this difference was very small. *In fact, the comparison of the two plots indicates that if there was no anchimeric assistance in the solvolysis of* **9**, *the maximum rate factor attributable to anchimeric assistance in the solvolysis of exo-2-tosyloxynorbornane* (**1**) *would be less than 5.*

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Carbonium Ions. III.
Acetolysis of 2-Arylethyl Tosylates

Sir:

In the analysis of solvolytic reactions involving primary and secondary arenesulfonate esters with neighboring aryl groups it has been proposed for many years that neighboring aryl group bridging can occur in the ionization step as one of the reaction paths leading to products.[1,2] In systems of the type shown in eq 1 this analysis leads to the conclusion that there are two

$$ArCH_2CH_2OTs \xrightarrow{HOAc} ArCH_2CH_2OAc + HOTs \qquad (1)$$

competing paths for displacement of tosylate, which are designated as k_Δ and k_s. These paths are simultaneous reactions, each with its own characteristics, and there is no crossover between them. The k_Δ path involves aryl participation, as the tosylate group leaves, to give phenonium ion and this accounts for scrambling of the two carbons of the ethyl side chain.[3] The k_s path involves direct S$_N$2 displacement by nucleophile. Winstein and coworkers[2] have pointed out that only a fraction (F) of the phenonium ions goes on to product, while a fraction $(1 - F)$ returns to covalent starting material. This dictates that the relationship between the rate constants for these two paths and the titrimetric rate constant will be $k_t = Fk_\Delta + k_s$. The rate constant for scrambling in the starting material will be $k_{14} = (1 - F)k_\Delta$.

It has been proposed by Brown and coworkers[4] that there are serious inconsistencies in the preceding theory.

In an extension of methods used by earlier workers[2d,5] a complete analysis of all rate constants (k_t, k_Δ, k_s, and k_{14}) and F factors for the acetolysis of 2-phenylethyl tosylate has been carried out[6] in the absence of acetate ion. Using the methods previously described[6] the acetolysis of 2-*p*-chlorophenylethyl, 2-*p*-methylphenylethyl, and 2-*p*-methoxyphenylethyl tosylates in the absence of acetate ion have been analyzed. In each case the product acetate was shown to be stable to rearrangement in the reaction mixture. The per cent rearrangement in the product acetate for each compound was determined at two temperatures for the initial stage of reaction (time = 0) and the final stage of reaction (time = ∞) and the results are shown in Table I.

Table I. Rearrangement in Product of Acetolysis of 2-Arylethyl-1-^{14}C Tosylates (0.5 *M*)

Aryl group	Temp, °C	% rearr at time = 0	% rearr. at time = ∞
p-Chlorophenyl	90	3.0	11.7
	115	4.4	15.5
Phenyl[a]	90	11.9	30.3
	115	14.6	33.4
p-Methylphenyl	90	35.4	47.4
	115	35.8	48.4
p-Methoxyphenyl	65	43.7	48.8
	90	43.4	49.6

[a] Data for the phenyl compound taken from ref 6.

Using standard literature procedures[2d,7] the titrimetric rate constants, k_t, and the rate constants for scrambling of the starting tosylate, k_{14}, were determined under conditions identical with those used for the product rearrangement studies and these are shown in Table II. Also shown in Table II are the values for various other rate constants and parameters calculated by the procedure given earlier.[6] For those rate constants and parameters calculated by the time = 0 and time = ∞ methods, Table II shows the average of the two approaches with the difference between each method and the average being shown as the ± error. Some of the values in Table II can be compared to the results of earlier workers. Jenny and Winstein[2d] studied the *p*-methoxyphenylethyl tosylate at one temperature and the values they obtained were $k_t^{75} = 6.9 \times 10^{-6}$ sec^{-1}, $k_{14}^{75} = 1.91 \times 10^{-5}$ sec^{-1}, $k_\Delta^{75} = 2.6 \times 10^{-5}$ sec^{-1}, $F = 0.266$. The values we obtain for k_Δ and F are slightly different from those of Jenny and Winstein. We would caution against a rigorous interpretation based on the magnitude of F since its determination is rather sensitive to a number of factors.

Since k_s is influenced only by the inductive effects of the aryl group and its substituent while k_Δ is a function of the electron-donating ability of the aryl group the trends observed for k_s and k_Δ in Table II are reasonable. The ranges of $\Delta S^{\ddagger}$ for the k_Δ and k_s paths are in agreement with predictions.[2] The relative relationship of k_Δ and k_t is summarized in Table III to dramatize why k_t values alone should not be used as a test for participation. It should be noted in Table II that determination

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[1] (a) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949); (b) D. J. Cram, *ibid.*, **71**, 3875 (1949); (c) D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963); (d) D. J. Cram, *ibid.*, **86**, 3767 (1964); (e) D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967).

[2] (a) S. Winstein, *Bull. Soc. Chim. France*, 55C (1951); (b) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953); (c) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956); (d) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958); (e) S. Winstein and R. Baker, *J. Am. Chem. Soc.*, **86**, 2071 (1964); (f) L. Eberson, J. P. Petrovich, R. Baird, D. Dyckes, and S. Winstein, *ibid.*, **87**, 3504 (1965); (g) A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968).

[3] The definition % scrambling = 2 × % rearrangement will be used.

[4] (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965); (b) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967); (c) H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968).

[5] J. W. Clayton and C. C. Lee, *Can. J. Chem.*, **39**, 1510 (1961).

[6] J. L. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Jones, *J. Amer. Chem. Soc.*, **91**, 1154 (1969).

