mechanistic significance assigned to k_Δ, we should expect a correlation of k_Δ values with solvolysis rates (k_t) of neophyl-OTs,[5b] for which ionization occurs with phenyl participation at a rate equal to k_t and dependent on solvent ionizing power but not nucleophilicity. On the other hand, the k_s process should depend on a blend of nucleophilicity and ionizing power for which the simple EtOTs should be a rather good model.[5b] Thus, k_s would be expected to correlate rather well with k_t values for EtOTs.

As illustrated in Figure 1, a good linear free-energy correlation exists between log k_Δ for *n*-PrOTs and log k_t for neophyl-OTs. The slope of the least-squares line is 0.846 with a mean deviation of 0.08 log unit for the fit of the AcOH, HCOOH, and CF_3COOH points. Similarly, log k_s is linear in log k_t for EtOTs. The slope is 0.925 with a mean deviation of 0.01 log unit for the four solvents. With the aid of the log k_Δ plot 0.002% k_Δ is estimated in EtOH.

For *i*-BuOTs solvolysis in EtOH, AcOH, and HCOOH, k_s was approximated by assigning the yield of unrearranged *i*-Bu solvolysis product to the k_s route, the remainder being assigned to k_Δ due to H participation as in IIa and CH_3 participation as in IIb. Listed in Table II are the k_t, k_s, and composite k_Δ values. A good correlation exists between log k_s for *i*-BuOTs and log k_t for EtOTs at 75°. The slope of the least-squares line is 0.86, with a mean deviation of 0.02 log unit for the fit of the EtOH, AcOH, and HCOOH points.

Solvent correlations for *n*-PrOTs and *i*-BuOTs strongly support the interpretation of solvolysis on the basis of discrete k_Δ and k_s processes in EtOH, AcOH, HCOOH, and CF_3COOH. Isotope effects are also reasonable.[3c] For k_Δ the β-deuterium isotope effects are *ca.* 1.8, while for k_s the range is 1.06 to 1.28. The $\Delta S^{\ddagger}$ values seem to be characteristically lower[2c] for MeOTs and EtOTs, which solvolyze by the k_s route, than for *i*-BuOTs and neoPenOTs, which solvolyze mainly by the k_Δ route.

It is clear that the major shift from k_s to k_Δ in the solvolysis of *n*-PrOTs occurs in going from HCOOH to CF_3COOH. For *i*-BuOTs, the shift occurs between EtOH and AcOH. For neoPenOTs, k_Δ is dominant even in EtOH where the 92.7% rearranged products[4f] are ascribed to the k_Δ process due to CH_3 participation (see III) and the 7.3% neoPenOEt[4f] is assigned to k_s. In AcOH, k_t for neoPenOTs is already >99.97% k_Δ.[11] The least-squares line for the plot of log k_Δ for neoPenOTs at 75° *vs.* neophyl-OTs has a slope of 0.833 for the solvents EtOH, AcOH, HCOOH, and CF_3COOH. The mean deviation for the fit of the points is 0.25 log unit.

It is interesting to examine the k_Δ and k_s rate constants for the primary alkyl tosylates as regards their variation with structure. For k_Δ the ROTs structure sequence is PhEt $\gtrsim$ *i*-Bu $\gtrsim$ neoPen > *n*-Pr, while for k_s the ROTs structure sequence is Et $\simeq$ *n*-Pr > PhEt > *i*-Bu > neoPen.

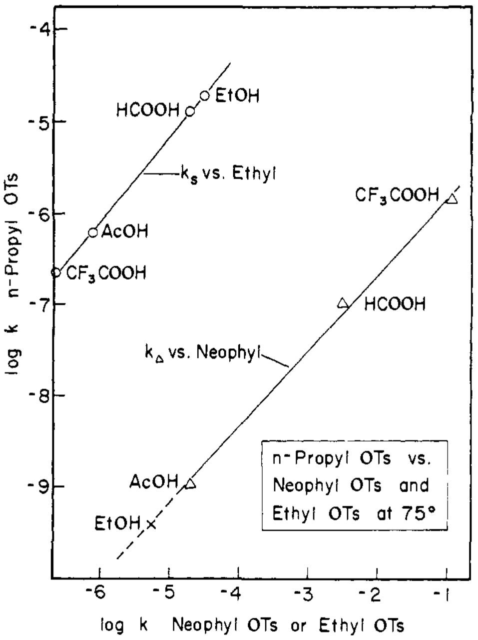

Figure 1. Trifluoroacetolysis of simple primary alkyl toluenesulfonates.

