

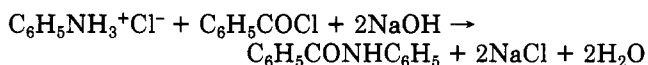
that pyridine transport from water into chloroform is relatively slow, approximately as fast as the transport of aniline from water to chloroform. Given that both aniline and pyridine are transporting into chloroform at comparable rates, it is not surprising that the pyridine is somewhat less effective as a phase-transfer catalyst under these conditions.

The retention of the excellent yield of benzanilide under these conditions indicates that aniline competes very effectively for benzoylpyridinium ion while it is still in the chloroform phase. Benzoylpyridinium ion is formed as pyridine transports into the chloroform phase, at approximately the same rate at which aniline transports into chloroform. The balancing of the rates of generation of the reactive species and the arrival of its coreactant apparently optimizes the kinetic catalysis with a minimum loss of the reactive benzoylpyridinium ion to the aqueous phase, where it would hydrolyze.

The above analysis also speaks to the point of whether or not pyridine may truly act catalytically, that is, in less than stoichiometric ratios. To do so, pyridine used to activate one benzoylpyridinium chloride would have to be released after reaction in order to activate another benzoyl chloride. For reactions that would recycle entirely within one phase, as the aqueous pyridine-catalyzed reaction appears to do, this would be a straightforward process. For true phase-transfer catalysis, pyridine would have to transport between phases for each cycle of catalysis. Since aqueous pyridine does show significant rate enhancement with respect to the uncatalyzed reaction, it seems quite feasible that it could function as a recycling (substoichiometric) catalyst, even under our relatively unusual conditions of mass-transport limited reaction. Under the more normal conditions of vigorous mixing, true catalytic activity is much more feasible and is observed.^{7,8}

Improved Method for Two-Phase Amide Synthesis.

A slight modification of our approach allows for a very convenient synthetic method for amide preparation. The aniline is dissolved in aqueous acid and placed over a benzoyl chloride solution in CCl₄. No reaction takes place until the aniline is liberated by titration with aqueous base. Aniline thus can be released in a controlled fashion, subsequently entering the organic phase where it reacts with benzoyl chloride to form benzanilide, which precipitates. The HCl released in the amide-forming reaction requires that 2 equiv of base be titrated for each amide formed.



This method compares very favorably with the traditional method of amide synthesis from aryl acid chlorides, the Schotten-Baumann method.¹² Unlike the Schotten-Baumann method, there is never an excess of base, which could compete with the amine. Furthermore, the product precipitates nicely from CCl₄ solution. If the base titration is continued to a relatively high pH, any benzoic acid side product will be extracted into the aqueous solution, making isolation of the final product simpler.

A similar two-phase method of amide synthesis from amine hydrochlorides has been reported.¹³ In that case, a toluene solution of acid chloride is heated with an aqueous amine hydrochloride solution. Presumably HCl is gradually driven off to initiate the phase transfer of the amine. The current base titration method is essentially based on the same premise but employs much milder conditions and offers a much higher yield in the case of benzanilide.

Summary

These results indicate that the two-phase reaction of benzoyl chloride with aniline ordinarily occurs in the organic phase, and the reaction can be limited by aniline transport under conditions of very slow mixing. Pyridine acts as an inverse phase transfer catalyst for the transport of benzoyl chloride (as benzoylpyridinium chloride) into the aqueous phase, where it hydrolyzes to benzoic acid. Under appropriate conditions, both processes can be observed; both the product yields and the reaction rates can be analyzed in terms of the competition of the two pathways. Optimum yields of benzanilide product are obtained by utilizing aqueous pyridine catalysis or by slow neutralization of aqueous anilinium hydrochloride by base titration.

Acknowledgment. This work comprised the undergraduate honors thesis project of J.A.Y. and was presented by J.A.Y. at the 42nd Northwest Regional Meeting of the American Chemical Society, Bellingham, Washington, June 18, 1987. Partial financial support was provided by the U.S. Department of Energy, Advanced Energy Projects Division of the Office of Basic Energy Sciences, Grant DE-FG06-85ER-13389.

Registry No. Aniline, 62-53-3; benzoyl chloride, 98-88-4; pyridine, 110-86-1.

(12) Vogel, A. *Textbook of Practical Organic Chemistry*, 4th ed.; Longman: Essex, England, 1978; p 682.

(13) Shama, S. A.; Tran, T. L. *J. Chem. Ed.* 1978, 55, 816.

