Nucleophilic solvent participation in the solvolysis of 4-methoxybenzyl bromide and chloride

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The solvolysis of 4-methoxybenzyl chloride (1) and bromide (3), and 1-(4-methoxyphenyl)ethyl chloride (4) in a variety of solvents were carried out. The observation of linear correlation using the dual-parameter Grunwald–Winstein equation, and the positive azide salt effect indicate significant nucleophilic solvent participation for 1 and 3. A smaller deviation of log k (in 100% 2,2,2-trifluoroethanol) for the bromide 3 than chloride 1 in the log $k - Y_{BnX}$ plots reveals a lesser extent of nucleophilic participation and is also in harmony with the greater nucleofugality of the bromide ion. The use of a low k_{Br}/k_{Cl} ratio as evidence for the presence of solvent participation is discussed. The observed α-deuterium kinetic isotope effect of 1.08 to 1.21 measured for 1 and 3 is inconsistent with the magnitude generally considered for a concerted mechanism.

Introduction

The solvolysis of substituted benzyl halide has been an attractive theme of mechanistic study since the pioneering work on solution kinetics of arylmethyl chlorides carried out by Olivier in 1922.[1,2] In exploring the change of mechanism with structure in aliphatic nucleophilic substitutions, Ingold suggested that the reaction of benzyl halides "belongs to the mechanistic border region"[3] of unimolecular (S_N1) and bimolecular (S_N2) reactions based on the kinetic order and rate of reaction. On the other hand, benzyl chloride has been used as an example to demonstrate the necessity of including a new parameter, solvent nucleophilicity (N) [eqn. (1)],[4] in addition to the solvent

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

ionizing power (Y) in the correlation analysis of solvent effects with the solvolytic reactivity in the limiting process proposed previously [eqn. (2)].[5]

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

Later work on kinetic isotope effects led to different conclusions. Studies of primary chlorine[6,7] and carbon[7] isotope effects on substituted benzyl chlorides by Fry *et al.* indicated a mechanistic spectrum ranging towards S_N1 with electron-donating groups, and towards S_N2 with electron-withdrawing groups. The chlorine kinetic isotope effect was also employed to evaluate ion pairing in the solvolysis of *para*-substituted benzyl chlorides.[8] Work done by others on carbon-14 and α-deuterium isotope effects showed an S_N2 character for reactions of unsubstituted and 4-methylbenzyl chlorides.[9] However, the observed secondary deuterium kinetic isotope effect for the solvolysis of 4-methylbenzyl-α-d_2 chloride in aqueous ethanol and 2,2,2-trifluoroethanol revealed the mechanism was "near limiting".[10] In addition, the solvolysis of 4-methoxybenzyl bromide in 80% aqueous dioxane was considered to proceed *via* an S_N1 mechanism.[11]

Nevertheless, the study of substituent effects on the solvolysis of arylmethyl chlorides by using Hammett-type correlation analysis suggested the 4-methoxybenzyl substrate,[10] or those containing a substituent more activating than 2-naphthyl,[12] solvolysed with a limiting S_N1 mechanism. An S_N1 mechanism for 4-methoxybenzyl chloride (1)[13] was proposed from studies of the solvolytic reactivity in a large variety of aqueous binary

1 X = Cl	**2** Y = Cl
3 X = Br	**4** Y = 4-OCH₃
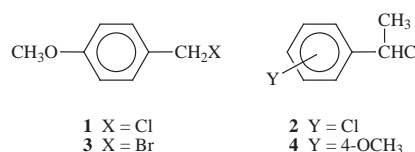
solvents and product selectivity, and was generally accepted.[14] Amyes and Richard reported the solvolysis of 1 in the presence of azide ion was stepwise in 50% aqueous trifluoroethanol, and was concurrently stepwise and concerted in aqueous acetone.[15] Solvolysis in aqueous acetone containing pyridine or thiourea was also considered to involve concurrent substitution of uni- and bi-molecular process.[16,17] Moreover, a good correlation has been found for log k of solvolyses for 1-phenylethyl chloride (2) with that for 1.[13] Since nucleophilic solvent intervention was recently proved to be involved in the solvolysis of 2,[18] it was desirable to reexamine the solvolysis of 1. In the present work, evidence for a significant nucleophilic solvent intervention in the solvolysis of 4-methoxybenzyl bromide (3) and of 1 will be presented.

