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SOLVOLYSES OF SUBSTITUTED NAPHTHYLMETHYL TOSYLATES. IMPORTANCE OF THE EXTENT OF SOLVATION IN DELOCALIZED CATIONIC TRANSITION STATES ON THE CORRELATION OF SOLVOLYTIC REACTIVITIES#

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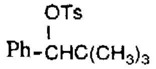
Abstract: Grunwald-Winstein correlation analyses of solvolytic reactivities for 2,2,2-trifluoro-1-naphthylethyl tosylates **2-4** were found to show linear relationships with that of 2,2-dimethyl-1-naphthylpropyl tosylate **5** but not with that of 2,2-dimethyl-1-phenylpropyl or adamantyl tosylate, from which the importance of solvation of delocalized cationic transition state could be demonstrated.

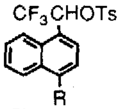
In applying the Grunwald-Winstein equations, $\log(\underline{k}/\underline{k}_o) = \underline{m}\underline{Y}$ (1)[1] and/or $\log(\underline{k}/\underline{k}_o) = \underline{m}\underline{Y} + \underline{l}\underline{N}$ (2),[2] to correlate solvolytic reactivities of benzylic substrates, we recently demonstrated the necessity of using new scales of solvent ionizing power ($\underline{Y}_{BnX}$) based on 2-aryl-2-adamantyl derivatives.[3-5] The failure in the application of the corresponding $\underline{Y}_X$ scales[6] was attributed to the solvation at cationic transition states. The different extent of solvation of the localized charge on 1-adamantyl cation and the delocalized benzylic cation makes the $\underline{Y}_X$ scale inapplicable to the benzylic substrates. Now we like to report that neither adamantyl tosylates nor 2,2-dimethyl-1-phenylpropyl tosylate **1**[7-9] can be used as a suitable reference standard to correlate the solvolytic reactivity of naphthylmethyl tosylates **2-4**. The observed linear relationships between the logarithm of the rate constants for **2-4** against that for 2,2-dimethyl-1-naphthylethyl tosylate **5** clearly demonstrate the importance of solvation which is different between the delcoalized naphthylmethyl cations and benzylic cations.

2,2-Dimethyl-1-phenylpropyl tosylate(**1**), 2,2,2-trifluoro-1-(α-naphthyl)-ethyl tosylate(**2**),[10] 2,2,2-trifluoro-1-(4'-methyl-α-naphthyl)ethyl tosylate (**3**), 2,2,2-trifluoro-1-(β-naphthyl)ethyl tosylate (**4**), and 2,2-dimethyl-1-(β-naphthyl)ethyl tosylate(**5**) were prepared from the corresponded alcohols by conventional method.[11] The first order solvolytic rate constants were measured at least in duplicate by conductimetric (±2%) or titrimetric (±3%) method. The pertinent data are summarized in **Table 1**.

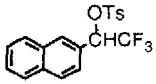


$\mathrm{Ph\text{-}\overset{OTs}{C}HC(CH_3)_3}$

1



2 R=H **3** R=CH$_3$



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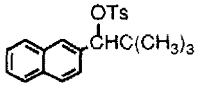

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Table 1. Pertinent solvolytic rate constants for tosylates **1**-**5**.