Correlation of the Rates of Solvolysis of 2-Adamantyl 2,2,2-Trifluoroethanesulfonate: A Y_{OTf} Scale¹

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Specific rates of solvolysis of 2-adamantyl 2,2,2-trifluoroethanesulfonate (tresylate), determined in a variety of organic and aqueous organic solvents at 25 and/or 50 °C, have been used for the determination of a scale of solvent ionizing power (Y_{OTf}). The Y_{OTf} values give an excellent linear correlation with Y_{OTs} values, with a very small intercept and a slope of essentially unity. Additional Y_{OTs} values (for 2,2,2-trifluoroethanol-ethanol mixtures) have been determined from the specific rates of solvolysis of 2-adamantyl *p*-toluenesulfonate.

Several months ago, we presented² a scale of solvent ionizing power for a 2,2,2-trifluoroethanesulfonate (tresy-

late) leaving group (Y_{OTf}) based upon the rates of solvolysis of 2-adamantyl tresylate. The recent publication³ of a

Table I. First-Order Rate Coefficients^a for the Solvolysis of 2-Adamantyl 2,2,2-Trifluoroethanesulfonate^b and Y_{OTr} Values

$T, ^\circ\text{C}$	$10^6k, \text{s}^{-1}$			
	80% EtOH ^c	MeOH	EtOH	$\text{CH}_3\text{CO}_2\text{H}$
25.00	3.15 ± 0.07^d	0.245 ± 0.002^d	$(0.0410)^{d,e}$	0.373 ± 0.009^d
35.00		1.25 ± 0.04	0.212 ± 0.005	1.86 ± 0.03
35.40	14.0 ± 0.1			
42.50	36.7 ± 0.5	3.84 ± 0.03	0.704 ± 0.008	
45.00				7.50 ± 0.11
50.05	101 ± 1	11.4 ± 0.3^d	2.32 ± 0.04^d	$(15.1)^e$
55.00				28.9 ± 0.3
60.10			8.76 ± 0.10	
Y_{OTr}^f	0.000	-1.110	-1.886	-0.927
Y_{OTr}^g	0.00	-0.92	-1.75	-0.61

^a With associated standard deviations. ^b Concentration ca. 0.0055 M. ^c On a volume-volume basis at 25 °C. ^d Reference 3 reports values of $3.11 \times 10^{-6} \text{ s}^{-1}$ for 80% ethanol at 25.0 °C, an extrapolated value of $0.281 \times 10^{-6} \text{ s}^{-1}$ for methanol at 25.0 °C, an extrapolated value of $0.0495 \times 10^{-6} \text{ s}^{-1}$ for ethanol at 25.0 °C, a value of $0.371 \times 10^{-6} \text{ s}^{-1}$ for acetic acid at 25.0 °C, a value of $11.6 \times 10^{-6} \text{ s}^{-1}$ for methanol at 50.0 °C, and a value of $2.25 \times 10^{-6} \text{ s}^{-1}$ for ethanol at 50.0 °C. ^e Calculated from data at other temperatures. ^f $\log(k/k_0)_{2\text{AdOTr}}$ at 25 °C, where k_0 refers to the specific rate in 80% ethanol. ^g From ref 14.

limited number of Y_{OTr} values prompts us to publish our extensive study of 2-adamantyl tresylate solvolysis. For comparison with the Y_{OTr} values for ethanol-2,2,2-trifluoroethanol (TFE) mixtures, we have determined Y_{OTr} values for these solvents from a study of the solvolysis of 2-adamantyl *p*-toluenesulfonate (tosylate).

Tresylates react about 100 times faster than the corresponding tosylates and slightly slower than pentafluorobenzenesulfonates;⁴ for example, about 20 times slower for the 2-adamantyl esters in aqueous ethanol.⁵ Tresylates^{2-4,6} and pentafluorobenzenesulfonates^{4,5} are frequently used to bridge the reactivity gap between moderately good leaving groups, such as halide and tosylate ions, and the excellent anionic leaving groups, such as trifluoromethanesulfonate (triflate), fluorosulfonate, and perchlorate. As an *O*-trimethylsilylating agent, trimethylsilyl tresylate is 1.4×10^4 times as reactive as trimethylsilyl chloride.⁷ Fisher and Shiner⁸ have studied the solvolysis of 2-adamantyl tresylate in three aqueous organic solvents. More recently, a study of this compound (and also of the isomeric 1-adamantyl tresylate) has been reported for five pure organic and six aqueous organic solvents.³ Fărcașiu⁹