Trifluoroacetic acid is certainly an effective solvent for bringing out k_Δ. Even more effective is FSO_3H, and in the following communication[12] we report the results of a study of solvolysis of the simple primary alkyl tosylates in this solvent.

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[11] The acetolysis of neoPenOTs at 125° in the presence of 0.036 *M* NaOAc yields 0.03 ± 0.007% neoPenOAc. However, all the evidence indicates that most of this small amount can be ascribed to the reaction with NaOAc.

[12] A. Diaz, I. L. Reich, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5637 (1969).

Solvolysis of Primary Tosylates in Fluorosulfuric Acid[1]

Sir:

As reported in the preceding communication,[2] CF_3COOH is quite effective in increasing k_Δ/k_s ratios in solvolysis of simple primary tosylates. Another such solvent is concentrated H_2SO_4, as is reported by Myhre in an accompanying communication.[3a] In this communication we report on the solvolysis of primary tosylates in FSO_3H. This solvent, with its extremely low nucleophilicity and tremendously high ionizing power, is even more effective in promoting high k_Δ/k_s ratios. In FSO_3H, even *n*-PrOTs reacts completely by the anchimerically assisted k_Δ route, as do *i*-BuOTs and neoPenOTs.

Solvolyses in FSO_3H were followed directly by nmr[4] in nmr tubes[5] at preset probe temperatures determined before and after the run from the temperature-sensitive chemical shifts of MeOH. The solvolysis of *n*-PrOTs was followed using the disappearance of the signals for the α-H at δ 4.28 and the γ-H at δ 0.85 as *n*-PrOTs forms isopropyl product. The *p*-methyl and aromatic proton signals were used as standards. Good first-order rate constants (k_t) were observed between 5 and 90% reaction, and the infinities were 100%. Added $KFSO_3$ reduces k_t, k_t being *ca.* inversely proportional

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[1] Research sponsored by the National Science Foundation.

[2] I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5635 (1969).

[3] (a) P. C. Myhre and E. Evans, *ibid.*, **91**, 5641 (1969); (b) P. C. Myhre and K. S. Brown, *ibid.*, **91**, 5639 (1969).

[4] All chemical shifts are relative to CH_2Cl_2 at δ 5.30.

[5] After the initial nmr spectrum was recorded, MeOTs, EtOTs, and *n*-PrOTs could be recovered from the reaction solution in 90, 91, and 75%, yield, respectively.

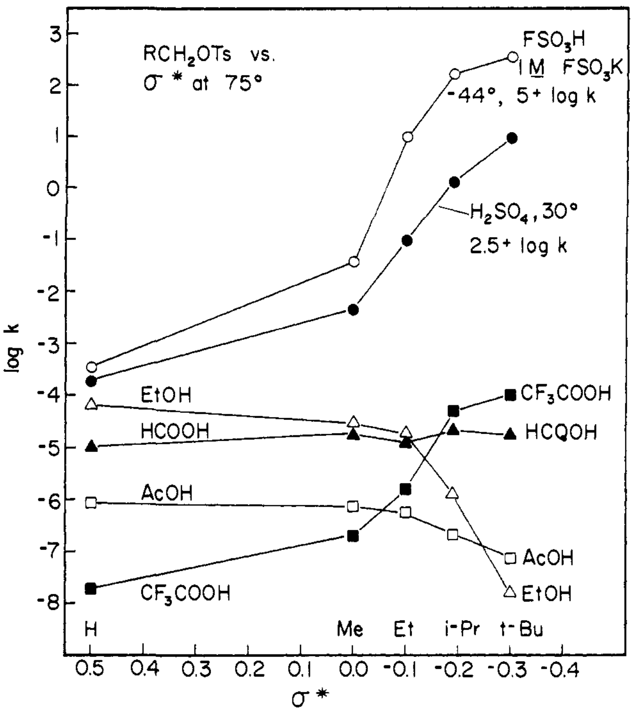

Figure 1. Solvolysis of primary tosylates in various solvents.

