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Concerning the Extents of Nucleophilic Participation in Solvolyses of *p*-Methoxybenzyl Halides†

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The solvolyses of *p*-methoxybenzyl chloride (**1**) in 39 solvents are well correlated using an extended form of the Grunwald–Winstein equation; a claim that nucleophilic participation is greater than in the solvolyses of the corresponding bromide **2** is discussed.

The solvolyses of *p*-methoxybenzyl chloride (**1**) have been among the most extensively studied.[1–6] Using literature data,[5] we have previously applied the three-term form of the extended Grunwald–Winstein equation [eqn. (1)] and have found an appreciable sensitivity towards changes in all of the three variables involved (Table 1). In eqn. (1), k and k_0 are the specific rates of solvolysis in a given solvent and in 80% ethanol, respectively; l is the sensitivity to changes in solvent nucleophilicity (N_T);[7,8] m is the sensitivity to changes in solvent ionizing power (Y_{Cl});[9] h is the sensitivity to changes in the aromatic ring parameter (I);[3] and c is a constant (residual) term. It was emphasised that the results should be treated with caution because solvolysis in only one fluoroalcohol-containing solvent was included in the 27-solvent data set.

$$\log(k/k_0) = lN_T + mY_{Cl} + hI + c \qquad (1)$$

Recently, a study of the specific rates of solvolysis has been presented[2] involving 14 additional solvents containing 2,2,2-trifluoroethanol (TFE), and the data for the twelve for which N_T, Y_{Cl} and I values are all available have been added to the previous analyses (Table 1 and Fig. 1).

Accompanying the new data[2] was a comparison of the specific rates of solvolysis in 40% ethanol and 97% TFE (k_{40E}/k_{97T}), two solvents differing by only 0.08 Y_{Cl} units but by 2.56 N_T units. For solvolyses of 1-adamantyl chloride, the ratio has a value of 0.83 and for solvolyses involving nucleophilic participation the ratio will tend to increase in value. This treatment, however, neglects effects associated with the aromatic ring parameter and, accordingly, values *lower* than 0.83 were observed for **1** (0.70) and for benzhydryl chloride (0.18). We can make a rough approximation, based on previous analyses,[3,10] of an h value of about one for each aromatic ring capable of entering into conjugation during ionisation.

Coupled with the difference in I values of 0.74, we can estimate that the lower limits ($l = 0$) for the k_{40E}/k_{97T} ratios will be 0.15 and 0.03, respectively, suggesting a measure of nucleophilic participation by the solvent, and consistent with the l values of 0.25 ± 0.06 for **1** (Table 1) and 0.30 ± 0.07 for benzhydryl chloride.[3]

Liu *et al.*[1] have duplicated many of the new measurements and have also determined specific rates for solvolyses of the corresponding bromide, *p*-methoxybenzyl bromide (**2**), in 16 solvents, including TFE and TFE-ethanol mixtures. Analyses were carried out using eqn. (1) and essentially identical l, m and h values were obtained for solvolyses of **1** and **2** (last two entries of Table 1). The sensitivities obtained for the solvolyses of **1** are very similar, irrespective of whether 14, 27 or 39 data points are incorporated, suggesting a very robust data set.[11]

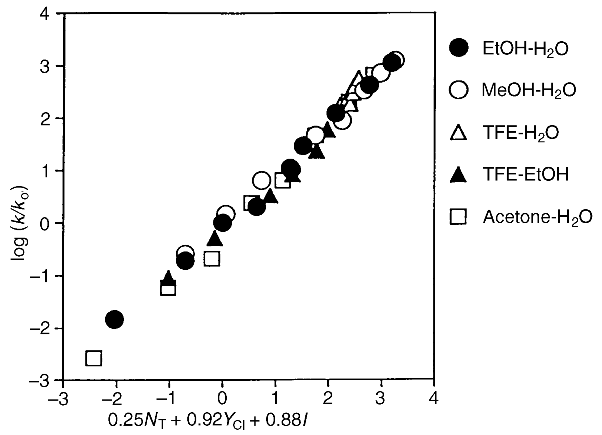
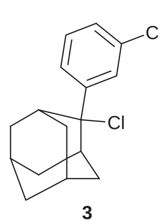


Fig. 1 Plot of $\log(k/k_0)$ for solvolyses of *p*-methoxybenzyl chloride at 25.0 °C against ($0.25N_T + 0.92Y_{Cl} + 0.88I$)

In view of the close similarity of the two correlations, it is surprising that one of the major conclusions drawn from the study[1] was that there was more nucleophilic participation during solvolyses of **1** than during solvolyses of **2**. This was based on an application of Y_{BnX} scales[12] to the $\log(k/k_0)$ values. In particular, the deviations of the 100% TFE point from the correlation against Y_{BnX} were investigated, with a smaller deviation for **2** than for **1**.