Table II. Enthalpies (ΔH^\ddagger) and Entropies (ΔS^\ddagger) of Activation for Solvolysis of 2-Adamantyl 2,2,2-Trifluoroethanesulfonate^a

solvent	$\Delta H^\ddagger_{298}, \text{kcal/mol}$	$\Delta S^\ddagger_{298}, \text{cal/mol K}$
80% EtOH ^b	25.8 ± 0.2	$+3.0 \pm 0.6$
MeOH ^c	28.7 ± 0.1	$+7.5 \pm 0.5$
EtOH ^c	29.8 ± 0.6	$+7.5 \pm 2.0^d$
$\text{CH}_3\text{CO}_2\text{H}$	27.5 ± 0.3	$+4.2 \pm 1.2$

^a Calculated using data of Table I and with associated standard errors. ^b On a volume-volume basis at 25 °C. ^c Based on two temperatures (50.0 and 75.0 °C), values for ΔH^\ddagger and ΔS^\ddagger of 27.9 kcal/mol and 5.1 cal/mol K for MeOH and of 28.6 kcal/mol and 4.1 cal/mol K for EtOH have been reported (ref 3). ^d Standard error estimated using the fractional error for the specific solvolysis rate associated with the 35 °C determination.

Table III. First-Order Rate Coefficients^a for the Solvolysis of 2-Adamantyl *p*-Toluenesulfonate^b in Mixtures^c of Ethanol (E) with Water or 2,2,2-Trifluoroethanol (T)

$T, ^\circ\text{C}$	$10^6k, \text{s}^{-1}$				
	80% EtOH	100% T	80% T-20% E	60% T-40% E	40% T-60% E
25.00	$(2.3)^{d,e}$	144 ± 2^f	21.8 ± 0.3	3.76 ± 0.11	$(0.84)^d$
40.30	22.4 ± 0.3				
50.00	95.5 ± 1.2				29.2 ± 0.6
59.80	319 ± 3				98.2 ± 1.4
70.20					352 ± 4

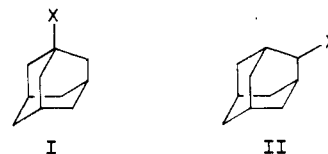
^a With associated standard deviations. ^b Concentration ca. 0.005 M. ^c On a volume-volume basis at 25 °C. ^d Calculated from the data at other temperatures. ^e A value of $2.4 \times 10^{-8} \text{ s}^{-1}$ has been reported (ref 14). ^f A value of $151 \times 10^{-8} \text{ s}^{-1}$ has been estimated (ref 14).

has studied the solvolyses of 1-substituted 2-adamantyl tresylates.

The original Grunwald-Winstein equation (eq 1) defines a scale of solvent ionizing power (Y) based on the solvolysis of *tert*-butyl chloride.¹⁰ In eq 1, k/k_0 represents the

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

specific rate of solvolysis in the solvent under consideration (k) relative to that in 80% ethanol (k_0), the standard solvent. The sensitivity (m) to changes in solvent ionizing power is defined as unity for the standard substrate. If a scale of solvent ionizing power is desired in which nucleophilic participation by the solvent is minimized, use of a 1-adamantyl (I)¹¹ or a 2-adamantyl (II)¹²⁻¹⁴ derivative as the standard substrate has been recommended.¹⁵



Results

Solvolyses in Ethanol, Methanol, Acetic Acid, and 80% Ethanol. Specific rates of solvolysis were determined at four temperatures in the 25–60 °C range. Throughout

(1) Abstracted, in part, from the Ph.D. Dissertation of D.C.H., Northern Illinois University, August 1988.

(2) Presented at the 193rd National Meeting of the American Chemical Society, Denver, Colorado, April 5–10, 1987; Abstract ORGN7.

(3) Takeuchi, K.; Ikai, K.; Shibata, T.; Tsugeno, A. *J. Org. Chem.* **1988**, *53*, 2882.

(4) Crossland, R. K.; Wells, W. E.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4217.

(5) Hawkinson, D. C.; Kevill, D. N. *J. Org. Chem.* **1988**, *53*, 3857.

(6) Examples of the use of tresylate as a leaving group, in systems other than adamantyl, include: (a) Richter, S.; Bregovec, I.; Sunko, D. E. *J. Org. Chem.* **1976**, *41*, 785. (b) Shiner, V. J., Jr.; Seib, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 862. (c) Lenoir, D.; Röhl, W.; Weiss, E.; Wenke, G. *Tetrahedron Lett.* **1976**, 1991. (d) Petty, R. L.; Ikeda, M.; Samuelson, G. E.; Boriack, C. J.; Onan, K. D.; McPhail, A. T.; Meinwald, J. *J. Am. Chem. Soc.* **1978**, *100*, 2404. (e) Creary, X. *J. Org. Chem.* **1979**, *44*, 3938. (f) McDonald, R. N.; Curi, C. A. *J. Am. Chem. Soc.* **1979**, *101*, 7116 and 7118. (g) Shiner, V. J., Jr.; Tai, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 436. (h) Lenoir, D.; Frank, R. M. *Chem. Ber.* **1981**, *114*, 3336. (i) Banert, K.; Kirmse, W.; Wroblowsky, H.-J. *Chem. Ber.* **1983**, *116*, 3591.