to $KFSO_3$ concentration, as is illustrated in Table I. The products of reaction are *i*-$PrOSO_2F$ (multiplet at δ 5.45 and doublet at δ 1.55) and *p*-toluenesulfonyl fluoride.[6] The solvolysis of 2,2-d_2-1-PrOTs is somewhat slower, k_H/k_D being *ca.* 2.4 at −50°. The isopropyl product in this case shows no signal at δ 5.45 while the methyl singlet at δ 1.55 integrates for 5.1 ± 0.3 protons, supporting isopropyl product formation *via* simple 1,2-hydride shift.[7,8]

Table I. Solvolysis Rate Constants for *n*-PrOTs[a] in FSO_3H

Temp, °C	$KFSO_3$, *M*	10^3k,[b] sec^{-1}
−61		0.281 ± 0.026
−54		1.12 ± 0.16
−50		1.13 ± 0.01
−44		5.35 ± 0.58
−27.5		11.6 ± 1.0
−27.5	0.25	3.03 ± 0.01
−27.5	0.50	1.77 ± 0.23
−27.5	0.75	11.4 ± 0.01
−27.5	1.0	0.930 ± 0.008
−17	1.0	2.42 ± 0.04
−17	1.5	1.65
−10	1.0	4.98 ± 0.04
−7.5	1.0	6.30
−5	1.0	8.42 ± 0.28

[a] 0.50 *M* ROTs. [b] Average of two to four runs.

The solvolysis of MeOTs, followed using the shift of the alkyl methyl proton signal from δ 3.98 to 4.23, shows good first-order kinetics. In the absence of salt the reaction proceeds to a 17% MeOTs-83% $MeOSO_2F$ equilibrium mixture. The addition of $KFSO_3$ drives the reaction to completion and reduces the rate as in the case of *n*-PrOTs. The solvolysis of EtOTs in FSO_3H containing 1.0 *M* $KFSO_3$, followed using the shift in the α-proton signal from δ 4.35 to 4.74, showed good first-order kinetics (Table II).

Table II. Rates of Solvolysis for Some Primary RCH_2OTs[a] in FSO_3H Containing 1.0 *M* $KFSO_3$

RCH_2OTs	Temp, °C	10^3k, sec^{-1}	Rel *k*
MeOTs	−44[b]	3.4×10^{-6}	1.0
MeOTs	+50	0.817 ± 0.17	
MeOTs	+62	2.57 ± 0.07	
MeOTs	+82	13.3 ± 0.3	
EtOTs	−44[b]	4.0×10^{-4}	120
EtOTs	+16	0.451 ± 0.011	
EtOTs	+28.5	1.36 ± 0.03[c]	
EtOTs	+45	6.6	
EtOTs	+53	9.9 ± 1.6	
n-PrOTs	−44[b]	0.11[b]	3.2×10^4
i-BuOTs	−44	1.83 ± 0.05	5.4×10^5
neoPenOTs	−44	3.87 ± 0.23	1.1×10^6

[a] 0.5 *M* ROTs. [b] Extrapolated value. [c] Lit.[3b] 1.1×10^{-3} sec^{-1} at 30°.

At −78° in FSO_3H, *i*-BuOTs gave rise extremely rapidly to the *t*-butyl cation[9a] with its nmr signal at δ 3.85, this species being observed in *ca.* 60% yield. Since the 2-butyl cation rearranges rapidly[9a,c] to *t*-butyl in FSO_3H, it is not clear what portions of the ionization are due to methyl and hydrogen participation, respectively. It is probable that methyl participation is quite competitive with that of hydrogen since methyl participation is increasingly important in the solvent sequence,[2,3a] AcOH < HCOOH < CF_3COOH < H_2SO_4. In FSO_3H containing 1 *M* $KFSO_3$, the disappearance of *i*-BuOTs is sufficiently slow to permit following the reaction at −44°. Good first-order rate constants were obtained following the disappearance of the γ-proton signal at δ 0.9 (Table II). Under these conditions only products of decomposition were observed. The results with neoPenOTs parallel those with *i*-BuOTs. In FSO_3H at −77°, neoPenOTs gave rise very rapidly to the *t*-amyl cation,[9b] observed in *ca.* 77% yield. The solvolysis at −44° in FSO_3H containing 1 *M* $KFSO_3$, followed with the aid of the α-proton signal at δ 3.92 in the neoPenOTs, showed good first-order behavior (Table II).

