J. Org. Chem. **1996,** *61,* 1523−1525

On the Significance of Electrophilic Pull in Solvolysis. Abnormally Low Tosylate/Bromide Rate Ratio and Unusually High Reactivity for 1-(2,6-Dimethylphenyl)-2,2-dimethyl-1-propyl Bromide

Kwang-Ting Liu*,[†,‡] and Chung-Shin Tang[†]

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

Received September 29, 1995

The importance of solvation of leaving groups on reactivities has been known from the rate enhancement due to the presence of a small amount of water in the ethanolysis of benzhydryl chloride ever since the beginning of the study of solvolytic mechanisms.[1] A "push−pull mechanism" for solvolysis has been proposed,[2] but it was considered to be controversial.[3] Although attention has been paid to electrophilic assistance by acid or by metal ions,[4] specific electrophilic solvation is often included in the scales of solvent-ionizing power, such as Y.[5] A four-parameter equation has been used for the correlation analysis of solvolytic reactivities,[6] from which the contribution of the electrophilic assistance might be evaluated if a sufficient number of data, 20 or more, are available.[7] A double-difference method using four solvents was also suggested in order to estimate electrophilic solvent assistance.[8] However, in the latter case, the highly ionizing solvent hexafluoro-2-propanol should be employed, and thus this method was not applicable to many reactive substrates. Now we would like to report evidence of significant influence on reactivities due to the electrophilic pull of leaving anions from the solvolysis of 1-aryl-2,2-dimethyl-1-propyl bromides **1B**−**4B** and tosylates **1T**−**4T** and to propose the use of low tosylate/bromide rate ratio as a criterion for the presence of this effect.

1B	R=H	**1T**	R=H
2B	R=2-Me	**2T**	R=2-Me
3B	R=2, 6-Me$_2$	**3T**	R=2, 6-Me$_2$
4B	R=i-Pr	**4T**	R=i-Pr

(Structures)

Results and Discussion

In a previous study, the solvolysis of tosylates **1T**−**3T** was found to show discrepancy[9] between the theoretical[10] and experimental trend of $\Delta H^‡$, although the trend of $\Delta G^‡$ was the same in both cases. It was considered to be the result of the neglect of significant solvation of leaving anion in calculations.[9] To verify this proposal, 1-phenyl-, 1-(2-methylphenyl)-, 1-(2,2-dimethylphenyl)-, and 1-(2-isopropylphenyl)-2,2-dimethyl-1-propyl bromides (**1B**−**4B**) and the tosylate **4T** were prepared and solvolyzed. Conductimetrical rate constants were measured at least in duplicate (±2%). Pertinent rate data are given in Table 1. Results of correlation analyses with Y_{BnX}[11−13] are listed in Table 2. Rearranged product was not observed.

Table 1. Solvolysis Rate Constants for Bromides 1B−4B and Tosylate 4T

	k (s^{-1}), 25 °C				
solvent	**1B**	**2B**	**3B**	**4B**	**4T**
90E		1.11×10^{-6}			1.04×10^{-4}
80E	4.18×10^{-7}	3.87×10^{-6}	4.83×10^{-7}	1.38×10^{-6}	3.08×10^{-4}
70E	1.33×10^{-6}	1.23×10^{-5}	1.70×10^{-6}	4.06×10^{-6}	7.88×10^{-4}
60E	4.59×10^{-6}	3.94×10^{-5}	5.65×10^{-6}	1.21×10^{-5}	1.96×10^{-3}
80A	6.22×10^{-8}	4.94×10^{-7}			3.48×10^{-5}
70A	2.87×10^{-7}	2.65×10^{-6}	4.10×10^{-7}	1.13×10^{-6}	1.68×10^{-4}
60A	1.42×10^{-6}	1.43×10^{-5}	1.87×10^{-6}	5.05×10^{-6}	6.36×10^{-4}
50A	6.50×10^{-6}	6.62×10^{-5}	9.53×10^{-6}	2.59×10^{-5}	2.65×10^{-3}
100M		2.78×10^{-6}	2.72×10^{-7}	1.18×10^{-6}	2.64×10^{-4}
90M	8.63×10^{-7}	1.03×10^{-5}	1.20×10^{-6}	4.94×10^{-6}	8.78×10^{-4}
80M	3.22×10^{-6}	3.58×10^{-5}	4.09×10^{-6}	1.74×10^{-5}	2.49×10^{-3}
60M	3.00×10^{-5}	3.04×10^{-4}	3.85×10^{-5}	1.55×10^{-4}	1.60×10^{-2}
100T	6.92×10^{-5}	8.31×10^{-4}	3.96×10^{-4}	1.04×10^{-3}	1.26×10^{-1}
8T2E	9.37×10^{-6}	9.46×10^{-5}	3.72×10^{-5}	8.51×10^{-5}	1.88×10^{-2}
6T4E	1.51×10^{-6}	1.45×10^{-5}	4.21×10^{-6}	9.25×10^{-6}	2.76×10^{-3}
4T6E	2.16×10^{-7}				4.96×10^{-4}

