

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

*J. Chem. Research (S)*,  
1997, 18–19†

Kwang-Ting Liu,\* Chien-Pu Chin, Yen-Shyi Lin and Meng-Lin Tsao

Department of Chemistry, National Taiwan University, Taipei, Taiwan 107, Republic of China

The necessity of establishing a new  $Y_{\text{xBnBr}}$  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)<sup>1</sup> or (2)<sup>2</sup>] 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  $Y_{\text{BnX}}$  scales<sup>3</sup> for correlation analyses of solvent effects. Later work on the solvolysis of *tert*-butyl(2-naphthyl)methyl<sup>4,5</sup> and diarylmethyl<sup>5</sup> 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  $Y_{\text{x}}$  by adding a term, an aromatic ring parameter  $I$ , to the original Grunwald–Winstein equations to derive eqns. (3) and (4), instead of using  $Y_{\text{BnX}}$  with the simpler eqns.

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

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

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

$$\log(k/k_0) = mY + hI \quad (3)$$

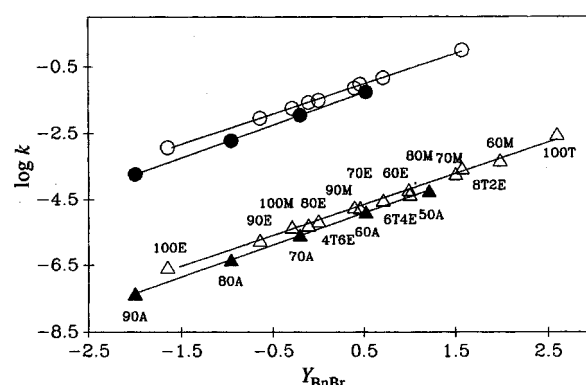
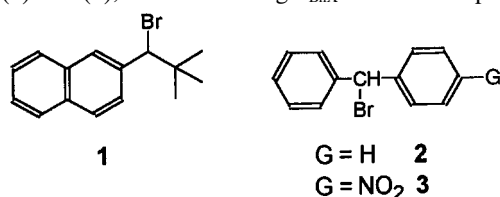


Fig. 1 Correlations of  $\log k$  for **1** ( $\Delta$ ) and **2** ( $\circ$ ) against  $Y_{\text{BnBr}}$ : solid symbols denote values of  $k$  measured in aqueous acetone

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

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

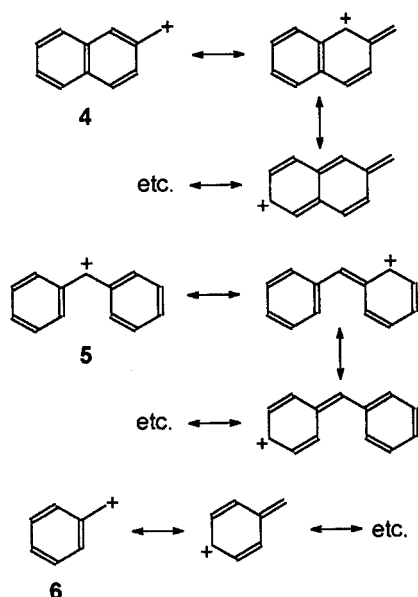
<sup>a</sup>E = ethanol, A = acetone, M = methanol, T = 2,2,2-trifluoroethanol. Figures shown are percentages v/v in water; 80T20E indicates T–E (80 : 20 v/v) (likewise for 60T40E and 40T60E). <sup>b</sup>Based on **1**. <sup>c</sup>From data measured at other temperatures. <sup>d</sup>Calculated from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

\*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

$$\log(k/k_0) = mY + lN + hI \quad (4)$$

However, deficiencies in the use of eqns. (3) or (4) have already been pointed out.<sup>9</sup> 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  $\rho$  value found in less nucleophilic solvents. The regression using eqn. (2) with  $Y_{\text{xBnBr}}$  and  $N_{\text{T}}$ , or using eqn. (4) with  $Y_{\text{Br}}$ ,  $N_{\text{T}}$  and  $I$  only gave correlations with  $R = 0.96$ . It is remarkable that the use of eqn. (2) with  $Y_{\text{BnBr}}$  and  $N_{\text{T}}$  yielded linear correlations with  $R = 0.988$ . It is likely that in the benzhydryl bromide containing a strong deactivating substituent, such as 4- $\text{NO}_2$ , the positive charge delocalises mainly over the unsubstituted phenyl ring in the cationic transition state, and thus  $Y_{\text{BnBr}}$ , not  $Y_{\text{xBnBr}}$ , is the choice for the correlation analysis.

