Solvolysis of *tert*-Butyl(2-naphthyl)methyl and Some Benzhydryl Bromides. A New *Y* Scale for Benzylic Bromides with Extended Charge Delocalisation†

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The necessity of establishing a new Y_{xBnBr} scale based on log k values for *tert*-butyl(2-naphthyl)methyl bromide is demonstrated by the results of correlation analysis of solvolytic reactivities of benzhydryl bromides and 4-nitrobenzhydryl bromide.

Single- or dual-parameter Grunwald–Winstein equations [eqns. (1)[1] or (2)[2]] have been widely employed in the correlation study of solvolytic mechanisms. The sensitivity to changes in solvent ionising power *Y* and in nucleophilicity *N* is measured by the coefficients *m* and *l*, respectively. Our recent studies on the solvolysis of a number of secondary and tertiary benzylic substrates led to the development of several new Y_{BnX} scales[3] for correlation analyses of solvent effects. Later work on the solvolysis of *tert*-butyl(2-naphthyl)methyl[4,5] and diarylmethyl[5] systems suggested the necessity of using an additional reference standard for correlating the reactivities of systems with extended charge delocalisation over a naphthalene ring or two phenyl rings at the transition state. On the other hand, Kevill and co-workers proposed retention of the use of Y_X by adding a term, an aromatic ring parameter *I*, to the original Grunwald–Winstein equations to derive eqns. (3) and (4), instead of using Y_{BnX} with the simpler eqns.

(1) or (2).[6,7] More recently, they applied our published data in a preliminary report[5] to argue the advantage of using eqns. (3) and (4).[8]

$$\log (k/k_0) = mY \tag{1}$$

$$\log (k/k_0) = mY + lN \tag{2}$$
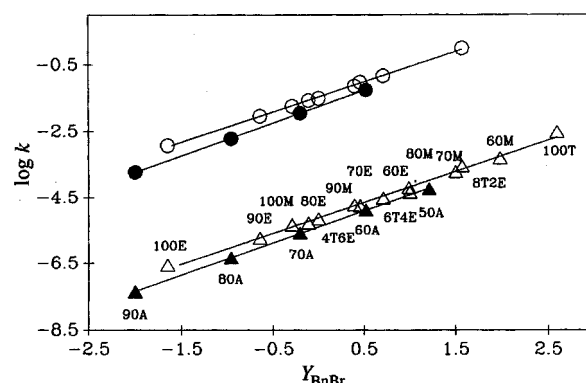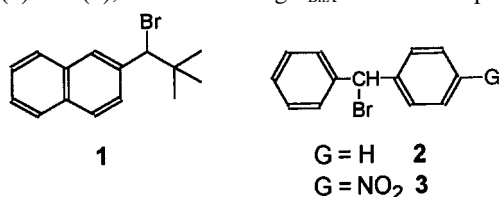
$$\log (k/k_0) = mY + hI \tag{3}$$

Fig. 1 Correlations of log *k* for **1** (△) and **2** (○) against Y_{BnBr}: solid symbols denote values of *k* measured in aqueous acetone

Table 1 Y_{xBnBr} values and solvolysis rate constants for bromides **1–3**

| Solvent[a]	*k*/s (25 °C)			Y_{xBnBr}[b]
	1	**2**	**3**	
100E	2.79×10^{-7c}	1.20×10^{-3}		-1.40
90E	1.83×10^{-6c}	8.86×10^{-3}	7.80×10^{-6c}	-0.585
80E	7.03×10^{-6c}	3.04×10^{-2}	2.63×10^{-5}	0.00
70E	1.74×10^{-5}	9.27×10^{-2}	6.39×10^{-5}	0.394
60E	4.52×10^{-5}		1.60×10^{-4}	0.808
90A	4.40×10^{-8c}	1.88×10^{-4}		-2.20
80A	4.63×10^{-7c}	1.91×10^{-3}	$3.33 \times 10^{-6c,d}$	-1.18
70A	2.63×10^{-6c}	1.11×10^{-2}	1.15×10^{-5}	-0.427
60A	1.30×10^{-5c}	5.45×10^{-2}	4.42×10^{-5}	0.267
50A	5.74×10^{-5}		1.62×10^{-4}	0.912
100M	4.66×10^{-6c}	1.76×10^{-2}	1.14×10^{-5}	-0.179
90M	1.84×10^{-5}	7.15×10^{-2}	4.49×10^{-5}	0.418
80M	6.15×10^{-5}		1.40×10^{-4}	0.942
70M	1.90×10^{-4}			1.43
60M	4.81×10^{-4}		9.62×10^{-4}	1.84
100T	2.92×10^{-3}		2.89×10^{-4}	2.62
80T20E	2.78×10^{-4}	9.75×10^{-1c}	9.92×10^{-5}	1.60
60T40E	3.01×10^{-5}	1.43×10^{-1}	3.23×10^{-5}	0.632
40T60E	5.32×10^{-6}	2.64×10^{-2}		-0.121

[a]E = ethanol, A = acetone, M = methanol, T = 2,2,2-trifluoroethanol. Figures shown are percentages v/v in water; 80T20E indicates T–E (80 : 20 v/v) (likewise for 60T40E and 40T60E). [b]Based on **1**. [c]From data measured at other temperatures. [d]Calculated from literature values (E. A. Jeffery, R. K. Bansal, L. J. Andrews and R. M. Keefer, *J. Org. Chem.*, 1964, **29**, 3365).