A major problem with this approach is that the substrates used to establish the Y_{BnCl} scale (compound **3**) and the Y_{BnBr} scale (compound **4**) are themselves not very similar. The h/m ratios should match for solvolyses of one substrate to be considered a good similarity model for solvolyses of a second,[3] and values have been reported[3,13] of 1.83 ± 0.30 for **3** and 1.32 ± 0.17 for **4**. The use of Y_{BnCl} as a similarity model for the solvolyses of **1** will seriously overestimate the importance of the hI term, leading[3] to an apparent, and spurious, increase in the l value. When



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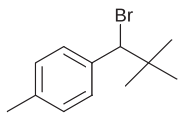

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Table 1 Correlation of the specific rates of solvolysis of *p*-methoxybenzyl chloride (**1**) at 25.0 °C using the Grunwald–Winstein approach and various combinations of N_T, Y_{Cl}, and I parameters.[a,b]

n^c	l^d	m^d	h^d	c^e	R^f	F^g
39		0.80 ± 0.02		-0.11 ± 0.26	0.9842	1144
	-0.03 ± 0.07 $(0.64)^h$	0.79 ± 0.03		-0.12 ± 0.27	0.9843	560
		0.82 ± 0.02	0.53 ± 0.11	-0.17 ± 0.21	0.9902	902
	0.25 ± 0.06	0.92 ± 0.03	0.88 ± 0.13	-0.11 ± 0.18	0.9934	874
27^i	0.30 ± 0.05	0.93 ± 0.02	1.26 ± 0.13	-0.06 ± 0.13	0.9968	1188
14^j	0.24 ± 0.09	0.92 ± 0.06	0.83 ± 0.24		0.987	
$13^{j,k}$	0.23 ± 0.10	0.87 ± 0.07	0.80 ± 0.24		0.982	

[a] Data from refs. 1 and 5. [b] Including the terms of eqn. (1) as indicated by the sensitivities reported. [c] Number of solvents. [d] With associated standard errors. [e] Accompanied by the standard error of the estimate. [f] Correlation coefficient. [g] *F*-test value. [h] Probability that the contribution to the linear free energy relationship is insignificant (recorded when > 0.005). [i] From ref. 3. [j] From ref. 1. [k] For *p*-methoxybenzyl bromide (**2**).

the extents of nucleophilic participation by the solvent are approximately equal, use of the Y_{BnBr} scale will result in a smaller l value, reflected in turn in a smaller deviation for the 100% TFE point.

While **3** has a negligible l value (0.05 ± 0.10) for its solvolyses,[13] an l value of 0.17 ± 0.06 has been reported[13] for solvolyses of **4** and it has, at a reduced level, the same defects[9,14] as *tert*-butyl chloride, the substrate used for the original Y scale.[15] Accordingly, use of Y_{BnBr} in conjunction with N_T will lead to anomalously low l values. Since the l values (and the resultant deviations in plots against Y_{BnX} values) are anomalously large for chlorides and anomalously small for bromides, there is the illusion of a larger degree of nucleophilic participation for the solvolyses of the chloride.

Liu *et al.*[1] reported α-deuterium isotope effects for solvolyses of **1** and **2** in the range of 1.08 to 1.21 per deuterium, exactly the values to be expected[16] for a limiting or near limiting solvolysis. This is nicely consistent with the proposal[3] that the nucleophilic assistance within the solvolyses of **1** and **2** involves a solvation of the developing carbocation, rather than a process involving appreciable covalent attachment, for which lower values would be anticipated.

Experimental

The simple and multiple regression analyses were carried out using the ABSTAT statistical package (Anderson-Bell, Arvada, Colorado, USA).

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