In conclusion, the present work demonstrates the necessity of establishing a new  $Y_{\text{xBnBr}}$  scale, and the advantage of employing this and the  $Y_{\text{BnBr}}$  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	$n$	$R$	$m$ ( $\sigma$ ) <sup>a</sup>	$I$ ( $\sigma$ )	$h$ ( $\sigma$ )
2	$Y_{\text{xBnBr}}$	13	0.999	0.993 (0.015)		
	$Y_{\text{Br}}$ /	11	0.978	0.661 (0.056)		1.28 (0.21)
	$Y_{\text{Br}}$ $N_{\text{T}}$ /	11	0.995	0.861 (0.051)	0.475 (0.098)	1.55 (0.11)
3	$Y_{\text{xBnBr}}$	15	0.906	0.611 (0.081)		
	$Y_{\text{xBnBr}}$ $N_{\text{T}}$	15	0.966	0.833 (0.078)	0.301 (0.073)	
	$Y_{\text{BnBr}}$ $N_{\text{T}}$	15	0.988	0.860 (0.043)	0.310 (0.040)	
	$Y_{\text{Br}}$ /	14	0.880	0.532 (0.087)		0.25 (0.29)
	$Y_{\text{Br}}$ $N_{\text{T}}$ /	14	0.958	0.779 (0.081)	0.362 (0.087)	0.71 (0.21)

<sup>a</sup>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  $Y_{\text{Br}}$ <sup>10</sup> gave only poor correlations (correlation coefficient  $R < 0.90$ ). With  $Y_{\text{BnBr}}$ ,<sup>3</sup> 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.  $Y_{\text{BnBr}}$  plots were realized (Fig. 1). Statistical analysis<sup>11</sup> 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-naphthyl)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,  $Y_{\text{xBnBr}}$  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  $N_{\text{T}}$  values<sup>12</sup> were used for the nucleophilicity term. Excellent linear correlations were found for 2 in eqn. (1) against  $Y_{\text{xBnBr}}$  ( $R = 0.998$ ). No apparent deviation from linearity was noted. The corresponding  $m$  value of 0.996 indicated a limiting  $S_{\text{N}}1$  mechanism for the solvolysis of 2. The application of eqn. (3) gave a less satisfactory result ( $R = 0.978$ ). Although the addition of an  $N_{\text{T}}$  term [eqn. (4)] also yielded an excellent linear relationship ( $R = 0.995$ ), the unreasonable large  $I$  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  $Y_{\text{BnBr}}$  or  $Y_{\text{xBnBr}}$  nor eqn. (3) showed good correlations. A non-limiting  $S_{\text{N}}1$  mechanism has already been proposed<sup>5</sup> 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.  $\text{C}_{15}\text{H}_{17}\text{Br}$  requires C, 64.99; H, 6.18%).

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

Financial support from the National Science Council, Republic of China, is gratefully acknowledged.

Received, 23rd August 1996; Accepted, 4th October 1996  
Paper E/6/05861B

### References

- E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 1948, **70**, 846.
- S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, 1951, **73**, 2700.
- K.-T. Liu, *J. Chin. Chem. Soc.*, 1995, **42**, 607, and references cited therein.
- K.-T. Liu, H.-Y. Hsu and J.-S. Yang, *Tetrahedron Lett.*, 1992, **33**, 3327.
- K.-T. Liu, C.-P. Chin, Y.-S. Lin and M.-L. Tsao, *Tetrahedron Lett.*, 1995, **36**, 6919.
- D. N. Kevill, N. HJ. Ismail and M. J. D'Souza, *J. Org. Chem.*, 1994, **59**, 6303.
- D. N. Kevill and M. J. D'Souza, *J. Chem. Soc., Perkin Trans. 2*, 1995, 973.
- D. N. Kevill and M. J. D'Souza, *J. Chem. Res.*, 1996, (S) 286; (M) 1649.
- K.-T. Liu, *J. Chem. Soc., Perkin Trans. 2*, 1996, 327.
- T. W. Bentley and G. Llewellyn, *Progr. Phys. Org. Chem.*, 1990, **17**, 121.
- J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, Wiley, New York, 2nd edn., 1988, ch. 3.
- (a) D. N. Kevill and S. W. Anderson, *J. Chem. Res. (S)*, 1991, 356; (b) D. N. Kevill and M. J. D'Souza, *J. Chem. Res. (S)*, 1993, 174.
- D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, New York, 3rd edn., 1988.