(7) Hergott, H. H.; Simchen, G. *Justus Liebigs Ann. Chem.* **1980**, 1718.

(8) Shiner, V. J., Jr.; Fisher, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 2553.

(9) (a) Fărcașiu, D. *J. Am. Chem. Soc.* **1976**, *98*, 5301. (b) Fărcașiu, D. *J. Org. Chem.* **1978**, *43*, 3878.

(10) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.

(11) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5977.

(12) 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.

(13) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540.

(14) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

(15) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1.

each kinetic run, constant integrated first-order rate coefficients were observed. Averages of all of the integrated first-order rate coefficients for duplicate runs, along with Y_{OTr} values defined at 25.0 °C, are reported in Table I. The specific rates of solvolysis in ethanol at 25.0 °C and in acetic acid at 50.05 °C were obtained by interpolation within plots of $\log(k/T)$ against T^{-1} . Table II presents the enthalpies (ΔH^\ddagger) and entropies (ΔS^\ddagger) of activation, calculated by using the experimental data reported in Table I.

Solvolyses in Solvents of Varying Ionizing Power. Specific rates of solvolysis have been determined for the following aqueous organic solvent systems: 100–50% ethanol, 100–50% methanol, 95–50% acetone, 95–50% dioxane, 100–50% TFE (six compositions for each of the above listed systems), and 97–80% HFIP (three compositions). The solvolyses in formic acid and in four ethanol–TFE mixtures were also studied. Since Y_{OTs} values were not available for ethanol–TFE mixtures, the specific rates of solvolysis of 2-adamantyl tosylate were determined for three of the compositions (the Y_{OTs} value for the fourth was then obtained by interpolation). The first-order rate coefficients for the solvolysis of 2-adamantyl tosylate are reported in Table III.

In Table IV are listed the averages of all of the integrated first-order rate coefficients from duplicate runs for 2-adamantyl tresylate solvolysis in each of the solvents studied, with the exception of those already listed in Table I. Calculated Y_{OTr} values and Y_{OTs} values (the latter largely from the literature^{14,16–19}) are also listed within Table IV. For most of the solvents, rate data were obtained at 25.0 °C. For solvents in which the solvolysis was extremely slow at 25.0 °C (90% ethanol, 95 and 90% acetone, and 95 and 90% dioxane), kinetic studies were conducted at 50.0 °C. Some solvolyses of intermediate reactivity were studied at both 25.0 and 50.0 °C.

Discussion

In the recently published study of 2-adamantyl tresylate solvolysis by Takeuchi and co-workers,³ the solutions were buffered by a slight excess of 2,6-lutidine or, in the case of acetic and formic acids, sodium acetate or sodium formate. We found, in our study, that all of the solvolyses proceeded to the predicted infinity titer, with constant first-order rate coefficients being observed over the considerable extent of reaction for which the kinetics was followed; accordingly, no buffer was added. For nine solvents, the first-order rate coefficients obtained by Takeuchi and co-workers³ are in good agreement with our values obtained in the absence of buffer. For two organic solvents, the values are lower than our values: by 18% for TFE and by 56% for formic acid. Although it cannot be taken as proof of the superiority of our values for these two solvents, it is worthy of note that our values would lie better on the plot of Y_{2AdOTr} against Y_{2AdOTs} , which is presented.³

For the slower reacting solvent systems, the Y_{OTs} values are not directly available from 2-adamantyl tosylate solvolysis. Values can be obtained indirectly from a study¹⁷ of 1-adamantyl tosylate in these solvents. Since the rates of solvolyses of 1-adamantyl tosylate are slightly more sensitive to solvent variation than the rates of solvolyses of 2-adamantyl tosylate,¹⁶ it has been suggested¹⁸ that Y_{OTs}