Results and discussion

Solvolytic rate constants for 1, 3, 4-methoxybenzyl-α-d chloride (1-d), 4-methoxybenzyl-α-d bromide (3-d) and 1-(4-methoxyphenyl)ethyl chloride (4) in various solvents were measured conductimetrically, with the exception of those for the study of salt effects which were monitored by a titrimetric method. The results for 1, 3, and 4 are listed in Table 1. In most cases, the rate constants for 1 and 3 are in good agreement with the data in the literature.[13,18]

Correlation analyses of log k in Table 1 against Y[18–20] [eqn. (2)], and against Y and N_{OTs},[21] or Y and N_T[22] [eqn. (1)] were carried out, and the results are shown in Table 2. It is obvious that for 1 and 3 the single-parameter eqn. (2) does not yield a good linear correlation as compared with the use of eqn. (1), no matter which Y scale is used. Improved linearity could be found if Y_{Cl} was replaced by Y_{BnCl} in the correlation analysis using eqn. (1) or eqn. (2).[23] An insignificant difference between the use of N_{OTs} and N_T was seen, although less data points had been used in the former case due to the lack of N_{OTs} for several solvents. An excellent linear relationship ($R = 0.994$) was observed for bromide 3 when Y_{BnBr} and N_{OTs} were used in the dual-parameter eqn. (1).

On the contrary, Table 2 showed an excellent linear relationship between log k and Y_{BnCl} [eqn. (2)], but not Y_{Cl}, in the case of the secondary chloride **4**. No linear correlation was observed even if the dual-parameter eqn. (1) with Y_{Cl} and N_T was used. Therefore, a nucleophilic solvent participation is likely to be

Table 1 Solvolysis rate constants for halides **1**, **3** and **4**

Solvent[a]	k/s^{-1} (25 °C)		
	1	**3**	**4**
100E	$1.67 \times 10^{-5\,b}$	2.35×10^{-4}	$2.17 \times 10^{-2\,g}$
90E	2.19×10^{-4}	2.29×10^{-3}	$2.45 \times 10^{-1\,g,h}$
80E	1.16×10^{-3}	9.69×10^{-3}	1.55^{i}
70E	4.33×10^{-3}	3.05×10^{-2}	
60E	1.34×10^{-2}	9.09×10^{-2}	
90A	$3.04 \times 10^{-6\,b}$	5.89×10^{-5}	3.40×10^{-3}
80A	6.71×10^{-5}	8.57×10^{-4}	$7.21 \times 10^{-2\,g}$
70A	5.42×10^{-4}	4.80×10^{-3}	$6.55 \times 10^{-1\,j}$
60A	3.60×10^{-3}	2.68×10^{-2}	
100M	2.90×10^{-4}	3.31×10^{-3}	$3.94 \times 10^{-1\,k}$
90M	$1.65 \times 10^{-3\,b}$	1.55×10^{-2}	
80M	$7.37 \times 10^{-3\,b}$	5.45×10^{-2}	
100T	$2.04 \times 10^{-1\,c}$	$6.06 \times 10^{-1\,f}$	
80T20E	2.52×10^{-2}	9.30×10^{-2}	
60T40E	3.58×10^{-3}	1.72×10^{-2}	
40T60E	5.50×10^{-4}	3.80×10^{-3}	1.38^{l}
70Tw	$4.33 \times 10^{-1\,d}$		
50T	$4.79 \times 10^{-1\,e}$		