[7] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

Table II. Data for Acetolysis of 2-Arylethyl Tosylates (0.5 *M*)

Parameter or rate constant	Temp, °C	*p*-Chlorophenyl	Phenyl^a	*p*-Methylphenyl	*p*-Methoxyphenyl
10^7k_t, sec^{-1}	65				35.3
	75	2.14^b	2.72^b	8.44^b	109^b
	90	8.67	12.7	40.8	500
	115	70.2	127	430	
10^7k_{14}, sec^{-1}	65				45.6
	90	1.48	8.00	60.6	535
	115	22.8	80.6	645	
F	65				0.413 ± 0.010
	90	0.319 ± 0.058	0.318 ± 0.044	0.346 ± 0.024	0.466 ± 0.017
	115	0.211 ± 0.002	0.368 ± 0.052	0.352 ± 0.028	
10^7k_s, sec^{-1}	65				3.2 ± 1.3
	75	1.97 ± 0.08^b	2.07 ± 0.10^b	2.0 ± 0.5^b	8.5 ± 5.9^b
	90	7.96 ± 0.19	8.92 ± 0.76	8.4 ± 3.3	35 ± 31
	115	64.1 ± 0.1	79.3 ± 10.6	78 ± 44	
10^7k_Δ, sec^{-1}	65				77.7 ± 1.3
	75	0.39 ± 0.06^b	2.39 ± 0.12^b	19.0 ± 0.6^b	228 ± 5^b
	90	2.19 ± 0.19	11.8 ± 0.8	92.3 ± 3.8	998 ± 29
	115	28.9 ± 0.1	128 ± 11	997 ± 44	
$\Delta S^\ddagger$ for k_Δ, eu		−11.9 ± 2.6	−14.6 ± 0.7	−10.9 ± 0.3	−10.6 ± 0.4
$\Delta S^\ddagger$ for k_s, eu		−24.7 ± 0.7	−21.5 ± 1.7	−24.3 ± 7.9	

[a] Data for the phenyl group taken from ref 6. [b] Calculated from rate data at other temperatures.

Table III. Relationship of k_Δ and k_t at 75° for Acetolysis of 2-Arylethyl Tosylate

Aryl group	Relative k_Δ	Relative k_t
p-Chlorophenyl	1.0	1.0
Phenyl	6.1	1.3
p-Methylphenyl	49	3.9
p-Methoxyphenyl	585	51

of rate constants for paths that make very minor contributions, k_Δ for *p*-chloro and k_s for *p*-methyl and *p*-methoxy, are subject to larger experimental errors than for those which make major contributions.

It is generally agreed that neophyl tosylates ionize with aryl participation and that k_t accurately measures the rate constant for ionization.[2,4b,8] The titrimetric rate constants for acetolysis of the neophyl tosylates having the same *para* substituents as were used in the 2-phenylethyl tosylates were determined and are given in Table IV. A plot of log k_t for the neophyl tosylates against the log k_Δ for the corresponding *para*-substituted 2-phenylethyl tosylates (Figure 1) shows a linear correlation with a slope of 0.98. This indicates strongly that k_Δ rate constants for 2-arylethyl tosylates are a true measure of ionization with participation by the aryl group. It should be noted that Hammett plots of log k_t for neophyl, log k_Δ for 2-arylethyl, and log k_t for 2-arylethyl tosylates *vs.* σ or σ^+ constants are all nonlinear for the substituents *p*-Cl, *p*-H, *p*-CH_3, and *p*-CH_3O.

Table IV. Titrimetric Rate Constants for Acetolysis of 2-Aryl-2-methyl-1-propyl Tosylates

Aryl group	Temp, °C	k_t, sec^{-1}	$\Delta S^\ddagger$, eu
p-Chlorophenyl	75	3.66×10^{-6}	−7.5
	100	5.14×10^{-5}	
Phenyl^a	50	9.87×10^{-7}	−6.2
	75	1.92×10^{-5}	
p-Methylphenyl	50	9.32×10^{-6}	−8.8
	75	1.41×10^{-4}	
p-Methoxyphenyl^b	50	1.28×10^{-4}	−6.1
	75	1.77×10^{-3} ^{c}	

[a] Values of $k_t = 9.92 \times 10^{-7}$ sec^{-1} at 49.6° and $k_t = 1.93 \times 10^{-5}$ sec^{-1} at 74.7° given by S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952). [b] Value of $k_t = 1.21 \times 10^{-4}$ sec^{-1} at 50° given in ref 2c. [c] Value taken from ref 2c.

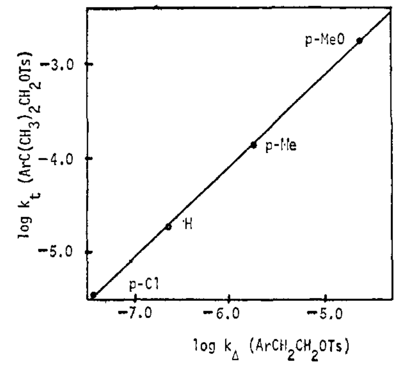

Figure 1. Hammett plot of log k_t for neophyl tosylates and log k_Δ for 2-arylethyl tosylates at 75° in 99.7% HOAc.

For the type of solvolysis shown in eq 1 the competing k_Δ and k_s concept enjoys overwhelming success in explaining all the known data including rate constants,[1,2,6] scrambling data,[1c,6] kinetic isotope effects,[9] stereochemistry,[6] substituent effects, solvent effects,[2] and entropies of activation.[1,2,6]

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(8) H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Amer. Chem. Soc.*, **87**, 1280 (1965).

(9) W. H. Saunders, Jr., S. Asperger, and D. H. Edison, *ibid.*, **80**, 2421 (1958); W. H. Saunders, Jr., and R. Glaser, *ibid.*, **82**, 3586 (1960).

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