Table 2. Correlation Analyses of log k for 1−4 against Y_{BnX}

substance	m	R	standard deviation	n
1B	0.897	0.994	0.028	14
2B	0.908	0.997	0.018	15
3B	1.05	0.991	0.043	13
4B	1.03	0.994	0.033	13
2T	1.00	0.996	0.024	16
3T	1.14	0.987	0.051	16
4T	1.16	0.977	0.061	16

The observation of excellent linear log $k - Y_{\mathrm{BnX}}$ correlations for **1B**−**4B** and **2T** but slight deviations from linearity for **3T** and **4T** suggested limiting S$_N$1 mechanisms and small steric retardation to resonance in the solvolytic transition state for tosylates **3T** and **4T**. Bromides, however, seem to be less sensitive to the bulkiness of *ortho* substituents. In addition, contrary to what was observed for the corresponding tosylates,[9] **3B** showed higher reactivity than that of the unsubstituted bromide **1B** in spite of steric inhibition of resonance due

---

[†] National Taiwan University.

[‡] National Central University.

(1) Farinacci, N. T.; Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 2542.

(2) Swain, C. G. *J. Am. Chem. Soc.* **1948**, *70*, 1119.

(3) Thornton, E. R. *Solvolytic Mechanisms*; Ronald Press: New York, 1964; pp 12−13.

(4) For review, see: Kevill, D. N. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1983; Part 2, The Chemistry of Halides, Pseudohalides and Azides, Chapter 20.

(5) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 43−45.

(6) Abraham, M. H.; Grellier, P. L.; Abboud, J.-L. M.; Doherty, R. M.; Taft, R. W. *Can. J. Chem.* **1988**, *66*, 2673.

(7) For example: Abraham, M. H.; Doherty, R. M.; Kamlet, M. J.; Harris, R. M.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1987**, 913.

(8) Doherty, R. M.; Abraham, M. H.; Harris, J. M.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.* **1986**, *51*, 4872.

(9) Liu, K.-T.; Tang, C.-S.; Chin, C.-P. *J. Chin. Chem. Soc. (Taipei)* **1994**, *41*, 351.

(10) Lee, I.; Kim, N. D.; Kim, C. K. *J. Phys. Org. Chem.* **1993**, *6*, 499.

(11) Y_{BnOTs} was derived form the rate of solvolysis for **1T**; see: Liu, K.-T.; Yang, J.-S.; Chang, S.-M.; Lin, Y.-S.; Sheu, H.-C.; Tsao, M.-L. *J. Org. Chem.* **1992**, *57*, 3041.

(12) Y_{BnOTs} for 80% methanol, 0.750, was obtained from $k = 6.02 \times 10^{-4}$/s; see: Tang, C.-S. M. S. Thesis, National Taiwan University, June 1994.

(13) For revised and extended Y_{BnBr} values, see: Liu, K.-T. *J. Chin. Chem. Soc. (Taipei)* **1995**, *42*, 607.