[a] For abbreviation of solvents: A = acetone, E = ethanol, M = methanol, T = 2,2,2-trifluoroethanol. Figures shown are percentages of volume in water, and that with w denotes weight percent; 80T20E indicates T–E (80 : 20 v/v) and likewise for 60T40E and 40T60E. [b] Ref. 11. [c] From k (s^{-1}) = 5.58 $\times$ 10^{-2} (11 °C), 2.04 $\times$ 10^{-2} (1 °C). [d] From k (s^{-1}) = 9.36 $\times$ 10^{-2} (11 °C), 2.85 $\times$ 10^{-2} (1 °C). [e] From k (s^{-1}) = 1.13 $\times$ 10^{-1} (11 °C), 8.11 $\times$ 10^{-2} (8 °C), 3.66 $\times$ 10^{-2} (1 °C). [f] From k (s^{-1}) = 9.74 $\times$ 10^{-2} (4 °C), 4.73 $\times$ 10^{-2} (−3.5 °C), 3.33 $\times$ 10^{-2} (−7 °C). [g] Ref. 16. [h] From k (s^{-1}) = 8.50 $\times$ 10^{-2} (14.4 °C), 5.35 $\times$ 10^{-2} (10 °C), 1.77 $\times$ 10^{-2} (0 °C). [i] From k (s^{-1}) = 9.71 $\times$ 10^{-2} (−0.3 °C), 4.06 $\times$ 10^{-2} (−7.4 °C). [j] From k (s^{-1}) = 3.84 $\times$ 10^{-2} (−0.3 °C), 1.57 $\times$ 10^{-2} (−7.4 °C). [k] From k (s^{-1}) = 8.32 $\times$ 10^{-2} (10.6 °C), 4.40 $\times$ 10^{-2} (5.2 °C), 2.37 $\times$ 10^{-2} (0 °C), 1.25 $\times$ 10^{-2} (−5.1 °C). [l] From k (s^{-1}) = 1.63 $\times$ 10^{-1} (5.2 °C), 9.12 $\times$ 10^{-2} (0 °C), 4.72 $\times$ 10^{-2} (−5.1 °C), 3.63 $\times$ 10^{-2} (−7.4 °C).

Table 2 Correlation analyses against different Y and N

Substrate	Parameters	n	R	m	(s.d.)[a]	l (s.d.)[a]
1	Y_{Cl}	18	0.972	0.841	(0.051)	
	Y_{Cl}, N_{OTs}	15	0.975	0.780	(0.063)	0.022 (0.107)
	Y_{Cl}, N_T	17	0.968	0.891	(0.079)	0.129 (0.114)
	Y_{BnCl}	17	0.975	0.819	(0.049)	
	Y_{BnCl}, N_{OTs}	15	0.986	0.904	(0.056)	0.309 (0.094)
	Y_{BnCl}, N_T	17	0.984	0.935	(0.057)	0.239 (0.085)
3	Y_{Br}	16	0.961	0.756	(0.066)	
	Y_{Br}, N_{OTs}	14	0.964	0.705	(0.076)	0.031 (0.112)
	Y_{Br}, N_T	16	0.956	0.834	(0.092)	0.139 (0.114)
	Y_{BnBr}	16	0.983	0.870	(0.044)	
	Y_{BnBr}, N_{OTs}	14	0.994	0.973	(0.040)	0.254 (0.051)
	Y_{BnBr}, N_T	16	0.992	0.994	(0.043)	0.195 (0.048)
4	Y_{Cl}	8	0.848	0.840	(0.215)	
	Y_{Cl}, N_T	8	0.933	1.034	(0.178)	1.317 (0.543)
	Y_{BnCl}	8	0.994	1.083	(0.047)	

[a] Standard deviation.

present in the solvolysis of **1** and **3**, but absent in the case of **4**. Additional convincing evidence is desirable for assurance. The study of the azide salt effect has long been an useful tool to elucidate the nucleophilic character of reactions,[24] and has been successfully applied to the solvolysis of benzylic substrates.[15,18,25] So we compared the kinetic salt effects on the solvolysis of **1** and **4** induced by adding sodium perchlorate and sodium azide, respectively. The results are presented in Table 3.

Since the experimental error for titrimetric rate constants in the presence of azide ion, $k(NaN_3)$, is ±3%, the azide salt effect, $k(NaN_3)/k(NaClO_4)$, of 1.05 for **4** could be considered negligible. However, the significant rate increment due to the addition of sodium azide indicates a positive azide salt effect for **1** in 80% acetone.[26] Although this effect may be interpreted in different ways,[15,24] our previous result in the solvolytic study of secondary benzylic chlorides[18] suggests that it is consistent with the presence of a nucleophilically assisted process in the solvolysis of **1**. The observation of the common-ion effect led to the conclusion that concurrent uni- and bi-molecular mechanisms operated in the solvolysis of 4-methoxybenzyl bromide[11] and chloride.[15,16] However, a small common-ion effect had also been found in the solvolysis of *tert*-butyl chloride,[27] a system for which nucleophilic solvent participation was confirmed in a later study.[28] Consequently, the common-ion effect in solvolysis is not necessarily the outcome of limiting S$_N$1 mechanisms, and a reconsideration of its meaning seems to be needed.