Solvent	k, s^{-1} (25°C)				
	1	**2**	**3**	**4**	**5**
90E	$3.52x10^{-5}$	$9.63x10^{-8}$ [a]	$8.32x10^{-6}$ [a]	$7.06x10^{-9}$ [a]	$8.19x10^{-4}$
80E	$1.07x10^{-4}$	$2.76x10^{-7}$ [a,b]	$2.31x10^{-5}$	$1.92x10^{-8}$ [a]	$2.37x10^{-3}$
70E	$2.88x10^{-4}$	$6.76x10^{-7}$ [a]	$5.31x10^{-5}$	$5.47x10^{-8}$ [a]	$4.75x10^{-3}$
60E	$7.60x10^{-3}$	$1.41x10^{-6}$ [a,b]	$1.14x10^{-4}$		$1.10x10^{-2}$
80A	$1.21x10^{-5}$	$1.60x10^{-8}$ [a]	$1.81x10^{-6}$ [a]	$7.81x10^{-10}$[a]	$1.60x10^{-4}$
70A	$5.90x10^{-5}$	$8.36x10^{-8}$ [a]	$7.35x10^{-6}$ [a]	$3.35x10^{-9}$ [a]	$7.50x10^{-4}$
60A	$2.48x10^{-4}$	$3.18x10^{-7}$ [a]	$2.67x10^{-5}$	$1.30x10^{-8}$ [a]	$2.50x10^{-3}$
50M	$1.17x10^{-2}$	$1.71x10^{-5}$	$1.54x10^{-3}$		
97T	$1.30x10^{-2}$	$2.03x10^{-5}$ [c]	$3.44x10^{-3}$	$2.53x10^{-6}$	0.345[a]
HOAc	$2.07x10^{-5}$	$6.34x10^{-9}$ [a,b]	$1.02x10^{-6}$ [a]	$4.27x10^{-10}$[a]	$1.03x10^{-4}$

[a]Extrapolated from data at other temperatures. [b]Lit. data[9] are $4.70x10^{-7}$ (80E), $3.32x10^{-6}$ (60E) and $9.13x10^{-9}$ (HOAc). Extrapolation is likely the cause of the difference. [c]Lit. data[10] is $1.79x10^{-5}$ (97T).

Both tosylates **1**[7-9] and **2**[10], have been found to solvolyze via limiting S_N1 mechanism without involving nucleophilic solvent assistance. However, no good linear relationship for log k - Y_{OTs} plots has been found in either case.[9,12] To account for the scattered plots, the solvation of delocalized cationic transition states was proposed in the case of **1**,[9] whereas the extrapolation of kinetic data and the presence of ion pair return were suggested in the case of **2**.[10] Comparisons of log k - mY_{OTs} plots for **2**-**5** revealed the independence of deviations on the relative reactivity of substrates or the relative stability of cationic intermediates. (**Table 2**)[13] Moreover, similar scatterings were observed in different cases regardless of the temperature at which reaction rates had been monitored. **Table 2** also showed no linear relationship with the dual-parameter eq. 2 was resulted. Thus, the alternative explanation by different extents of solvation in the transition state is likely the suitable one.[3-5,14] Deviation from linear log k - Y_{OTs} plots has also been found in other cases, such as 1-aryl-2,2,2-trifluoroethyl[8,15] and neophyl tosylates,[16] which could be rationalized similarly.

Table 2. Correlation analyses of log ks for **2**-**5** against Y_{OTs}.

	2	**3**	**4**	**5**
Eq. (1)	m = 1.08	m = 1.08	m = 1.16	m = 0.931
	(r = 0.943)	(r = 0.942)	(r = 0.912)	(r = 0.918)
Eq. (2)	m = 1.10	m = 1.06	m = 1.17	m = 0.919
	l = 0.073	l = -0.047	l = 0.027	l = -0.034
	(r = 0.946)	(r = 0.944)	(r = 0.912)	(r = 0.918)

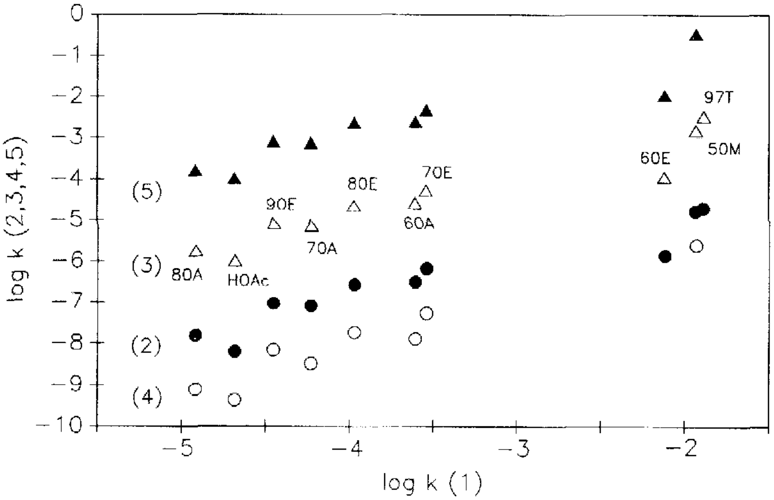


Figure 1. Correlations of log ks for **2**-**5** versus that for **1**.

