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SOLVOLYSIS REACTIVITIES OF ETHYL AND n-PROPYL TRIFLUOROMETHANESULFONATES IN TRIFLUOROETHANOL AND TRIFLUOROACETIC ACID.

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Winstein's recent report (1) on the solvolysis of primary alkyl tosylates in trifluoroacetic acid (TFA) complements our related results on the solvolysis of primary alkyl trifluoromethanesulfonates ("triflates") in TFA and trifluoroethanol (TFE). Despite the high solvolytic reactivity of primary alkyl triflates, it has been shown previously that the solvolysis of ethyl triflate in the usual solvents, such as acetic acid, is hardly more limiting in character than is the solvolysis of ethyl tosylate (2). Other solvolytic studies in TFA (1,3) and TFE (4) have demonstrated their comparatively low nucleophilicity and consequent usefulness in allowing the solvolytic formation of normally unstable carbonium ions. Accordingly, it is significant to study the possibly more limiting character of trifluoroacetolysis and trifluoroethanolysis of primary alkyl triflates by determining secondary deuterium isotope effects for ethyl triflate and rates and products for n-propyl triflate.

Ethyl triflate (EtOTf) and the deuterated ethyl triflates were prepared and characterized essentially as described previously (2), except that the procedure of Friedman (5) was used for $LiAlH_4$ reductions. n-Propyl triflate was prepared in a similar manner by the interaction of n-propyl iodide with CF_3SO_3Ag slurried in pentane. After filtration, the pentane was removed with an aspirator to leave a tan oil which was unstable over long periods at room temperature and could not be distilled. Analysis of this oil by nmr showed an otherwise pure mixture of n-propyl and isopropyl (36-50%) triflates, and this material was used without further purification.

Solvolysis rates in TFE* were determined in the usual titrimetric manner: aliquots were quenched in cold TFE and titrated potentiometrically (2) with KOH in TFE. Rates in TFA** were determined by quenching 2 ml aliquots in 7.5 ml of ice-cold propionic acid plus 0.5 ml of distilled $(CF_3CO)_2O$ and titrating potentiometrically with sodium acetate in acetic acid. This procedure was shown to give results reproducible and proportional to CF_3SO_3H concentration within 1%. Isopropyl triflate was found to solvolyze too rapidly to measure, and good first-order rates for n-propyl triflate could be obtained using isomer mixtures in all solvents studied. Acetolysis rates were determined as described previously (2). The results, together with related data, are given in Table I. Rearrangement of n-propyl triflate to give isopropyl products was followed by nmr. No rearrangement was visible in acetic acid, about 13% in TFE (by 100 Mc nmr), and >90% in TFA.

The interpretation of large β-deuterium isotope effects as an approximate indication of limiting character and large α-deuterium isotope effects as an indication of minimal involvement of nucleophiles in solvolysis has been well established (6). Using these criteria, the small size of the measured effects in both TFA and TFE suggests that EtOTf solvolyzes with little limiting character in either solvent. For comparison, isotope effects for isopropyl tosylate in TFA (3c) would lead us to expect both α-d_2 and β-d_3 effects of at least 1.46 for a near-limiting solvolysis. Myhre (7), for example, has reported rather large isotope effects (α-d_2 = 1.30 and β-d_3 = 1.58) for the apparently near-limiting solvolysis of ethyl tosylate in FSO_3H.

The large rate enhancement of n-propyl triflate relative to ethyl and the formation of isopropyl trifluoroacetate clearly indicate the occurrence of a limiting solvolysis with concerted hydrogen migration rather than formation of a primary alkyl carbonium ion. By similar arguments, limiting solvolysis apparently competes poorly with nucleophilic displacement in TFE and little, if

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* Halocarbon Products Co., Hackensack, N. J. -- dried over Linde 4A molecular sieves and distilled to give solvent containing 0.04 wt. % water by Karl-Fischer titration.

** Aldrich--twice distilled from H_2SO_4.

TABLE I

Summary of Solvolysis Rates

Substrate	n[a]	$10^5k_1\,\text{sec}^{-1}$ [b]	k_H/k_D	$k_{n\text{-}Pr}/k_{Et}$
Trifluoroacetic Acid,[c] 50.0°				
EtOTf	4	1.37 ± .04	---	---
CD_3CH_2OTf	2	1.19 ± .03	1.15 ± .04	---
CH_3CD_2OTf	2	1.21 ± .03	1.13 ± .04	---
n-PrOTf	2	13.9 ± 1.4	---	10.2
EtOTs[d]	2	0.00176	---	---
n-PrOTs[d]	-	0.0108	---	6.1
CD_3CH_2OTs[d,e]	-	1.16	1.16	---
CH_3CD_2OTs[d,e]	-	1.24	1.09	---
Trifluoroethanol,[f] 34.98°				
EtOTf	4	8.21 ± .44	---	---
CD_3CH_2OTf	2	7.54 ± .17	1.09 ± .05	---
CH_3CD_2OTf	2	7.27 ± .15	1.13 ± .05	---
n-PrOTf	2	6.25 ± 0.8	---	0.76
EtOTs[g]	-	0.534	---	---
Acetic Acid, 25.0°				
EtOTf[h]	9	5.27 ± .05	---	---
n-PrOTf	2	3.90 ± .06	---	0.74

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[a] Number of kinetic runs. [b] Rate constants were obtained using a nonlinear least-squares program (LSKIN1 - D. F. DeTar and C. E. DeTar, Computer Programs for Chemistry, Vol. 1, Benjamin, N.Y., 1969). Errors are either the average standard deviation of the runs or that computed by the method of R. B. Dean and W. J. Dixon, Anal. Chem., 23, 636 (1951), whichever is larger. [c] About 0.037-0.04M in substrate. [d] Data taken or extrapolated from Ref. 1. [e] Runs at 125.0°. [f] About 0.055M in substrate. [g] At 110°. Private communication from Professor Donald S. Noyce and R. L. Castenson. [h] Data from Ref. 2.

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at all, in acetic acid. Similar competition reactions between an internal nucleophile and solvent have been used previously as indications of solvent nucleophilicity (1,3,4a). Considering hydrogen as an internal nucleophile, our rearrangement data allow us to place the nucleophilicity of TFE between TFA and acetic acid and probably closer to acetic acid. A comparison of isotope effects for isopropyl tosylate in TFA (β-d_6 = 2.12 at 25°) (3c) and isopropyl brosylate in 97% aq. TFE (β-d_6 = 1.579 at 45°) (4b) confirms the comparison with TFA. Using the "apparent m" value for EtOTf in acetic and formic acids (2) and a Y value of 1.045 for TFE (4b), the rate calculated by the Grunwald-Winstein equation for EtOTf in TFE is approximately 10-fold faster than that observed. This difference is probably attributable to the lower nucleophilicity of TFE than acetic or formic acid.

These results confirm that normal solvolyses of primary alkyl systems involve exclusively participation by solvent or by an external or internal (neighboring group) nucleophile; primary carbonium ions are never involved. Furthermore, triflate and tosylate solvolyses are mechanistically similar; the utility of triflates lies primarily in their enhanced reactivity with normally sluggish systems.

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