The inconsistency between the amount of the azide product and the change in rate constants[24a] suggests the solvent intervention in the solvolysis of **1** is unlikely to be purely concerted S$_N$2 type, similar to the conclusion in the literature.[15] In the case of bromide **3**, no reproducible rate constant $k(NaN_3)$ could be obtained because no clear end point in the potentiometric titration had been obtained. Nevertheless, the relative significance of the nucleophilic solvent participation could be examined by other means. In the log $k - Y_{BnCl}$ and log $k - Y_{BnBr}$ plots (Figs. 1 and 2) the data points measured in nucleophilic solvents (aqueous acetone, ethanol and methanol, denoted as AEM) and those measured in isodielectric and poorly nucleophilic trifluoroethanol–ethanol mixtures (denoted as TE) are depicted in two split lines. The extent of deceleration for solvolysis in the poorly nucleophilic trifluoroethanol could then be estimated from the difference between the logarithm of the calculated k (●) from extrapolation of the AEM-line and that of the observed k (○). The significant deviation found in both cases is probably convincing evidence for the presence of nucleophilic solvent participation in the solvolyses. The smaller deviation for the bromide **3** (Δlog k = 0.722) than that for the chloride **1** (Δlog k = 1.26) reveals less nucleophilic participation and is in harmony with the greater nucleofugality of bromide ion.

The α-deuterium kinetic isotope effect (KIE) has widely been employed in the mechanistic study of substitution reactions for primary and secondary substrates.[29–31] A reaction with k_H/k_D close to or smaller than unity was considered to proceed with S$_N$2 mechanism or the like. Indeed, a "near limiting" mechanism for the solvolysis of 4-methylbenzyl chloride was concluded based on the observed α-D KIE of 1.08 to 1.15 per D,[11] whereas the solvolysis in the presence of azide ion gave very low KIE values, 0.996 to 1.004 per D, and supported the S$_N$2 processes.[10]

Table 3 Salt effects in the solvolysis of **1** and **4**

Substrate	[Salt]/M	$k(NaN_3)/s^{-1}$	$k(NaClO_4)/s^{-1}$	$k(NaN_3)/k(NaClO_4)$	RN$_3$ (%)[d]
1[a] (0.005 M)	0	$(6.71 \pm 0.02) \times 10^{-5\,c}$	$(6.71 \pm 0.02) \times 10^{-5\,c}$		
	0.02	$(7.63 \pm 0.08) \times 10^{-5}$	$(7.05 \pm 0.03) \times 10^{-5}$	1.08 ± 0.01	29.4
	0.04	$(9.71 \pm 0.09) \times 10^{-5}$	$(8.26 \pm 0.04) \times 10^{-5}$	1.18 ± 0.01	42.0
4[b] (0.005 M)	0	$(7.52 \pm 0.08) \times 10^{-4}$	$(7.52 \pm 0.08) \times 10^{-4}$		
	0.04	$(1.14 \pm 0.03) \times 10^{-3}$	$(1.09 \pm 0.02) \times 10^{-3}$	1.05 ± 0.03	

[a] In 80A at 25 °C. [b] In 90A at 10 °C. [c] From Table 1. [d] By titration (*cf.* ref. 25).

