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Solvolysis in Strong Acids. III. The Question of Alkyl–Oxygen Cleavage in Alkyl Tosylate Solvolysis[1]

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Simple primary alkyl *p*-toluenesulfonates solvolyze at markedly different rates in concentrated sulfuric acid. Mechanistic interpretations supported by investigations of first-formed products and kinetic isotope effects have been reported.[2] Recently, Harris has reviewed these and closely related studies within the general context of solvolytic substitution.[3,4] Our studies in this area have continued along several lines. One topic of interest has been the solvolytic behavior of some simple alkyl tosylates containing the trifluoromethyl group.[5]

Systems such as 2,2,2-trifluoroethyl tosylate and 1,1,1-trifluoro-2-propyl tosylate react most sluggishly under SN2-like conditions.[6] The remarkable stability of the 2,2,2-trifluoroethyldiazonium ion indicates that SN1-like reactions of these systems should also proceed with great reluctance.[7] Consequently, we were surprised to find that 2,2,2-trifluoroethyl tosylate and 1,1,1-trifluoro-2-propyl tosylate solvolyzed in the 85–100% sulfuric acid region at rates comparable to those of ethyl tosylate, but 3,3,3-trifluoro-1-propyl tosylate solvolyzed in sulfuric acid at rates significantly slower than those observed for methyl tosylate. Some of the relevant kinetic data are shown in Figure 1.[8] The fluorinated tosylates underwent solvolysis without rearrangement.

A consistent mechanistic representation that presumed alkyl–oxygen cleavage for the entire set of alkyl tosylates (Figure 1) was difficult to formulate. Further study of the seemingly aberrant fluorinated alkyl tosylates appeared necessary. We report here a correlated stereochemical and ^{18}O-labeling study which shows that solvolysis of 1,1,1-trifluoro-2-propyl tosylate in 98% sulfuric acid occurs with complete retention of configuration because solvolysis *does not* involve cleavage of the alkyl–oxygen bond.

An earlier survey study of asymmetric reductions with the lithium aluminum hydride–quinine complex indicated that a useful enantiomeric excess of (+)-1,1,1-trifluoro-2-propanol [(+)-1] could be produced by this reducing system.[9] After optimizing conditions, (+)-1 could be conveniently prepared in 30% enantiomeric excess by reduction of 1,1,1-trifluoroacetone at 25 °C with an ethereal slurry of the 1:1 complex. 1,1,1-Trifluoro-2-propanol-^{18}O (1-^{18}O) was prepared by hydration of anhydrous trifluoroacetone with 50 atom % $H_2{}^{18}O$ followed by acid-catalyzed dehydration and subsequent reduction with lithium aluminum hydride in diglyme.

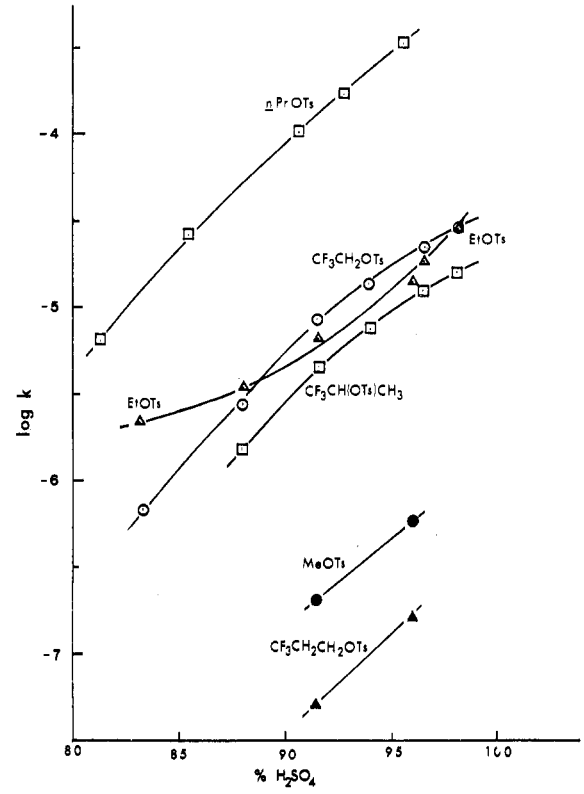
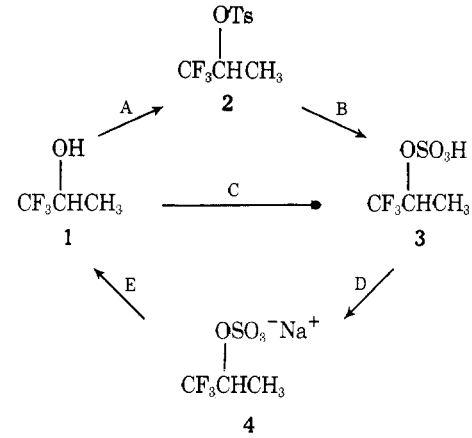


