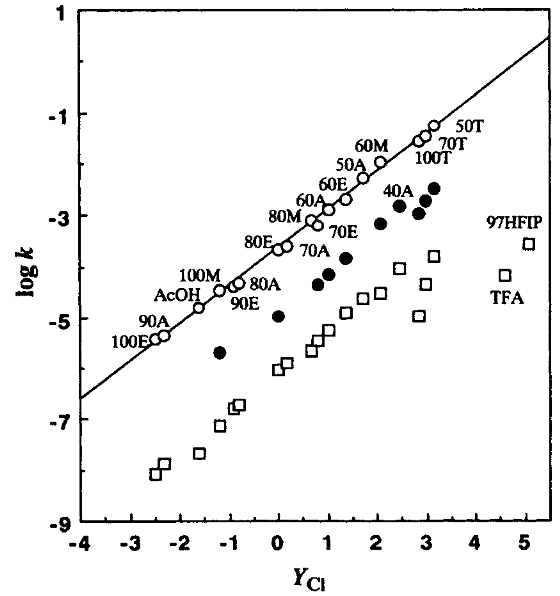


Figure 1. Plots of log *k* against Y_{Cl} for the solvolyses of (●) **2**, (□) **3** and (○) **4** at 25 °C. The points for **3** are shifted downward by 1 unit for clarity. For the references for Y_{Cl}, **2** and **3**, see text

It has been well recognized that downward deviations of the points for fluorinated alcohols [2,2,2-trifluoroethanol (TFE) and HFIP] and carboxylic acids (TFA, HCO_2H and AcOH) in the correlation with Y_{Cl} indicate the involvement of nucleophilic solvent intervention in non-fluorinated alcohols and aqueous organic solvents, such as aqueous ethanol, acetone and dioxane.[1c,d] As Figure 1 shows, the perfect fit of the points for AcOH, TFE, 70% TFE and 50% TFE for **4** to a single straight line ($m = 0{\cdot}75 \pm 0{\cdot}01$, $r = 0{\cdot}998$) is in accord with the essential absence of nucleophilic solvent intervention in the transition state of ionization.

Table 2. Correlation of specific rates of solvolysis of **2**–**4** against N_T[a] and Y_{Cl}[b] by using the extended Grunwald–Winstein equation (2)

Substrate	*n*[c]	*l*[d]	*m*[d]	*c*[d]	*r*[e]
2	10	0·10 ± 0·04[f]	0·82 ± 0·04[f]	0·13 ± 0·11[f]	0·996[f]
3	10	0·37 ± 0·04[f]	0·89 ± 0·04[f]	0·03 ± 0·11[f]	0·995[f]
4	17	−0·01 ± 0·02	0·74 ± 0·01	0·04 ± 0·02	0·998

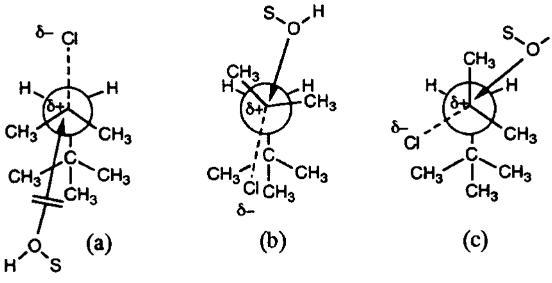
[a] Ref. 2.

[b] Ref. 1d.

[c] Number of solvents. Same solvents for **2** and **3**; see Refs 1e and 4.

[d] Using equation (2); with associated standard errors.

[e] Correlation coefficient.



Scheme 1

The rate data in Table 1 were also analysed using equation (2). As expected from the good straight line (Figure 1), the *l* value was $-0{\cdot}01 \pm 0{\cdot}02$. The results are summarized in Table 2 together with those of Kevill and D'Souza's analyses on the solvolyses of **2** and **3**.[1e] The *l* value increases in the order **4** $(-0{\cdot}01\pm0{\cdot}02) < $ **2** $(0{\cdot}10\pm0{\cdot}04) <$ **3** $(0{\cdot}37\pm0{\cdot}04)$, showing that the nucleophilic solvent intervention increases in this order.

It is worth pointing out that the magnitude of the *m* value decreases in the order **3** $(0{\cdot}89\pm0{\cdot}04) \geqslant$ **2** $(0{\cdot}82\pm0{\cdot}04) >$ **4** $(0{\cdot}74\pm0{\cdot}01)$. This order is opposite to that of reactivity in TFE (k/s^{-1} at 25 °C): **3** $(1{\cdot}04\times10^{-4})^{7b} <$ **2** $(1{\cdot}06\times10^{-3})^{4} <$ **4** $(2{\cdot}86\times10^{-2})$. A lower *m* value of a more activated chloride due to greater B-strain is in accord with an earlier transition state and, therefore, a reduced sensitivity to changes in solvent ionizing power.

The present study also gives an important insight into the magnitude of the relief of B-strain involved in the solvolysis of **4**. The previous work compared the rate of **4** with that of **3** in 80% ethanol at 25 °C to yield a **4**:**3** rate ratio of 22.[5] The **4**:**3** rate ratio obtained in this work in TFE is 275 by using the specific rate $1{\cdot}04\times10^{-4}\ \mathrm{s}^{-1}$ for **3**.[7b] Extrapolation of the plot for **4** in Figure 1 predicts the specific rates in TFA ($Y_{\mathrm{Cl}} = 4.6$)[1d] and 97% HFIP ($Y_{\mathrm{Cl}} = 5{\cdot}08$)[1d] to be 0·61 and $1{\cdot}4\ \mathrm{s}^{-1}$, respectively. By using these predicted specific rates and those reported for **3** in TFA[8] and 97% HFIP[9] at 25 °C ($6{\cdot}4\times10^{-4}$ and $2{\cdot}69\times10^{-3}\ \mathrm{s}^{-1}$, respectively), we obtain **4**:**3** rate ratios of 950 and 520, respectively. Evidently, the B-strain effect for **4** as measured by the solvolysis rate ratio has been underestimated by a factor of at least 40.

The essential absence of the nucleophilic solvent intervention and the presence of marked B-strain effect in the solvolyses of **4** suggest that the leaving chloride ion takes a locus that is antiperiplanar to the *tert*-butyl group [Scheme 1(a)]. In this conformation the nucleophilic solvent participation would be hampered by the bulky *tert*-butyl group. The other two conformations [Scheme 1(b) and (c)] permit nucleophilic solvent participation, but the steric strain may not be relieved: the steric strain would rather increase in the transition state owing to possible steric hindrance to ionization by the *tert*-butyl group, as has been demonstrated in the solvolyses of various U-shaped molecules.[10]

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