Table 4 α-Deuterium kinetic isotope effects in the solvolysis of **1** and **3**

Substrate	Solvent[a]	k (H)/s^{-1}	k (D)/s^{-1}	k (H)/k (D)
1, 1-d	90E	$(2.19 \pm 0.01) \times 10^{-4}$	$(2.00 \pm 0.02) \times 10^{-4}$	1.10 ± 0.01
	80A	$(6.71 \pm 0.02) \times 10^{-5}$	$(6.04 \pm 0.03) \times 10^{-5}$	1.11 ± 0.01
	100M	$(2.90 \pm 0.02) \times 10^{-4}$	$(2.49 \pm 0.02) \times 10^{-4}$	1.16 ± 0.01
	100T	$(2.04 \pm 0.01) \times 10^{-1}$	$(1.72 \pm 0.02) \times 10^{-4b}$	1.19 ± 0.01
	80T20E	$(2.52 \pm 0.02) \times 10^{-2}$	$(2.14 \pm 0.01) \times 10^{-2}$	1.18 ± 0.01
	40T60E	$(5.50 \pm 0.03) \times 10^{-4}$	$(4.86 \pm 0.02) \times 10^{-4}$	1.13 ± 0.01
	70Tw	$(4.33 \pm 0.02) \times 10^{-1}$	$(3.78 \pm 0.01) \times 10^{-1c}$	1.15 ± 0.01
	50T	$(4.79 \pm 0.03) \times 10^{-1}$	$(4.11 \pm 0.03) \times 10^{-1d}$	1.16 ± 0.01
3, 3-d	90E	$(2.27 \pm 0.02) \times 10^{-3}$	$(2.10 \pm 0.02) \times 10^{-3}$	1.08 ± 0.01
	80A	$(8.57 \pm 0.02) \times 10^{-4}$	$(7.85 \pm 0.02) \times 10^{-4}$	1.09 ± 0.00
	100M	$(3.25 \pm 0.02) \times 10^{-3}$	$(2.69 \pm 0.03) \times 10^{-3}$	1.21 ± 0.01
	80T20E	$(9.45 \pm 0.03) \times 10^{-2}$	$(8.02 \pm 0.02) \times 10^{-2}$	1.18 ± 0.01
	40T60E	$(3.80 \pm 0.02) \times 10^{-3}$	$(3.39 \pm 0.02) \times 10^{-3}$	$1,12 \pm 0.01$

[a] cf. Table 1 for abbreviations. [b] From k (s^{-1}) = 4.95 × 10^{-2} (11 °C), 1.88 × 10^{-2} (1 °C). [c] From k (s^{-1}) = 8.29 × 10^{-2} (11 °C), 2.55 × 10^{-2} (1 °C). [d] From k (s^{-1}) = 9.15 × 10^{-2} (11 °C), 2.85 × 10^{-2} (1 °C).

Table 5 Bromide/chloride rate ratios for **3** and **1**[a]

Solvent[b]	k_{Br}/k_{Cl}	Solvent[b]	k_{Br}/k_{Cl}	Solvent[b]	k_{Br}/k_{Cl}	Solvent[b]	k_{Br}/k_{Cl}
100E	14.1	90A	19.4	100M	11.4	100T	2.97
90E	10.5	80A	12.8	90M	9.39	80T20E	3.69
80E	8.35	70A	8.86	80M	7.39	60T40E	4.80
70E	7.04	60A	7.44			40T60E	6.91
60E	6.78						

[a] cf. Table 1 for rate constants. [b] cf. Table 1 for abbreviations.
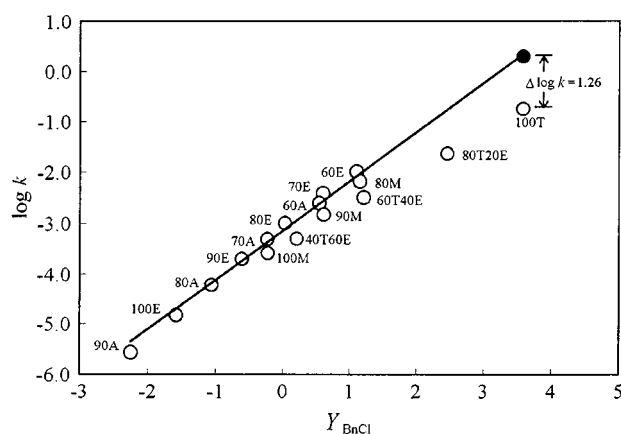
Fig. 1 Plots of log k for **1** against Y_{BnCl}
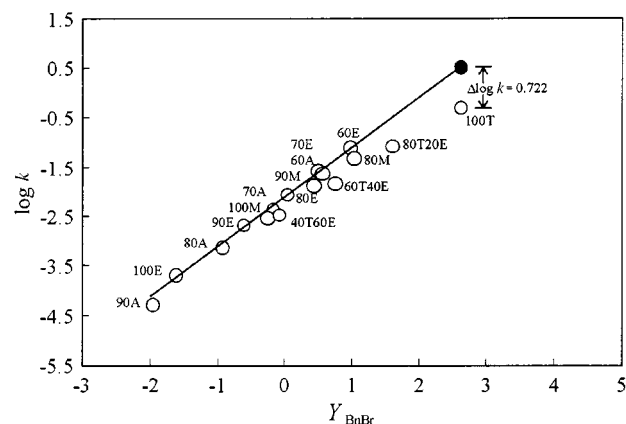
Fig. 2 Plots of log k for **3** against Y_{BnBr}

However, the solvolysis of 4-methoxybenzyl halides **1** and **3** was found "not limiting" in the present study. Thus, it would be expedient to study the effect of α-deuterium on the solvolytic reactivity in this system. The substrate pairs **1** and **1-**d and **3** and **3-**d, were solvolysed in a variety of solvents under identical conditions. The results are reported in Table 4. The observed

α-D KIE is in the range of 1.08 to 1.21, without any appreciable difference between those measured in highly nucleophilic or poorly nucleophilic solvents. Consequently, the magnitude of the α-D KIE might not be a suitable criterion for detecting the limiting mechanism of solvolysis as has long been proposed.

