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

		Rel k (ROTs)				
Solvent	Temp, °C	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.* 0.4:1.0:80:6.0×10^3:2.5×10^8:8.5×10^{11}:1.4×10^{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.

$$ROTs + FSO_3H \rightleftharpoons ROTsH^+ + FSO_3^- \qquad (1)$$

$$ROTsH^+ \longrightarrow R^+ + HOTs \qquad (2)$$

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).

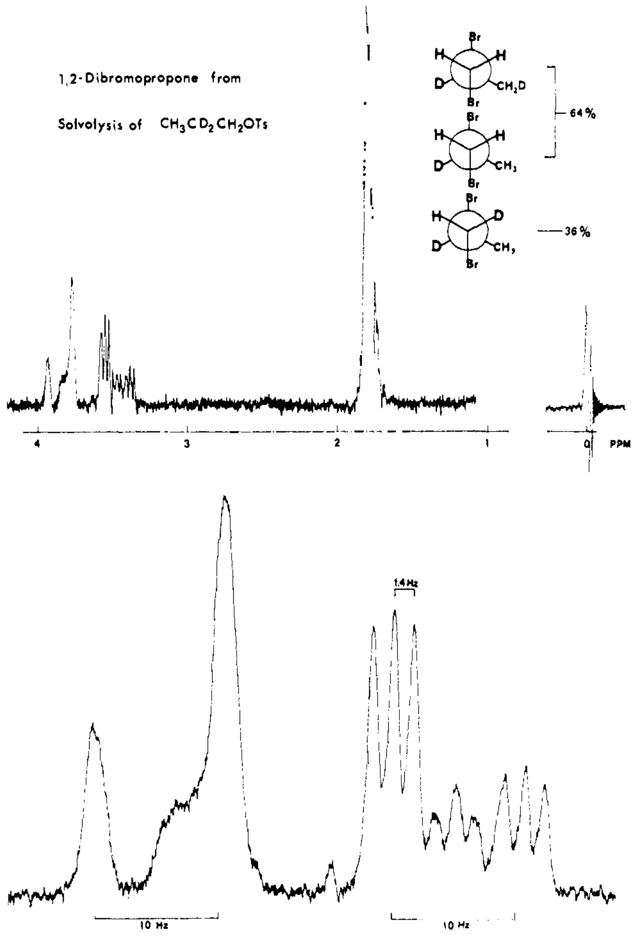

Figure 1. Nmr spectrum (CCl_4) of the 1,2-dibromopropane isolated from 96% sulfuric acid solvolysis of propyl-2,2-d_2 tosylate with bromine trapping. The expanded spectrum of the methylene proton region shows the anticipated **AB** quartet split by weak coupling with vicinal deuterium into a quartet of triplets. The absorptions at the A and B band origins, 22% of the area (36 mole %), represent the 1,2-dibromopropane-1,2-d_2 in the sample mixture.

