PERKIN 2

Comments on the utility of aromatic ring parameters in the correlation analysis of solvolytic reactivities for benzylic substrates

Kwang-Ting Liu

Department of Chemistry, National Taiwan University, Taipei 107, Taiwan, Republic of China
and
Department of Chemistry, National Central University, Chung-Li 320, Taiwan, Republic of China

The inclusion of the recently proposed aromatic ring parameter I with solvent ionizing power Y_X in Grunwald–Winstein correlation analyses of benzylic reactivities has been found to have several deficiencies and to be less informative in the understanding of solvolytic mechanisms than the use of Y_BnX alone.

Correlation analyses with single- or dual-parameter Grunwald–Winstein equations [eqns. (1)[1] or (2)[2]] have widely been used

$$\log(k/k_\mathrm{o}) = mY \tag{1}$$

$$\log(k/k_\mathrm{o}) = mY + lN \tag{2}$$

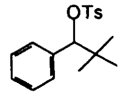
in the study of solvolytic mechanisms. The coefficients m and l are a measure of the sensitivity to the change in solvent ionizing power Y and in nucleophilicity N, respectively. The leaving group-dependent Y_x values[3] had been found to show dispersion in $\log k - Y_\mathrm{x}$ plots for benzylic substrates and thus new Y_BnX scales for benzylic bromides,[4] chlorides,[5] 4-nitrobenzoates[6] and tosylates†[7] were established[8] to take the solvation of the delocalized cationic transition state into consideration. Certain advantages, such as the detection of nucleophilic solvent intervention in the solvolysis of tertiary benzylic systems[9–11] were realised by employing new Y_BnX scales for correlation studies.

On the other hand, the necessity of Y_BnX scales was questioned by Kevill and D'Souza.[12,13] Recently, a new term, aromatic ring parameter I, was proposed to add to the original Grunwald–Winstein equations to adjust the observed dispersion [eqns. (3) and (4)].[14] Moreover, they used literature rate

$$\log(k/k_\mathrm{o}) = mY + hI \tag{3}$$

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

constants[4–7,9–11,15] for a number of secondary and tertiary benzylic substrates (**1–13**) in correlation analyses employing eqns. (3) and (4), and emphasized the utility of the parameter I.[16] However, several drawbacks in that approach have been overlooked and will be discussed in the present communication.



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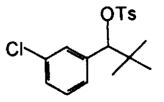

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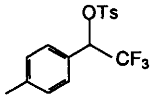

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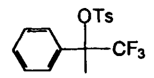

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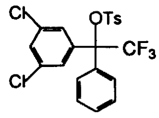

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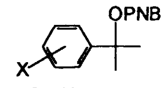
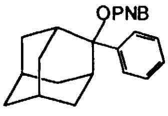


6a X = 4 - MeS
6b X = 4 - Me
6c X = 2 - Me
6d X = H



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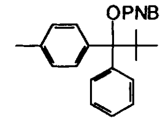

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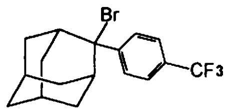

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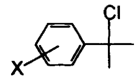
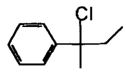


10a X = 2-Me
10b X = 3-Cl
10c X = 4-CF$_3$
10d X = H



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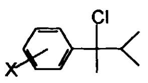
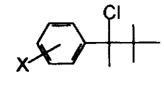


12a X = H
12b X = 3-Cl



13a X = H
13b X = 4-Me
13c X = 3, 4-(Me)$_2$

Comparison of the results of correlation analyses for five tosylates [α-*tert*-butylbenzyl tosylate **1**, α-*tert*-butyl-3-chlorobenzyl tosylate **2**, α-trifluoromethyl-4-methylbenzyl tosylate **3**, α-methyl-α-trifluoromethylbenzyl tosylate **4** and α-(3,5-dichlorophenyl)-α-trifluoromethylbenzyl tosylate **5**], six 4-nitrobenzoates [4-methylsulfanyl-, 4-methyl-, 2-methyl- and unsubstituted α,α-dimethylbenzyl 4-nitrobenzoates **6a–d**, 2-phenyl-2-adamantyl 4-nitrobenzoate **7** and α-*tert*-butyl-α-phenyl-4-methylbenzyl 4-nitrobenzoate **8**], 2-bromo-2-(4-trifluoromethylphenyl)adamantane **9** and 10 chlorides [2-methyl-, unsubstituted, 3-chloro- and 4-trifluoromethyl-α,α-dimethylbenzyl chlorides **10a–d**, α-ethyl-α-methylbenzyl chloride **11**, α-isopropyl-α-methylbenzyl and α-isopropyl-α-methyl-3-chlorobenzyl chlorides **12a** and **b**, α-*tert*-butyl-α,3,4-trimethylbenzyl, α-*tert*-butyl-α,4-dimethylbenzyl, and α-*tert*-butyl-α-methylbenzyl chlorides **13a–c**] using eqns. (1) and (3) are given in Table 1. An obvious drawback in using eqn. (3)