One of the striking features of the present data is the rate sequence for the primary tosylates in FSO_3H solvent. As summarized in Table III, the MeOTs-EtOTs-*n*-PrOTs-*i*-BuOTs-neoPenOTs sequence of solvolysis rates in FSO_3H is a steeply ascending one, namely, $1:120:3.3 \times 10^4:5.4 \times 10^5:1.1 \times 10^6$. This is more steeply ascending than in H_2SO_4,[3a] which in turn is more steeply ascending than in CF_3COOH.[2] The dramatic change in the trend of the solvolysis rates for the primary RCH_2OTs series, as solvent varies from EtOH[10] to

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(6) *p*-Toluenesulfonyl fluoride, mp 38–38.5°, with a correct carbon and hydrogen analysis, was recovered in 95.5% yield from the solvolysis of MeOTs: see W. Davies and J. H. Dick, *J. Chem. Soc.*, 2104 (1931).

(7) The presence of protonated cyclopropane intermediates gives rise to considerable hydrogen exchange with solvent (see ref 8).

(8) (a) R. L. Baird and A. A. Aboderin, *Tetrahedron Lett.*, 235 (1963); (b) R. L. Baird and A. A. Aboderin, *J. Amer. Chem. Soc.*, **86**, 252 (1964); (c) C. C. Lee and L. Gruber, *ibid.*, **90**, 3775 (1968).

(9) (a) G. A. Olah, *et al.*, *ibid.*, **86**, 1360 (1964); (b) G. A. Olah, *et al.*, *ibid.*, **87**, 2997 (1965); (c) M. Saunders, E. L. Hagen, and J. Rosenfeld, *ibid.*, **90**, 6882 (1968).

(10) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

Table III. Summary of Relative Rates of Some Primary Tosylates in Various Solvents

Solvent	Temp, °C	Rel k (ROTs) Me	Et	n-Pr	i-Bu	neoPen
EtOH[a]	75.0	4040	1750	1140	78	1.0
AcOH[a]	75.0	10	9.2	7.3	2.8	1.0
HCOOH[a]	75.0	1.0	1.8	1.2	2.2	1.8
CF_3COOH[b]	75.0	1.0	12.5	93	3060	6000
96% H_2SO_4[c]	30	1.0	26	530	7500	50,000
FSO_3H[d]	−44	1.0	118	3.3×10^4	5.4×10^5	1.14×10^6

[a] Reference 10. [b] Reference 2. [c] Reference 3a. [d] 1.0 M $KFSO_3$.

AcOH[10] to HCOOH[10] to CF_3COOH[2] to H_2SO_4[3a] to FSO_3H, is visually apparent in Figure 1 where log k_t is plotted *vs.* the Taft σ^* for R.[11] Thus, in going from EtOH to FSO_3H, the MeOTs/neoPenOTs rate ratio changes by a factor of *ca.* 10.[10] Of the solvolyzing solvents listed in Table III, FSO_3H seems to be the most efficient in promoting a high k_Δ/k_s ratio for a marginal RCH_2OTs case such as n-PrOTs.

Besides the structural rate sequences in the different solvents, it is interesting to compare the solvent–rate sequences for the different primary RCH_2OTs substrates. Thus, the solvent sequence of k_t values for MeOTs, whose solvolysis depends on a blend of nucleophilicity and ionizing power of solvent, is EtOH > AcOH < HCOOH > CF_3COOH < H_2SO_4 < FSO_3H, the smallest k_t being observed in CF_3COOH. For EtOTs and n-PrOTs, the variation of k_t with solvent is similar, but the changes are not as pronounced. Because of the k_Δ contribution, the k_t for n-PrOTs in CF_3COOH is now large enough that AcOH provides the smallest k_t. For i-BuOTs, with k_Δ now more dominant, the solvent sequence is EtOH > AcOH < HCOOH < CF_3COOH < H_2SO_4 < FSO_3H, k_t in CF_3COOH exceeding that in EtOH, AcOH, or HCOOH. Finally, for neoPenOTs, for which k_Δ is dominant in all six solvents, the solvent sequence reflects ionizing power but not nucleophilicity. For this substrate the sequence is EtOH < AcOH < HCOOH < CF_3COOH < H_2SO_4 < FSO_3H.