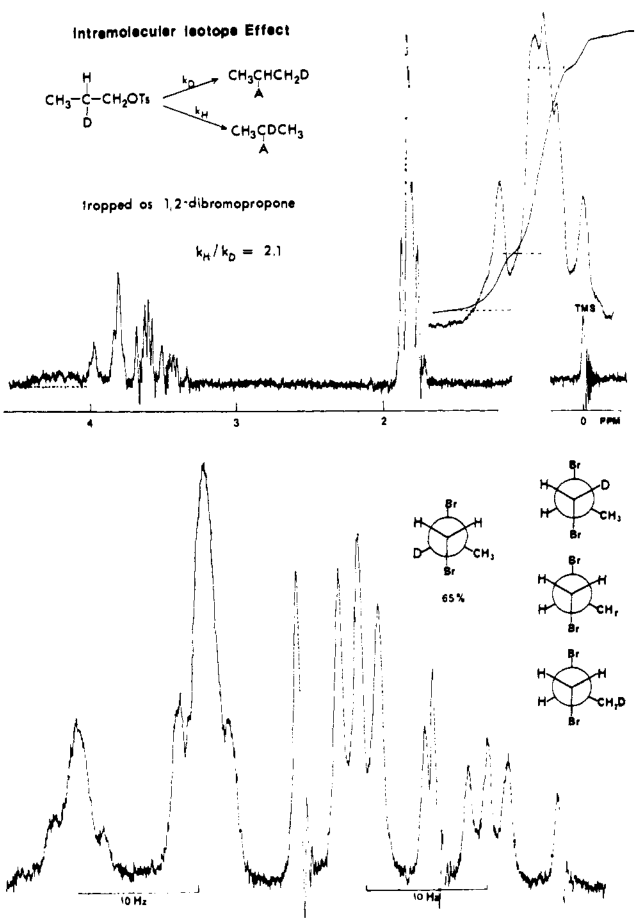

Figure 2. Nmr spectrum of 1,2-dibromopropane isolated from 96% H_2SO_4 solvolysis of propyl-2-d_1 tosylate with bromine trapping. The upper-right insert shows an expanded sweep and representative integral of the methyl proton region.

in conventional solvent systems (HOAc,[4] HCOOH,[4] H_2O[5]) but parallels the trends that are observed in CF_3COOH and HSO_3F.[3] The large rate spread in H_2SO_4 (*ca.* 5×10^4) appears to reflect a difference in the ability of alkyl groups to respond to increased demands for internal stabilization upon solvolysis in this weakly nucleophilic ionizing solvent.[6] The nature and timing of this internal response are delineated by isotope-effect measurements and first-formed product characterizations.

Solvolysis of CH_3CD_2OTs in 96% H_2SO_4 at 30° proceeds with <5% rearrangement after nine half-lives (nmr). The α-*d* (1.18 ± 0.02) and β-*d* (1.20 ± 0.03) isotope effects are larger than normal,[7] but they are significantly less than isotope effects associated with limiting solvolysis.[8]

By contrast, propyl tosylate undergoes solvolysis in 96% H_2SO_4 to yield greater than 95% isopropyl products.[9] The rate of solvolysis, monitored by the change in the aromatic proton pattern (nmr) or the formation of *p*-toluenesulfonic acid (uv),[10] is identical with the rate of rearrangement, monitored by the disappearance of the C-1 methylene proton absorption of propyl tosylate (nmr).[11]

Characterization of the solvolytic rearrangement of propyl tosylate as an intramolecular hydrogen transfer is complicated by the very rapid rate of exchange of the isopropyl methyl hydrogens with solvent H_2SO_4.[13,14] However, the ability to trap first-formed propene as 1,2-dibromopropane permits the necessary and sufficient tests. Thus, 1,2-dibromopropane was isolated (60% by preparative glpc) from H_2SO_4 solvolysis of propyl tosylate by conducting the reaction in the presence of vigorously mixed solutions of bromine and carbon

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[4] (a) S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, 74, 1120 (1952); (b) W. Pritzkow and K. Schoppler, *Chem. Ber.*, **89**, 834 (1962).

[5] R. E. Robertson, *Progr. Phys. Org. Chem.*, **4**, 213 (1967).

[6] Rates of solvolysis of propyl tosylate in concentrated H_2SO_4 show a good linear correlation with the h_0 function. This implicates the conjugate acid (neutral leaving group) as the reactive species in H_2SO_4 solvolyses.

[7] Compare with recent isotope effect data of A. Streitwieser, Jr., C. L. Wilkens, and E. Kiehlmann, *J. Amer. Chem. Soc.*, **90**, 1598 (1968).

[8] E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

[9] The major product is isopropyl hydrogen sulfate plus some isopropyloxonium ion. The product ratio can be simulated by mixing 96% H_2SO_4 with isopropyl alcohol: C. M. Suter and E. Oberg, *J. Amer. Chem. Soc.*, 56, 678 (1934).

[10] C. G. Swain and C. Morgan, *J. Org. Chem.*, **29**, 2097 (1964).