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† IUPAC nomenclature: tosylate = toluene-4-sulfonate.

Table 1 Comparison of correlation analyses of solvolytic reactivities using Grunwald–Winstein type eqns. (1) and (3)

	Eqn. (1) with Y_{BnX}[a]		Eqn. (3) with Y_X and I[b]		
Substrate	m	R	m	h	R
1	*c*		0.93	0.76 ± 0.08	0.997
2	0.979	0.999	0.91	0.59 ± 0.11	0.995
3	0.999	0.992	0.80	1.10 ± 0.27	0.988
4	0.964	0.996	0.85	0.86 ± 0.19	0.993
5	1.06	0.994	0.88	1.46 ± 0.24	0.993
6a	0.722	0.998	0.79	0.82 ± 0.07	0.998
6b	0.784	0.996	0.87	0.81 ± 0.09	0.997
6c	0.704	0.996	0.82	0.74 ± 0.09	0.996
6d	0.657	0.957	0.80	0.23 ± 0.18	0.983
7	*d*		1.03	1.32 ± 0.11	0.997
8	0.865	0.995	0.88	1.34 ± 0.17	0.997
9[e]	*f*		0.79	1.01 ± 0.15	0.991
10a	0.767	0.991	0.68	0.78 ± 0.12	0.995
10b	0.649	0.972	0.66	0.36 ± 0.23	0.982
10c	0.616	0.972	0.61	0.50 ± 0.34	0.975
10d	0.772	0.986	0.71	0.58 ± 0.28	0.989
11	0.818	0.990	0.75	0.70 ± 0.18	0.993
12a	0.852	0.994	0.74	0.94 ± 0.09	0.998
12b	0.760	0.991	0.71	0.85 ± 0.20	0.987
13a	0.748	0.987	0.79	0.80 ± 0.15	0.991
13b	0.887	0.997	0.86	1.10 ± 0.14	0.992
13c	0.954	0.997	0.82	1.33 ± 0.09	0.995

[a] From the literature: **1–5**, ref. 7; **6**, ref. 10; **7** and **8**, ref. 6; **9**, ref. 8; **10a**, ref. 15; **10b–d**, ref. 10; **11** and **12**, ref. 11; **13**, ref. 15. The standard error for m is smaller than 0.05. [b] Ref. 16 unless otherwise noted. The standard error for m is smaller than 0.07. [c] Reference standard for Y_{BnOTs}. [d] Reference standard for Y_{BnOPNB}. [e] Calculated from revised rate data for **9**, see ref. 8. [f] Reference standard for Y_{BnBr}.

is the large standard error associated with h in many cases, which makes the outcome of the correlation less reliable. For the analysis using eqn. (1) with Y_{BnX}, the deviation for m is invariably smaller than 0.05. Another disadvantage of including hI in the calculation is that more experimental data are needed for acceptable analyses using the dual-parameter eqn. (3) than for the single-parameter eqn. (1) or by employing the multi-parameter eqn. (4) compared with the dual-parameter eqn. (2).