In recent times, FSO_3H has become a very useful solvent for direct observation[12] of carbonium ions. It is thus interesting to place this solvent on a scale of ionizing power along with the more conventional solvents. Using the k_Δ for n-propyl tosylate,[2] which reflects ionizing power and not nucleophilicity, the relative rates at 30° for the solvent sequence EtOH–AcOH–HCOOH–CF_3COOH–H_2SO_4–FSO_3H (1.0 M $KFSO_3$)–FSO_3H are *ca.* $0.4:1.0:80:6.0 \times 10^3:2.5 \times 10^8:8.5 \times 10^{11}:1.4 \times 10^{13}$. The k_Δ for n-PrOTs is only 0.85 times as sensitive[2] to solvent change as is neophyl-OTs. Thus, a scale[13] based on neophyl-OTs makes FSO_3H *ca.* 10^{15} times more ionizing than AcOH.

Regarding the nature of the solvolysis of ROTs substrates in FSO_3H solvent, it is interesting that rate is depressed by $KFSO_3$, the rate tending to be approximately inversely proportional to the $KFSO_3$ concentration. This is in line with a rate-determining C–O heterolysis in the conjugate acid, $ROTsH^+$ (eq 2), a small amount of which is in equilibrium with the unprotonated ROTs in FSO_3H containing added $KFSO_3$ (eq 1). That the equilibrium in eq 1 should lie to the left is expected from what is known regarding the acidity[12] of FSO_3H and the basicity of ROTs substrates.[14] Thus, for the solvolysis rates in Tables I and II the ground-state ROTs substrates are largely unprotonated, while the corresponding transition states are fully protonated.

$$\mathrm{ROTs} + \mathrm{FSO_3H} \rightleftharpoons \mathrm{ROTsH^+} + \mathrm{FSO_3^-} \quad (1)$$

$$\mathrm{ROTsH^+} \longrightarrow \mathrm{R^+} + \mathrm{HOTs} \quad (2)$$

Acknowledgment. We thank Dr. P. Myhre for helpful discussions and information prior to publication about the behavior of the alkyl tosylates in concentrated H_2SO_4.

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[11] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 556 ff.

[12] R. J. Gillespie, *Accounts Chem. Res.*, 1, 202 (1968).

[13] S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Amer. Chem. Soc.*, 83, 618 (1961).

[14] Using the K_b for $MeOSO_2Me$ in H_2SO_4 of 10^{-4} mol/kg[15a] and the 10-fold increase in K_b for $MeNO_2$ between H_2SO_4 and FSO_3H,[15b] we can estimate a K_b of 10^{-3} mol/kg for $MeOSO_2Me$ in FSO_3H. On the basis of such a K_b, 0.4 M ROTs is only 5% protonated in FSO_3H and only 0.1% protonated in the presence of 1.0 M $KFSO_3$.

[15] (a) S. K. Hall and E. A. Robinson, *Can. J. Chem.*, 42, 1113 (1964); (b) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, 3, 1149 (1964).

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Solvolysis of Primary Alkyl Toluenesulfonates in Concentrated Sulfuric Acid. Evidence of Hydrogen Participation[1,2]

Sir:

The response of a hydrogen or an alkyl group to positive charge developing at neighboring carbon has long been a subject of study and discussion. In accompanying communications,[3] Winstein and coworkers show that the use of CF_3COOH and HSO_3F as solvents for solvolysis studies permits structural differentiation and characterization of this response in some of the simplest alkyl systems. We report here related studies of alkyl p-toluenesulfonate (tosylate) solvolysis in 96% H_2SO_4.

The pattern of solvolysis rates (10^5k, sec^{-1}, at 30°) of methyl (0.06), ethyl (1.55), propyl (32.1), isobutyl (450), and neopentyl (>3000) tosylate (0.2 M) in 96% H_2SO_4 presents a striking departure from that observed

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] P. C. Myhre and K. S. Brown, presented, in part, at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract P 194.

[3] (a) I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, 91, 5635 (1969); (b) *ibid.*, 91, 5637 (1969).