$$\log (k/k_0) = mY + lN + hI \tag{4}$$

However, deficiencies in the use of eqns. (3) or (4) have already been pointed out.[9] In this paper more rate data for *tert*-butyl(2-naphthyl)methyl   bromide   (**1**),   benzhydryl
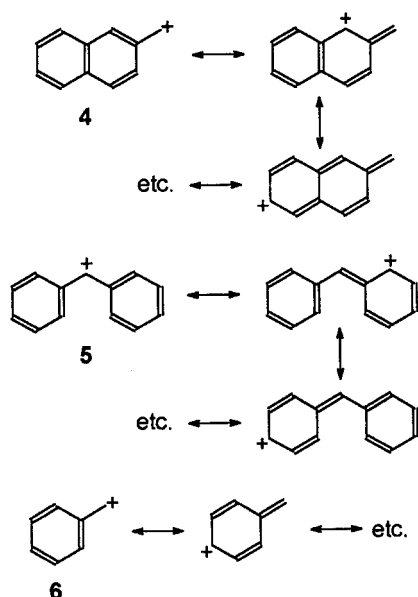
azide salt effect, the depression of data points corresponding to the k measured in ethanol–2,2,2-trifluoroethanol, and the more negative ρ value found in less nucleophilic solvents. The regression using eqn. (2) with Y_{xBnBr} and N_T, or using eqn. (4) with Y_{Br}, N_T and I only gave correlations with $R = 0.96$. It is remarkable that the use of eqn. (2) with Y_{BnBr} and N_T yielded linear correlations with $R = 0.988$. It is likely that in the benzhydryl bromide containing a strong deactivating substituent, such as 4-NO$_2$, the positive charge delocalises mainly over the unsubstituted phenyl ring in the cationic transition state, and thus Y_{BnBr}, not Y_{xBnBr}, is the choice for the correlation analysis.

In conclusion, the present work demonstrates the necessity of establishing a new Y_{xBnBr} scale, and the advantage of employing this and the Y_{BnBr} scales in the correlation analysis of solvolytic reactivities in order to have a better understanding of mechanisms.

Experimental

Bromides **1–3** were prepared by treatment of the corresponding alcohols with phosphorus tribromide in carbon tetrachloride. Spectral data, IR, proton and carbon NMR, are in line with the pro-

Table 2 Correlation analyses of log k for bromides **2** and **3**

Substrate	Parameters	n	R	m (σ)[a]	l (σ)	h (σ)
2	Y_{xBnBr}	13	0.999	0.993 (0.015)		
	Y_{Br}, I	11	0.978	0.661 (0.056)		1.28 (0.21)
	Y_{Br}, N_T, I	11	0.995	0.861 (0.051)	0.475 (0.098)	1.55 (0.11)
3	Y_{xBnBr}	15	0.906	0.611 (0.081)		
	Y_{xBnBr}, N_T	15	0.966	0.833 (0.078)	0.301 (0.073)	
	Y_{BnBr}, N_T	15	0.988	0.860 (0.043)	0.310 (0.040)	
	Y_{Br}, I	14	0.880	0.532 (0.087)		0.25 (0.29)
	Y_{Br}, N_T, I	14	0.958	0.779 (0.081)	0.362 (0.087)	0.71 (0.21)

[a]Standard deviation.

bromide (**2**) and 4-nitrobenzhydryl bromide (**3**) are reported, and a further example is provided to illustrate the drawback of incorporating hI term in the correlation analysis.

Bromides **1–3** were prepared by the conventional method from the corresponding alcohols. First-order solvolysis rate constants are listed in Table 1. Regression analyses of log k values against Y_{Br}[10] gave only poor correlations (correlation coefficient $R < 0.90$). With Y_{BrBr},[3] although both **1** and **3** yielded fairly good correlations ($R = 0.991$ and 0.988, respectively), obvious deviations for the data points measured in aqueous acetone in the log k vs. Y_{BnBr} plots were realized (Fig. 1). Statistical analysis[11] indicated the separation of two lines, those for aqueous acetone vs. those for all others, with a confidence level of $> 99\%$. The resemblance of the extent of charge delocalisation at the cationic transition state for the *tert*-butyl(2-napthyl)methyl cation (**4**) and benzhydryl cation (**5**), which are different from the benzyl cation (**6**), suggested the necessity of developing a new Y scale for accommodating the solvation of an extended delocalised system. Therefore, Y_{xBnBr}, was established based on the logarithms of the solvolytic rate constants for **1**.

Compilations of the results of regression analyses using different equations are shown in Table 2, in which N_T values[12] were used for the nucleophilicity term. Excellent linear correlations were found for **2** in eqn. (1) against Y_{xBnBr} ($R = 0.998$). No apparent deviation from linearity was noted. The corresponding m value of 0.996 indicated a limiting S$_N$1 mechanism for the solvolysis of **2**. The application of eqn. (3) gave a less satisfactory result ($R = 0.978$). Although the addition of an N_T term [eqn. (4)] also yielded an excellent linear relationship ($R = 0.995$), the unreasonable large l value (0.475), however, suggested that the result would be misleading and was likely to be an artifact. Consequently, the multiparameter eqn. (4) should be used with caution.

In the case of **3**, neither eqn. (1) with Y_{BnBr} or Y_{xBnBr} nor eqn. (3) showed good correlations. A non-limiting S$_N$1 mechanism has already been proposed[5] based on the observation of an

posed structure in all cases. The new compound **1**, mp 88–88.5 °C, had a correct elemental analysis (Found: C, 65.08; H, 6.45. C$_{15}$H$_{17}$Br requires C, 64.99; H, 6.18%).

Standard purification procedures[13] were employed to purified solvents for kinetic studies. The first-order rate constants were measured, at least in duplicate, conductimetrically to an accuracy of $\pm 2\%$.

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