Figure 1. First-order rates (s^{-1}) of solvolysis of some simple alkyl tosylates in concentrated sulfuric acid solutions at 30 °C. A plot of log k vs. % H_2SO_4.

Samples of chiral and isotopically labeled 1 were carried through the reaction cycles depicted in Scheme I as steps

Scheme I[a]



[a] A, TsCl—pyridine, —5° C; B, 98% H_2SO_4, 30° C; C, 98% H_2SO_4, 30° C; D, NaOH (aqueous), evaporation, extraction with CH_3OH; E, moist Et_2O—H^+, reflux.

A, B, D, E and steps C, D, E. The rotation of (+)-1 before and after passing through the reaction cycles was found to be identical within experimental error (Table I). The rotations of intermediates 3 and 4 were also found to be path independent (Table II). Finally, the oxygen-18 content of 1-^{18}O was found to be unchanged after passage through the reaction cycles (Table III).

The conclusions are clear. No step in the cycles involves measurable cleavage of the alkyl–oxygen bond. Complete retention of configuration is a trivial consequence of this fact.

Table I. Specific Rotations of (+)-1 before and after Passage through Reaction Cycles (Scheme I)

	$[\alpha]_\lambda^{25}$		
λ, nm	1 st mat.	1 via ABDE	1 via CDE
584	0.872	0.870	0.868
578	0.913	0.913	0.938
546	1.036	1.036	1.042
436	1.756	1.740	1.789
365	2.682	2.692	2.679

Table II. Specific Rotations of Intermediates in Reaction Cycles (Scheme I)

	$[\alpha]_\lambda^{25}$			
λ, nm	3[a,b] via AB	3[a,b] via C	4[c] via CD	4[c] via ABD
584	−3.21	−2.85	−1.78	−1.78
578	−3.34	−2.97	−1.84	−1.91
546	−3.78	−3.34	−2.19	−2.15
436	−6.36	−5.64	−3.69	−3.63

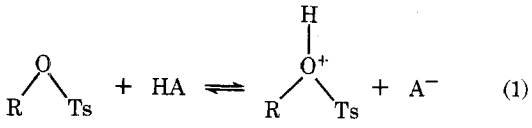
[a] $[\alpha]^{25}D$ of 1 used in these runs was +0.961. [b] In sulfuric acid reaction solution. Concentration uncertainties account for differences. [c] In aqueous solution.

Table III. ^{18}O Atom % of 1-^{18}O before and after Passage through Reaction Cycles (Scheme I)