The bromide/chloride rate ratios in Table 5 are worthwhile discussing. In contrast to the generally suggested ratio of about 40,[32] considerably smaller and variable ratios in the solvolysis of **1** and **3** were realized. The solvolytic reactivity ratios of substituted benzyl bromides and chlorides in ethanol–trifluoroethanol mixtures have been studied.[33] The insensitivity of k_{Br}/k_{Cl} in ethanol to a change in ring substituent and the increasing sensitivity in a medium containing more trifluoroethanol was ascribed to differences in the disposition of bromine and chlorine to form hydrogen bonds.[33,34] In trifluoroethanol (100T) at 85 °C the ratio k_{Br}/k_{Cl} was 2.86 for 4-methylbenzyl halides and was 4.91 for unsubstituted benzyl halides.[33] From the data in Table 1 the rate ratio for **3/1** in 100T can be found as 2.97 at 25 °C. Table 5 shows that the k_{Br}/k_{Cl} ratio increases with diminishing trifluoroethanol or water content in the medium, up to about 20 as the limit. Better solvation of anions in water and in trifluoroethanol than in common organic solvents, and a better solvation for the chloride ion than the bromide ion could be deduced from free energies of transfer of ions.[35] The decreasing k_{Br}/k_{Cl} ratios can be attributed to the acceleration of **1** due to the better solvation of chloride ions in a solvent containing more water or trifluoroethanol. It is similar to the observed k_{OTs}/k_{Br} ratios for 1-aryl-2,2-dimethyl-1-propyl systems, and can be considered as another example for the significance of electrophilic pull in solvolysis.[36]

Furthermore, the low k_{Br}/k_{Cl} ratio, about 3 (100T) to 20 (90A), in Table 5 is probably a characteristic of the non-limiting solvolysis. Nucleophilic solvent participation would make the electrophilic solvation of the leaving halide ion at the transition state less important in governing the solvolytic reactivity, and hence give a smaller difference between k_{Br} and k_{Cl}. On the other hand, both 2-halo-2-[4-(trifluoromethyl)phenyl]adamantanes (**5**)[37,38] and 1-*tert*-butyl-1-halo-1-(4-methyl)phenylmethanes (**6**),[18,39] are known to solvolyze via a limiting S$_N$1 mechanism, and higher k_{Br}/k_{Cl} ratios, about 10 (100T) to 50 (80A) have been found in these systems (Table 6). It also reveals

Table 6 Pertinent bromide/chloride rate ratios for **5** and **6**[a]

|	**5**				**6**			
	Solvent[b]	k_{Br}/k_{Cl}	Solvent[b]	k_{Br}/k_{Cl}	Solvent[b]	k_{Br}/k_{Cl}	Solvent[b]	k_{Br}/k_{Cl}
	90E	31.7	100M	45.6	80E	33.3	90M	35.6
	80E	29.0	90M	28.8	70E	27.2	70M	30.2
	80A	50.6	100T	9.50	60E	25.8	100T	10.7
	70A	43.3	80T20E	11.4	70A	47.3	80T20E	12.1
	60A	32.0	40T60E	24.5	60A	39.6	60T40E	16.9

[a] *cf.* Refs. 16, 32–34 for rate constants. [b] *cf.* Table 1 for abbreviations.

Table 7 Correlation analyses against Y_X, N_T and I

Substrate	Parameters	n	R	m (s.d.)[a]	l (s.d.)[a]	h (s.d.)[a]
1	Y_{Cl}, N_T, I	14	0.987	0.923 (0.061)	0.244 (0.094)	0.830 (0.237)
3	Y_{Br}, N_T, I	13	0.982	0.870 (0.074)	0.232 (0.098)	0.800 (0.236)

[a] Standard deviation.

the similar trend of the variation of k_{Br}/k_{Cl} ratio with the composition of solvent mixtures for **5** and **6**. Further study of this subject is in progress.