Table IV. First-Order Rate Coefficients for the Solvolysis of 2-Adamantyl 2,2,2-Trifluoroethanesulfonate^a in Organic and Aqueous Organic Solvents and Y_{OTr} Values^b

solvent ^{c,d}	T, °C	10^6k , s ⁻¹	Y_{OTr} ^e	Y_{OTs} ^f
90% EtOH	50.0	22.8 ± 0.2	-0.646	
	25.0		-0.715 ^g	-0.58
70% EtOH	25.0	9.81 ± 0.14	0.493	0.47
60% EtOH ^h	25.0	27.8 ± 0.4 ⁱ	0.945	0.92
50% EtOH	25.0	81.8 ± 2.4 ^j	1.414	1.29
90% MeOH	25.0	1.53 ± 0.01	-0.314	-0.17 ^k
80% MeOH	25.0	7.18 ± 0.15	0.357	0.47 ^k
70% MeOH	25.0	25.4 ± 0.3	0.906	1.02 ^k
60% MeOH	25.0	82.8 ± 1.2	1.419	1.52 ^k
50% MeOH ^h	25.0	432 ± 2	2.136	2.00 ^k
95% acetone	50.0	0.671 ± 0.005	-2.177	-2.54 ^l
90% acetone	50.0	1.93 ± 0.02 ⁱ	-1.718	-1.70 ^l
80% acetone	50.0	15.0 ± 0.2	-0.828	
	25.0	0.374 ± 0.005 ⁱ	-0.927	-0.79 ^l
70% acetone	50.0	63.6 ± 0.8	-0.200	
	25.0	1.81 ± 0.03	-0.242	-0.01 ^l
60% acetone	50.0	225 ± 5	0.348	
	25.0	7.94 ± 0.10	0.401	0.66
50% acetone ^b	50.0	809 ± 13	0.904	
	25.0	33.2 ± 0.3	1.022	1.26 ^k
95% dioxane	50.0	0.110 ± 0.002	-2.961	
90% dioxane	50.0	0.818 ± 0.009	-2.091	-2.06 ^l
80% dioxane	50.0	7.87 ± 0.06	-1.108	
	25.0	0.201 ± 0.005	-1.195	-1.10 ^l
70% dioxane	50.0	38.6 ± 0.6	-0.417	
	25.0	1.10 ± 0.01	-0.458	-0.42 ^m
60% dioxane	25.0	5.58 ± 0.10	0.248	
50% dioxane ^h	25.0	28.4 ± 0.4	0.954	
TFE ⁿ	25.0	161 ± 2 ⁱ	1.707	1.80
97% TFE	25.0	169 ± 1 ^j	1.730	1.83
90% TFE	25.0	196 ± 2	1.793	1.90 ^o
80% TFE	25.0	242 ± 3	1.844	1.94 ^o
70% TFE	25.0	292 ± 5 ^j	1.966	2.00
50% TFE ^p	25.0	460 ± 8	2.163	2.14
97% HFIP ^q	25.0	7860 ± 190	3.396	3.53 ^r
90% HFIP	25.0	2420 ± 80	2.885	2.90 ^r
80% HFIP	25.0	1260 ± 20	2.602	2.57 ^r
80% T-20% E	25.0	25.9 ± 0.2	0.915	0.977 ^s
60% T-40% E	25.0	4.54 ± 0.04	0.158	0.213 ^s
40% T-60% E	25.0	0.841 ± 0.013	-0.574	-0.437 ^s
20% T-80% E	25.0	0.181 ± 0.004	-1.240	-1.178 ^s
HCOOH	25.0	3160 ± 40 ^t	3.000	3.04

^a Concentration of ca. 0.0055 M unless otherwise noted; rate coefficients presented with standard deviations. ^b For additional values, see Table I. ^c With water as the other component, except for TFE–EtOH (T–E) mixtures. ^d On a volume–volume basis, at 25 °C, except for TFE–H₂O and HFIP–H₂O mixtures, which are on a weight–weight basis. ^e $\log(k/k_0)_{2AdOTr}$ at 25.0 or 50.0 °C, where k_0 refers to the specific rate in 80% ethanol. Y_{OTr} values at 50.0 °C for methanol, ethanol, and acetic acid are, respectively, -0.948, -1.638, and -0.825. ^f Values from ref 14 unless otherwise stated. ^g Interpolated from a plot of Y_{OTr} at 25.0 °C against Y (ref 10) for EtOH–H₂O mixtures. ^h Concentration ca. 0.0045 M. ⁱ Reference 3 reports values at 25.0 °C of $27.8 \times 10^{-6} \text{ s}^{-1}$ for 60% EtOH, $132 \times 10^{-6} \text{ s}^{-1}$ for TFE, $0.382 \times 10^{-6} \text{ s}^{-1}$ for 80% acetone, $1370 \times 10^{-6} \text{ s}^{-1}$ for HCOOH, and (extrapolated value) $79.2 \times 10^{-6} \text{ s}^{-1}$ for 50% EtOH; a value of $1.93 \times 10^{-6} \text{ s}^{-1}$ for 90% acetone at 50.0 °C was reported. ^j Reference 8 reports values at 25.0 °C of $81.7 \times 10^{-6} \text{ s}^{-1}$ for 50% EtOH, of $171 \times 10^{-6} \text{ s}^{-1}$ for 97% TFE, and of $298 \times 10^{-6} \text{ s}^{-1}$ for 70% TFE. ^k From ref 16. ^l Value obtained from data of ref 17, using eq 2 (ref 18). ^m Extrapolated value. ⁿ 2,2,2-Trifluoroethanol. ^o Interpolated value. ^p Concentration ca. 0.0034 M. ^q 1,1,1,3,3,3-Hexafluoro-2-propanol. ^r From ref 19. ^s This study.