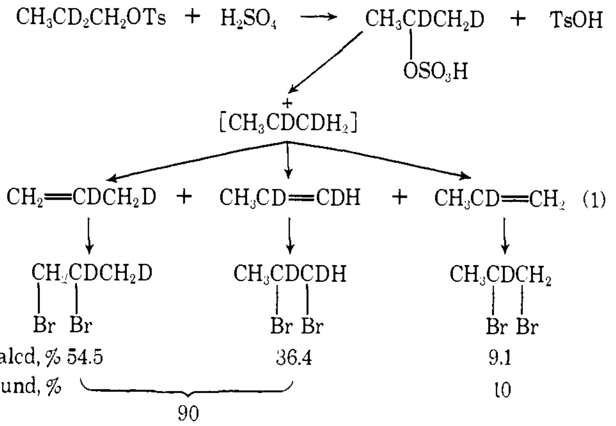
[11] For propyl-2,2-d_2 tosylate (0.2 *M*, 96% H_2SO_4), however, simultaneous measurements indicate that the rate of solvolysis (uv) is slightly slower (about 5%) than the rate of disappearance of the C-1 methylene protons (nmr). This observation is compatible with a small fraction of the solvolysis (with attendant deuterium scrambling) proceeding *via* a protonated cyclopropane.[12]

[12] G. J. Karabatsos, J. L. Fry, and S. Meyerson, *Tetrahedron Lett.*, 3735 (1967).

[13] No isopropyl methyl hydrogen can be detected in the nmr upon D_2SO_4 solvolysis of propyl tosylate; *cf.* N. C. Deno, *et al.*, *J. Amer. Chem. Soc.*, **90**, 6457 (1968).

[14] V. Gold and R. S. Satchell, *J. Chem. Soc.*, 1938 (1963).

tetrachloride. When D_2SO_4 was used, the dibromopropane isolated contained less than 1 atom % deuterium (mass spectrum). Solvolytic rearrangement of propyl-2,2-d_2 tosylate in 96% H_2SO_4 with bromine trapping of products yielded a mixture of dideuterio- and monodeuterio-1,2-dibromopropanes, consistent with the scheme shown in eq 1, where an isotope effect in elimination to form propene $(k_H/k_D)_{elim}$ of 2.0 is assumed,[15] and secondary isotope effects in elimination are neglected in the calculation of the product distribution. Mass spectral fragmentation patterns and the nmr spectrum (Figure 1) of the dibromide product are consistent with the distribution predicted.



Sulfuric acid solvolysis of propyl-2-d_1 tosylate and product trapping with bromine yielded mainly monodeuterio-1,2-dibromopropane. By integration of the methyl singlet with respect to the methyl doublet (Figure 2) and making appropriate corrections for deuterium affixed to the methyl carbon, an intramolecular (product) isotope effect $(k_H/k_D)_{intra}$ of 2.1 ± 0.3 was obtained. This value may be compared with the intermolecular (kinetic) isotope effect $(k_H/k_{\beta\text{-}d_2})$ of 1.85 ± 0.10 determined by both direct measurements of rates of solvolysis of propyl and propyl-2,2-d_2 tosylates and by competitive intermolecular rate studies.[16]

Application of bromine-trapping procedures to the 96% H_2SO_4 solvolysis of isobutyl tosylate at 0° led to the isolation and identification of a mixture of di- and tribromobutanes: 1,2-dibromo-2-methylpropane (**1**), 35%; *meso*- and *dl*-2,3-dibromobutane (**2**), 38%; 1,2,3-tribromo-2-methylpropane (**3**), 22%; other tribromobutanes (**4**), *ca.* 5%.[17] Parallel solvolysis of isobutyl-2-d_1 tosylate in 96% H_2SO_4 with bromine trapping yielded **1** (90% d_1), 21%; **2** (82% d_1), 55%; **3**, 13%; **4**, 11%. A product-distribution isotope effect $(k_H/k_D)_{prod}$ of 2.4 is estimated by assuming that products **1** and **3** represent hydrogen migration and **2** and **4** represent methyl migration. Competitive solvolysis of mixtures of isobutyl and isobutyl-d_1 tosylate yield a kinetic isotope effect $(k_H/k_{\beta\text{-}d_1})$ of 1.9 ± 0.1. Upon correction for the hydrogen:methyl migration ratio a value of 2.4 is obtained, in accord with the observed product-distribution isotope effect.