5 X = Br, Cl   **6** X = Br, Cl
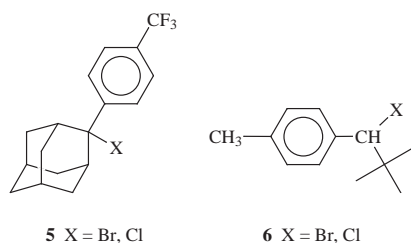
Lastly, Kevill and D'Souza recently proposed the use of a new term, aromatic ring parameter I, together with N_T and/or Y_X in eqns. (1) and (2) to examine the solvolytic behavior of benzylic substrates.[40] To study the nucleophilic solvent participation in benzylic solvolysis, a three-term equation [eqn. (3)] should be applied.

$$\log(k/k_o) = m Y_X + l N_T + h I \tag{3}$$

Among the drawbacks of such an approach,[41] a practical one is the need of sufficiently large number of experimental data for a reliable analysis. For example, an excellent correlation ($R = 0.996$) was found in the case of **1** if rate data in 28 solvents were used.[14c] However, with the rate data in Table 1, regression analyses using eqn. (3) could be carried out with only 13 (for **3**) or 14 (for **1**) data points.[42] Table 7 indicates similar results for the chloride **1** ($R = 0.987$), but a less satisfactory correlation for the bromide **3** ($R = 0.982$) as compared with those derived from eqn. (1) ($R = 0.994$ in Table 2). It could be considered as an additional example to illustrate the advantage of using the two-term equation [eqn. (1)] rather than the three-term equation [eqn. (3)].

Conclusions

From the present study we may conclude the presence of nucleophilic solvent participation in the solvolysis of 4-methoxybenzyl chloride (**1**) and bromide (**3**) from the regression analyses using the dual-parameter Grunwald–Winstein equation [eqn. (1)] with Y_{BnX} and N_{OTs} or N_T, and also from the observed positive azide salt effect. The smaller deviation of log k(100T) for the bromide **3** than chloride **1** in the log k − Y_{BnX} plots reveals less nucleophilic participation and is in harmony with the greater nucleofugality of bromide ion. The α-deuterium kinetic isotope effect of 1.08 to 1.21 measured for

1 and **3** is inconsistent with the magnitude generally observed for a concerted mechanism. Therefore, it might not be a suitable criterion for detecting the limiting mechanism of solvolysis.

Experimental

General
Proton and carbon-13 NMR spectra were recorded on a Bruker Model AC-200 instrument. IR spectra were measured on a Perkin-Elmer Model 983G spectrometer.

Materials
Commercially available spectral-grade or reagent-grade solvents were used directly for preparative purposes. They were purified following conventional methods[43] for kinetic studies. Doubly deionised water was used to prepare aqueous solvent mixtures for solvolysis. Halides **1** and **3** were prepared from the reaction of 4-methoxybenzyl alcohol (Aldrich) with thionyl chloride and phosphorus tribromide, respectively. 1-(4-Methoxyphenyl)ethyl chloride (**4**) was obtained as previously described.[18] Sodium borodeuteride reduction of 4-methoxybenzaldehyde yielded 4-methoxybenzyl-α-*d* alcohol, which was then transformed into **1**-*d* and **3**-*d*, respectively. Their IR and NMR spectra were found to be in harmony with the assigned structures.

Kinetic measurements
Conductimetric rate constants were measured at least in duplicate for general solvolytic studies. The conductivity cells containing solutions of 1×10^{-4} to 1×10^{-5} M were placed in a thermostat with a temperature variation of ±0.02 °C. A small amount (*ca.* 0.1%) of 2,6-dimethylpyridine was added to the solution in some cases to prevent curvature of the rate constant plot. Different cells were used for those runs for substrates in same solvent and at same temperature. The maximum error of k is ±2%. For the study of kinetic isotope effect, the solvolysis of the isotopic pairs were run side-by-side in the same thermostat. The potentiometric titration method was used for studying the salt effect. In the latter case, the concentration of substrate was 0.005 M. The maximum error of k(NaN₃) is ±3%.

Rate constants monitored at other temperatures were extrapolated to those at 25 °C by using Arrhenius plot. (See footnotes in Tables 1, 3 and 4.)

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