values, based on 1-adamantyl tosylate solvolysis, should be obtained using eq 2. We have previously²⁰ used Y_{OTs} values for aqueous acetone obtained in this way, and Table

$$Y_{OTs} = 0.868 \log(k/k_0)_{1AdOTs} + 0.027 \quad (2)$$

(16) Bentley, T. W.; Carter, G. E. *J. Org. Chem.* **1983**, *48*, 579.
 (17) Kevill, D. N.; Kolwyck, K. C.; Weitz, F. L. *J. Am. Chem. Soc.* **1970**, *92*, 7300.
 (18) Allard, B.; Casadevall, E. *Nouv. J. Chim.* **1985**, *9*, 565.
 (19) Allard, B.; Casadevall, E. *Nouv. J. Chim.* **1983**, *7*, 569.

(20) Kevill, D. N.; Bahnke, R. W. *Tetrahedron*, accepted for publication.

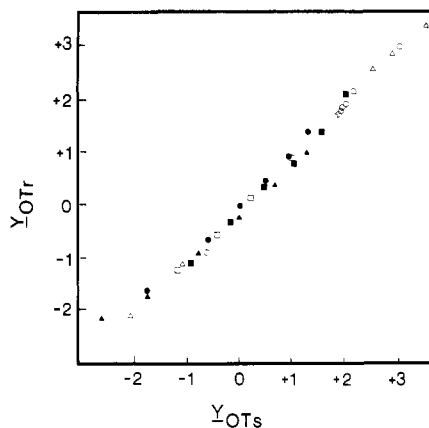


Figure 1. Grunwald-Winstein solvent ionizing power: plot of Y_{OTr} against Y_{OTs} . The symbols are as follows: (●) aqueous ethanol; (■) aqueous methanol; (▲) aqueous acetone; (○) formic acid, acetic acid, and aqueous TFE; (△) 90 and 80% dioxane and aqueous HFIP; (□) TFE-EtOH.

Table V. Slopes (m) and Intercepts (c) for Plots of Y_{OTr} against Y_{OTs} .

solvent ^a	n^b	m	c	r^c
EtOH/H ₂ O ^d	6	1.08 ± 0.02	-0.02 ± 0.02	0.999
MeOH/H ₂ O ^d	6	1.08 ± 0.03	-0.14 ± 0.04	0.998
acetone/H ₂ O ^e	6	0.83 ± 0.03	-0.18 ± 0.04	0.998
acetone/H ₂ O ^d	4	0.95 ± 0.02	-0.20 ± 0.02	0.999
dioxane/H ₂ O ^e	3	1.02 ± 0.01	0.02 ± 0.01	1.000
TFE/H ₂ O ^d	6	1.24 ± 0.17	-0.51 ± 0.32	0.966
HFIP/H ₂ O ^d	3	0.82 ± 0.01	0.49 ± 0.04	1.000
TFE/EtOH ^d	6	1.01 ± 0.01	-0.09 ± 0.02	1.000

^a On a volume to volume basis, except for TFE/H₂O and HFIP/H₂O mixtures, which are on a weight to weight basis. ^b Number of solvents examined in given composition range. ^c Correlation coefficient. ^d Y_{OTr} values at 25.0 °C. ^e Y_{OTr} values at 50.0 °C.

IV contains these and also new values for aqueous dioxane mixtures. It is of interest that a plot of Y_{2AdOTr} against Y_{1AdOTr} shows³ an identical slope (0.868) with that used in eq 2, giving strong support to the relationship.

The Y_{OTr} and Y_{OTs} values of Table I and those entries of Table IV for which both Y_{OTr} and Y_{OTs} values are reported (except for 70% dioxane, where the extrapolated Y_{OTs} is rather approximate) are plotted in Figure 1. An excellent linear free energy relationship (LFER) plot is obtained with a slope of 1.000 ± 0.014 and intercept of -0.070 ± 0.022 ($n = 35$, $r = 0.997$). When the point for 95% acetone is omitted, the correlation is slightly improved, with a slope of 1.018 ± 0.011 and an intercept of -0.096 ± 0.018 ($n = 34$, $r = 0.998$). For 95% acetone, there could well be a significant error in the Y_{OTs} value because of a relatively large adjustment in obtaining the value by use of eq 2; a $\log(k/k_0)_{1AdOTs}$ value of -2.95 is converted into a Y_{OTs} value of -2.54 . Where available, Y_{OTr} values obtained at 25.0 °C were used in the construction of Figure 1. However, four of the 35 values are from measurements at 50.0 °C (Table IV). Several systems were studied at both 25.0 and 50.0 °C, and these show that, although $|Y_{OTr}|$ values tend to be slightly lower at the higher temperature, the differences are sufficiently small to justify plotting Y_{OTr} values from both temperatures on the same LFER plot.