If the h value is a function of the π electron density adjacent to the reaction site as proposed,[14] the resonance contribution of the aryl ring in the solvolytic transition state would be reflected in the magnitude of h. That is, a more electron-donating substituent in the substrate would have been expected to give a larger value of h in the regression analysis using eqn. (3). However, this was not always the case. Although a decrease in the h value was found for tosylates **1** (0.76) *vs.* **2** (0.59), chlorides **12a** (0.94) *vs.* **12b** (0.85) and **13b** (1.10) *vs.* **13a** (0.80) as the substituent became more electron-withdrawing, no such trend was shown for 4-nitrobenzoates **6a** (0.82) *vs.* **6b** (0.81) or chlorides **10b** (0.36) *vs.* **10c** (0.50). High h values for **5** (1.46) and **8** (1.34) were attributed to the existence of two α aryl groups.[16] However, from the inversed $k(4\text{-}CF_3)/k(3\text{-}CF_3)$ rate ratios observed for several highly congested tertiary benzylic substrates it has already been shown that only one aryl ring in **5**[17] and **8**[18] contributes to the resonance stabilization of the cationic transition state.[19] Furthermore, an increasing order of h values (0.58 to 0.70, then to 0.94) was found for **10d**, **11** and **12a**, contrary to the well known retardation of resonance due to the bulkiness of α alkyl groups.[20,21] Consequently, no relationship between the h value and the effective resonance contribution can be concluded.

The behaviour for the solvolysis of **6d** was considered 'puzzling' because a low and relatively uncertain h value was obtained from the analysis using eqn. (3) (0.23 ± 0.18) or eqn. (4) (0.42 ± 0.16).[16] The correlation coefficient R showed only a small improvement (0.983 to 0.990) with the multi-parameter eqn. (4). 'Nucleophilic assistance' was suggested,[16] as had already been recognised.[9] However, the variation of nucleophilic solvent intervention due to the change in the electronic effect by ring substitution or the change in steric effect by an *ortho* or α alkyl group, which has been demonstrated from $\log k - Y_{BnX}$ plots,[9–11,15] cannot be disclosed from the regression analysis using eqns. (3) or (4).

In conclusion, concerning the number of data needed for analyses, the reliability of the statistical result and the information yielded, the utility of the hI term would be limited and less preferable than Y_{BnX} in the understanding of solvolytic mechanisms.

Acknowledgements

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References

1 S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, 1948, **70**, 846.
2 S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, 1951, **73**, 2700.
3 T. W. Bentley and G. Llewellyn, *Progr. Phys. Org. Chem.*, 1990, **17**, 1211.
4 K.-T. Liu and H.-C. Sheu, *J. Chin. Chem. Soc. (Taipei)*, 1991, **38**, 29.
5 K.-T. Liu and H.-C. Sheu, *J. Org. Chem.*, 1991, **56**, 3021.
6 K.-T. Liu, H.-I Chin and C.-P. Chin, *J. Phys. Org. Chem.*, 1991, **4**, 463.
7 K.-T. Liu, J.-S. Yang, S.-M. Chang, Y.-S. Lin, H.-C. Sheu and M.-L. Tsao, *J. Org. Chem.*, 1992, **57**, 3041.
8 K.-T. Liu, *J. Chin. Chem. Soc. (Taipei)*, 1995, **42**, 607.
9 K.-T. Liu, L.-W. Chang and P.-S. Chen, *J. Org. Chem.*, 1992, **57**, 4791.
10 K.-T. Liu, P.-S. Chen, C.-R. Hu and H.-C. Sheu, *J. Phys. Org. Chem.*, 1993, **6**, 122; 433.
11 K.-T. Liu and P.-S. Chen, *J. Chem. Res. (S)*, 1994, 310.
12 D. N. Kevill and M. J. D'Souza, *J. Phys. Org. Chem.*, 1992, **5**, 287.
13 D. N. Kevill and M. J. D'Souza, *J. Chem. Res. (S)*, 1993, 332.
14 D. N. Kevill, N. HJ Ismail and M. J. D'Souza, *J. Org. Chem.*, 1994, **59**, 6303.
15 K.-T. Liu, P.-S. Chen, P.-F. Chiu and M.-L. Tsao, *Tetrahedron Lett.*, 1992, **33**, 6499.
16 D. N. Kevill and M. J. D'Souza, *J. Chem. Soc., Perkin Trans. 2*, 1995, 973.
17 K.-T. Liu and M.-Y. Kuo, *Tetrahedron Lett.*, 1985, **26**, 355.
18 K.-T. Liu, *J. Chin. Chem. Soc. (Taipei)*, 1992, **39**, 617.
19 K.-T. Liu and M.-Y. Kuo, *J. Chem. Soc., Chem. Commun.*, 1987, 640.
20 W. Duismann and C. Ruchardt, *Chem. Ber.*, 1973, **106**, 1083.
21 H. Tanida and H. Matsumura, *J. Am. Chem. Soc.*, 1973, **95**, 1586.

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