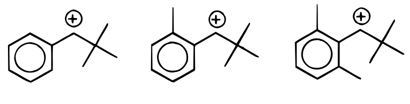
0022-3263/96/1961-1523$12.00/0

Table 3. Activation Parameters for the Solvolysis of Substrates 1B−3B

	$\Delta H^{\ddagger}$ (kcal/mol)			$\Delta S^{\ddagger}$ (eu)			$\Delta G^{\ddagger}$ (kcal/mol)		
solvent	**1B**	**2B**	**3B**	**1B**	**2B**	**3B**	**1B**	**2B**	**3B**
70E	24.5	22.9	25.2	−3.3	−4.3	−0.3	25.5	24.1	25.3
60E	23.7	22.1	24.5	−3.5	−4.6	−0.2	24.7	23.4	24.6
70A	24.3	22.8	25.2	−6.7	−7.4	−3.3	26.4	25.0	26.1
60A	23.5	21.1	24.5	−6.3	−9.9	−2.4	25.4	24.0	25.2
50A	22.8	20.5	23.0	−5.6	−8.9	−4.2	24.5	23.1	24.3
90M	24.1	22.9	25.2	−5.5	−4.4	−1.2	25.7	24.2	25.5
8T2E	23.1	22.3	24.8	−6.0	−3.9	−0.1	24.9	23.5	24.8
80E	21.0	20.3	21.2	−10.9	−8.9	−7.8	24.3	22.9	23.5
80E	21.7	20.7	22.3	−12.3	−11.1	−8.2	25.4	24.0	24.8

Scheme 1

AM1 Calculations : (ref. 10)



1 **2** **3**

$\Delta H^{\neq}$	2.8	<	3.3	<	4.7	kcal/mol
$\Delta S^{\neq}$	3.2	<	5.6	<	4.0	e.u.
$\Delta G^{\neq}$	1.8	>	1.6	<	3.5	kcal/mol

Experimental Data :

k(OTs)	**2T**	>	**1T**	>	**3T**	(ref. 9)
$\Delta G^{\neq}$	**2T**	<	**1T**	<	**3T**	
$\Delta H^{\neq}$	**2T**	<	**1T**	<	**3T**	
k(Br)	**2B**	>	**3B**	>	**1B**	(This Work)
$\Delta G^{\neq}$	**2B**	<	**3B**	<	**1B**	
$\Delta H^{\neq}$	**2B**	<	**1B**	<	**3B**	

Table 4. Tosylate/Bromide Rate Ratios for 1−4

solvent	**1T/1B**	**2T/2B**	**3T/3B**	**4T/4B**
80E	256	114	29.8	223
70E	217	106	23.2	194
60E	166	76.7	17.4	162
70A	199	122	22.1	149
60A	175	96.5	19.1	126
50A	166	82.9	16.3	103
90M	246	122	27.8	178
80M	187	94.4	22.4	143
60M	147	79.6	20.0	103
100T	181	115	18.4	122
80T20E	265	149	24.6	221
60T40E	299	166	30.2	298

to 2,6-dimethyl substituents. Another effect is likely to be involved to account for the difference between the order of reactivity observed in the present study and in the case of tosylates.[9] On the other hand, experimental activation parameters for **1B**−**3B** (Table 3) reveal that neither $\Delta G^{\ddagger}$ nor $\Delta H^{\ddagger}$ is consistent with the trends obtained from AM1 calculations (Scheme 1).[14,15] Neglect of solvent effect[16] is again the most probable explanation.

Analysis of the tosylate/bromide rate ratios in Table 4 is worthwhile. The $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ values for **1** and **4** are close to each other, within 30% difference in general, and are of the same order of magnitude observed for 2-adamantyl analogs.[17] However, the ratios are comparatively smaller for **2** and **3**, especially in the latter case where $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ is only about 1/10 of that for **1**. Since *k* for **3** has been considered to be abnormally large (*vide supra*), the lower rate ratio is likely due to the fast reaction of bromides. Moreover, OTs/Br rate ratios for **4** are invariably higher than those for **2**, which could be attributed to the relief of ground-state strain,[18] not to the separation of charges or the stability in the transition state.[19,20] It is interesting to note that the smallest ratio was observed in the case of **3**, despite an increasing strain introduced by the second *o*-methyl group. In addition, for each substrate decreased $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios were observed in specific solvent mixtures, such as aqueous ethanol or ethanol−trifluoroethanol, containing more water or more trifluoroethanol. Since the literature data[21] for free energies of transfer of ions indicated better solvation of anions in water and in trifluoroethanol than in common organic solvents, the influence of solvation of leaving anions on the solvolytic reactivities should be taken into consideration.