The treatment of solvolysis reactions of alkyl derivatives in terms of two competing pathways, anchimerically assisted (k_Δ) and anchimerically unassisted (k_s), has long been advocated and repeatedly explored by Winstein and coworkers.[19] Inherent in this treatment is the expectation that assistance by a neighboring group should become increasingly important as the nucleophilicity of the ionizing solvent decreases.[20] The 96% H_2SO_4 as well as the CF_3COOH[3a] solvolysis studies of primary alkyl tosylates appear as striking realizations of this expectation. The rate-limiting character of hydrogen transfer in H_2SO_4 solvolysis of propyl and isobutyl tosylates is substantiated by the near congruence of the intermolecular (kinetic) and intramolecular (product) isotope effects. Bromine trapping permits estimates of hydrogen:methyl migration rates under solvolytic conditions that do not permit direct detection of first-formed products.

The apparent enhancements of k_Δ processes observed in weakly nucleophilic solvents such as CF_3COOH and H_2SO_4 are indeed instructive. They lead one to reconsider the question: can solvolytic conditions be found which force neighboring hydrogen participation of simple ethyl derivatives? Experiments directed toward an answer are the subject of the next communication.[21]

Acknowledgment. We thank Professor S. Winstein and Dr. A. Diaz for a number of helpful discussions and information prior to publication concerning solvolysis of alkyl tosylates in CF_3COOH and HSO_3F.

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[15] S. Ehrenson, S. Seltzer, and R. Diffenbach, *J. Amer. Chem. Soc.*, **87**, 563 (1965).

[16] Competitive rate studies were conducted by solvolyzing equimolar mixtures of labeled and unlabeled alkyl tosylates and isolating the unconsumed alkyl tosylates from measured aliquots. The extent of over-all reaction was determined by uv analysis,[10] and the H/D ratio in the unconsumed reactant was determined by mass spectrometry.

[17] Substitution accompanying addition is well documented.[18] We presume that the tribromobutanes isolated are formed by substitution followed by addition.

[18] P. B. D. de la Mare and R. Bolton, "Electrophilic Addition to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966.

[19] S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **75**, 148 (1953).

[20] A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968), and references cited therein.

[21] P. C. Myhre and E. Evans, *ibid.*, **91**, 5641 (1969).

[22] National Science Foundation Undergraduate Research Participant, 1965–1966.

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Solvolysis of Ethyl Tosylate in HSO_3F

Sir:

Accumulating data provide important support for the view that neighboring group participation in solvolysis reactions is strongly enhanced in weakly nucleophilic ionizing solvents.[1] Correlations of the effect of these solvents on the k_Δ and k_s modes of solvolysis of simple primary alkyl tosylates have been discussed in the accompanying communications.[1g,h] Propyl tosylate exhibits a striking change in solvolytic behavior upon variation of solvent: <1% rearrangement in HCOOH,[2] 89% rearrangement in CF_3COOH,[1g] and essentially

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[1] (a) S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, **78**, 4801 (1956); (b) P. E. Peterson, *et al.*, *ibid.*, **89**, 5902 (1967), and references therein; (c) J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968); (d) A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968); (e) W. G. Dauben and J. L. Chitwood, *ibid.*, **90**, 6876 (1968); (f) P. C. Myhre and K. S. Brown, *ibid.*, **91**, 5639 (1969); (g) I. L. Reich, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635 (1969); (h) A. Diaz, I. L. Reich, and S. Winstein, *ibid.*, 5637 (1969).

[2] C. C. Lee and J. E. Kruger, *Can. J. Chem.*, **44**, 2343 (1966).