The slopes, intercepts, and correlation coefficients for individual mixed solvent systems have been computed separately, and these results are presented in Table V. In each case a good correlation is obtained. For aqueous TFE mixtures, five of the points are closely bunched, and heavy weight is given to the 50% TFE point, such that the values for the slope and intercept will be less reliable than for the

Table VI. Relative Rates of Solvolysis of 2-Adamantyl Sulfonates at 25.0 °C

solvent	OTs ^a	OTr ^b	PFBS ^c	OTf ^d
80% EtOH	1	131	2590	891 000
MeOH	1	84.5	2050	977 000
EtOH	1	95.3	2790	871 000
CH ₃ CO ₂ H	1	63.2	407	77 600

^a Specific rates of solvolysis of 2-adamantyl *p*-toluenesulfonate from ref 14. ^b Specific rates of solvolysis of 2-adamantyl 2,2,2-trifluoroethanesulfonate from Table I. ^c Specific rates of solvolysis of 2-adamantyl pentafluorobenzenesulfonate from ref 5. ^d Specific rates of solvolysis of 2-adamantyl trifluoromethanesulfonate from ref. 21.

other mixed solvent systems. All of the slopes are close to unity, and the intercepts are modest. Except for the TFE-water system, the correlation coefficients are in excess of 0.998.

When the Y_{OTr} values of Tables I and IV are plotted against Y_{OTf} values^{21,22} the correlation is much inferior to the correlation with Y_{OTs} values.³ This behavior is to be expected because of the poor correlation²¹ of Y_{OTf} with Y_{OTs} ; data that correlate well with one scale must correlate poorly with the other one.

A comparison of the specific rates of solvolysis of four 2-adamantyl sulfonates (tosylate,¹⁴ tresylate, pentafluorobenzenesulfonate,⁵ and triflate²¹) is presented in Table VI. The order of reactivity OTs < OTr < PFBS < OTf is an agreement with the observation of Sheppard²³ that the inductive electron-withdrawing abilities of the pentafluorophenyl and 2,2,2-trifluoroethyl groups are intermediate between those of phenyl and the powerful electron-withdrawing trifluoromethyl group and the observation⁴ that (as expected) increases in the electron-withdrawing ability of the substituent on sulfur strongly enhance the solvolytic reactivity of sulfonate esters.

There has been considerable discussion recently^{20-22,24,25} concerning the extent to which scales of solvent ionizing power Y_X , established for an anionic leaving group X, can be applied to solvolyses with a different leaving group. For 1-adamantyl halides the scales for X = Cl, Br, or I correlate well with each other and reasonably well with Y_{OTs} .^{26,27} Among the halide ion leaving groups, differences in slope of the Y value correlations were rationalized as being due to reduced sensitivity to solvent ionizing power as the size of the leaving group increases, allowing better internal charge distribution.²⁷ This in turn would be expected to influence the extent of electrophilic solvent assistance,²⁸ with the leaving groups showing the better internal charge distribution tending to be less dependent upon electrophilic solvation for stabilization. For some solvents at least, other leaving groups, principally triflate,^{21,22} perchlorate,^{22,24} and picrate²² required quite different Y_X values from those operating for halide or tosylate leaving groups, leading to the suggestion that each leaving group requires its own Y_X scale. Recently carried out studies of adamantyl esters with pentafluorobenzenesulfonate,⁵ 2-(trimethylamino)ethanesulfonate ([2]betylrate),²⁰ nitrate,^{1,2} heptafluorobutyrate,²⁵ trifluoroacetate,²⁵ and (in the present study)

(21) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* 1985, 50, 3330.

(22) Bentley, T. W.; Roberts, K. *J. Org. Chem.* 1985, 50, 4821.

(23) Sheppard, W. A. *J. Am. Chem. Soc.* 1970, 92, 5419.

(24) Kevill, D. N.; Bahari, M. S.; Anderson, S. W. *J. Am. Chem. Soc.* 1984, 106, 2895.

(25) Bentley, T. W.; Roberts, K., submitted for publication. We thank Dr. Bentley for providing us with a preprint of this manuscript.