The heat of hydration of benzenesulfonate ion was found to be smaller than that of iodide ion,[22] and thus, should be even smaller than that of bromide ion.[21] Consequently, it is likely that the high reactivity for **3B** and the low $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratio for **2** and **3** in all solvent systems are due to the better solvation of bromide ions.[23] The observation of a "normal" rate ratio for **4** could be attributed to the balance of a rate enhancement by solvation of leaving anion for the bromide and an acceleration due to the relief of steric strain for the tosylate. Generally speaking, for benzylic substrates in which the resonance stabilization of cationic transition state of solvolysis is less effective due to steric factors, the significance of solvation of leaving group will be more profound. In other words, the importance of electrophilic pull[2] of the leaving bromide ion, not tosylate, might be very influential on the solvolytic reactivity.[25] Moreover, the observation of a low tosylate/bromide rate ratio may be used as a diagnosis for indicating the significance of electrophilic pull in solvolysis. Further studies are in progress.

Experimental Section

General Remarks. Capillary melting points are uncorrected. Elemental analyses were done in the Microanalytical Laboratory at the Department of Chemistry, National Taiwan University.

Materials. Solvents for the kinetic studies were spectral grade or anhydrous solvents were freshly distilled before use.[26] Literature procedures were used for the preparations of tosylate **4T**[11] and bromides **1b**−**4b**.[27] The products were purified by

---

[14] Although no general trend of $\Delta S^{\ddagger}$ could be realized, the least negative value was invariably found for **3B** and might be attributed to a relatively more dissociated transition state.[15]

[15] Schaleger, L. L.; Long, F. A. *Adv. Phys. Org. Chem.* **1963**, *1*, 1.

[16] Kollman, P. *Chem. Rev.* **1993**, *93*, 2395.

[17] Fry, J. L.; Lancelot, C. J.; Lam, L. K. M.; Harris, J. M.; Bingham, R. C.; Raber, D. J.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2538.

[18] Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189.

[19] Hoffmann, H. M. R. *J. Chem. Soc.* **1965**, 6762.

[20] Bentley, T. W.; Christl, M.; Kemmer, R.; Llewellyn, G.; Oakley, J. E. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2531.

[21] Marcus, Y. *Pure Appl. Chem.* **1983**, *55*, 977.

[22] Morris, D. F. C. *Tetrahedron* **1958**, *4*, 423.

[23] One reviewer pointed out that for the 2-adamantyl system a higher tosylate/bromide rate ratio in acetic acid than in 80% ethanol was recorded.[17] However, the rate constant for the bromide at 25 °C was extrapolated from data at 150 and 174.6 °C[24] and might be uncertain.

[24] Fry, J. L.; Lam, L. K. M.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2542.

[25] In a recent paper, bromide was considered as an intermediate type concerning hydrogen bond susceptibility. See: Mitsuhashi, T.; Hirota, H.; Yamamoto, G. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 824.

[26] Perrin, D. D.; Armarogo, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

recrystallization from *n*-hexane or by chromatography over amine-washed alumina. Spectral data were found to compatible with the assigned structures, and acceptable elemental analyses (C and H) were obtained for new compounds (see the supporting information).

Kinetic Measurements. Conductimetric rate constants were measured by using the system developed in this laboratory.[28] Solutions of $10^{-4}-10^{-5}$ M were employed. In some cases, the addition of a small amount of 2,6-lutidine to the solution was found to be necessary to prevent curvature of the rate constant plot.

All reactions were followed to at least 2 half-lives and gave excellent first-order behavior with correlation coefficients of greater than 0.995. Rate constants measured at other temperature were used to calculate activation parameters and to estimate the rate constant, which could not be measured directly at 25 °C (see the supporting information).

Product Analyses. The product of solvolysis in aqueous acetone was isolated and was identified as the corresponding alcohol by its proton NMR spectrum.

Acknowledgment. We thank the National Science Council of the Republic of China (NSC 84-2113-M-002-003) for financial support.

Supporting Information Available: Characterization data and rate constants for prepared compounds (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO951776Z

---

(27) Liu, K.-T.; Sheu, H. C. *J. Chin. Chem. Soc. (Taipei)* **1991**, *38*, 29.

(28) Sheu, H.-C.; Liu, K.-T. *Proc. Natl. Sci. Counc. ROC (A)* **1993**, 17.