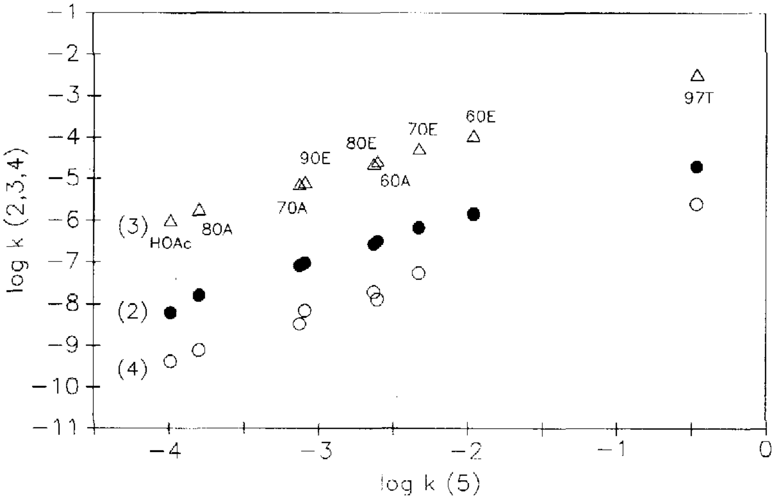
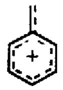


Figure 2. Correlations of log ks for **2**-**4** versus that for **5**.

Correlation analyses of logarithms of solvolysis rate constants for naphthylmethyl tosylates **2**-**5** vs. that for benzylic tosylate **1** were shown in **Figure 1**. The correlation coefficients r were 0.967 for **2**, 0.982 for **3**, 0.963 for **4** and 0.982 for **5**. Obviously, the extent of delocalization of the partial positive charge developed in the transition state (**6**) for benzylic substrates differs from that for naphthylmethyl substrates (**7**). Therefore, it is plausible that the extent of solvent interaction is also different. Indeed, **Figure 2** showed excellent linear correlations between the solvent-dependent log ks for **5** with those for **2** (m = 0.972, r = 0.992), **3** (m = 0.983, r = 0.999), and **4** (m= 1.07, r = 0.993), respectively.



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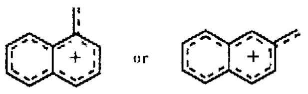

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Consequently, in the cationic transition state the solvation effect is different not only between adamantyl and benzylic moieties[3-5,9,14] but also between benzylic and naphthylmethyl moieties. The present result on the significant variation of solvent effects on the solvolysis of adamantyl, benzylic and naphthylmethyl tosylates suggests that no universal $\underline{Y}$ scale could be applicable to all substrates. It also clearly illustrates the important role the charge dispersion-dependent solvation of the cationic transition states plays in the linear free energy relationship involved in solvolytic reactions. Further studies in this aspect are in progress.

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REFERENCES AND NOTES

#Dedicated to Professor Herbert C. Brown on the occasion of his eightieth birthday.

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12. Correlation coefficient $\underline{r} = 0.976$[9] or 0.986.[8] The difference is likely due to the revised $\underline{Y}_{OTs}$ values[6] were utilized in the former case.
13. It is likely that the difference of $\underline{m}$ and $\underline{r}$ for **2** between the literature data($\underline{m} = 0.94$, $\underline{r} = 0.978$)[10] and those in **Table 2** is from the different solvent systems employed and the rate constants calculated. Nevertheless, such differences would not affect the conclusion obtained in this case or the latter ones (**Figures 1** and **2**).
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