(26) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* 1982, 104, 5741.

(27) Bentley, T. W.; Carter, G. E.; Roberts, K. *J. Org. Chem.* 1984, 49, 5183.

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

tresylate have found that the Y_X values correlate quite well with Y_{OT_8} with slopes of close to unity. This suggests that the problems associated with leaving group variation may not be as severe as previously thought. Indeed, Figure 1 represents an instance where modest rate differences, resulting from a modest variation in the leaving group from tosylate to tresylate, lead to an excellent LFER plot of unit slope.

Either the tresylate or the pentafluorobenzenesulfonate would fill the gap between the extremely good leaving groups, such as triflate, and the moderately good leaving groups, such as tosylate, with the pentafluorobenzenesulfonate being a slightly better nucleofuge.^{4,5} In solvolysis studies, the tresylate has the advantage of a higher solubility in the more aqueous solvents, and it is possible to examine a wider range of a mixed aqueous organic solvent. The tresylate also has the advantage that its esters can be prepared under mild conditions by conversion of the sulfonyl chloride to the sulfene followed by addition of the alcohol,⁴ a route not available for the preparation of pentafluorobenzenesulfonate esters. A factor favoring the use of pentafluorobenzenesulfonates is that while both acid chlorides are commercially available, the pentafluorobenzenesulfonyl chloride is less than one quarter of the cost of the 2,2,2-trifluoroethanesulfonyl chloride.²⁹

Experimental Section

Materials. The purifications of acetone, dioxane, ethanol, and methanol were as previously described.¹⁷ The purifications of acetic acid,³⁰ formic acid,³¹ 1,1,1,3,3,3-hexafluoro-2-propanol,³² and

2,2,2-trifluoroethanol³³ were also performed by previously reported procedures. 2-Adamantanol (Aldrich) was recrystallized from hexane prior to use. The 2,2,2-trifluoroethanesulfonyl chloride (Willow Brook Labs) was used without further purification.

2-Adamantyl 2,2,2-Trifluoroethanesulfonate. The general procedure of Crossland, Wells, and Shiner⁴ for preparation of tresylate esters was used to convert 2-adamantanol (6.00 g, 0.039 mol), in 200 mL of dry dichloromethane, into 2-adamantyl tresylate by treatment with triethylamine and 2,2,2-trifluoroethanesulfonyl chloride. The crude product was recrystallized from hexane to give 10.24 g (87%) of 2-adamantyl tresylate, mp 73–74 °C (lit.^{3,34} mp 76 °C): ¹H NMR (CDCl₃) δ 1.58–2.21 (m, 14), 3.89 (q, 2, J = 8.69 Hz, OSO₂CH₂CF₃), 5.04 (s, 1, CHOSO₂CH₂CF₃); IR (KBr pellet) includes peaks at 905, 920, 1090, 1140, 1180, 1190, 1255, 1275, 1335, 1385, 2918 cm⁻¹. Anal. Calcd for C₁₂H₁₇SO₃F₃: C, 48.32; H, 5.74; S, 10.75; F, 19.11. Found: C, 48.28; H, 5.80; S, 10.99; F, 18.26.

Kinetic Procedures. The kinetic procedures paralleled those reported⁵ for 2-adamantyl pentafluorobenzenesulfonate. The formolysis was followed by quenching each aliquot in a freshly prepared solution consisting of 5 mL of 0.025 wt % bromocresol green in acetic acid and 20 mL of dioxane at 0 °C. The quenched aliquots were then titrated with a standardized (ca. 4.2 × 10⁻³ N) solution of sodium acetate in acetic acid.³⁵ For runs in solvents containing the relatively expensive 1,1,1,3,3,3-hexafluoro-2-propanol, the size of the aliquots was reduced to 1 mL, and 10 mL of reactant solution was used.

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(31) Winstein, S.; Marshall, H. *J. Am. Chem. Soc.* **1952**, *74*, 1120.

(32) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1244.

(33) Rappoport, Z.; Kaspi, J. *J. Am. Chem. Soc.* **1974**, *96*, 4518.

(34) The short communication⁸ reporting the preparation of 2-adamantyl tresylate gives only a melting point. Accordingly, we report additional characterization data that we have obtained.

(35) Winstein, S.; Holness, N. *J. Am. Chem. Soc.* **1955**, *77*, 5562.

(29) Tresyl chloride has recently become reavailable (Aldrich) after a period of several years. Our sample had been purchased an appreciable number of years before this study was undertaken.

(30) Winstein, S.; Hanson, C.; Grunwald, E. *J. Am. Chem. Soc.* **1948**, *70*, 812.