	^{18}O atom %	
1 st mat.	1 via ABDE	1 via CDE
24.6 ± 0.3	24.4 ± 0.3	24.3 ± 0.3

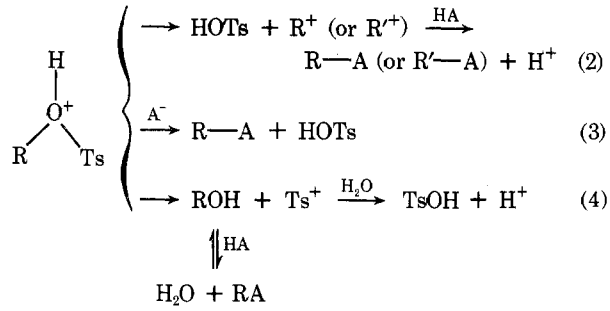
The implications of this result remain to be explored more fully. Previous discussions of solvolytic displacement of alkyl tosylates in strong acids have implicitly assumed alkyl–oxygen bond cleavage. In many cases this assumption appears to be required by product, label scrambling, and kinetic isotope effect data.[2-4] The solvolytic behavior of the 1,1,1-trifluoro-2-propyl system (and presumably the 2,2,2-trifluoroethyl system) shows that accessible, fundamentally different paths of solvolysis do exist. The dominance of one path over others seems to be a fairly sensitive function of alkyl group structure.

Since cleavage of the alkyl–oxygen bond does not occur in sulfuric acid solvolysis of 1,1,1-trifluoro-2-propyl tosylate, two possibilities remain, cleavage at the oxygen–sulfur bond or cleavage at the sulfur–aromatic carbon bond. The latter mode, presumably an electrophilic replacement of the alkoxysulfonylium cation ($ROSO_2^+$) by a proton, is discounted since no clear rationale is available to explain the sensitivity of solvolysis rate to alkyl group structure. Cleavage at the oxygen–sulfur bond could be accommodated within an expanded version of the mechanistic scheme previously suggested.[2a,3b] This scheme requires prior protonation of the substrate before cleavage.[10] For purposes of discussion the site of protonation is restricted to the alkyl oxygen atom, eq 1.



(1)

Given this, a partitioning among at least three paths can be proposed.



The first two paths, eq 2 and 3, represent conventional dissociative (SN1-like) and associative (SN2-like) solvolytic displacements. The third path, eq 4, is simply the complementary dissociative path that could occur when cleavage at the alkyl carbon–oxygen bond is very slow.[10b] Thus with the assumption that both sulfur–oxygen as well as alkyl–oxygen cleavages are slow for methyl tosylate and 3,3,3-trifluoro-1-propyl tosylate, the enhanced rates of solvolysis of 1,1,1-trifluoro-2-propyl tosylate and 2,2,2-trifluoroethyl tosylate might be rationalized in terms of leaving group tendencies of the respective alcohols. It seems reasonable to anticipate that the significantly higher K_A's of trifluoroethanol ($10^{-12.4}$) and 1,1,1-trifluoro-2-propanol ($10^{-11.8}$) with respect to methanol ($10^{-15.5}$) and 3,3,3-trifluoro-1-propanol would be reflected in better leaving group qualities for the former. Note, however, that this rationalization requires the implicit assumption that the K_A's of the alkyl tosylate conjugate acids are less influenced by alkyl group structure than are the rates of sulfur–oxygen cleavage.

If the assumptions made are valid, fairly conventional mechanistic arguments may explain the result reported within the larger context. However, a central question remains. Which tosylates of the set of fairly inert alkyl tosylates (methyl, ethyl, 3,3,3-trifluoro-1-propyl) solvolyze in whole or in part by paths other than alkyl–oxygen cleavage? The α-trifluoromethylalkyl systems may well be aberrant with respect to the previously assumed norm, but the issue remains open until studies in progress are completed.

This study points out the danger in tacit assumption of a given mode of bond cleavage in strong acid solvolysis, particularly when kinetic data are the sole indicators.

Experimental Section

Fluorinated alcohols and ketones were purchased from PCR, Inc., Gainesville, Fla. Water (50 atom % excess ^{18}O) was obtained from Bio-Rad Laboratories. NMR spectra were recorded on a Varian A-60 spectrometer. Rotation measurements were made with the use of a Perkin-Elmer 141 polarimeter. ^{18}O analyses were made with the use of a Perkin-Elmer Hitachi RMU 6D spectrometer.

(+)-1,1,1-Trifluoro-2-propanol. The preparation was patterned after the work of Cervinka and Belovsky.[11] A number of trials were made. The following conditions appeared to give the best yield and greatest enantiomeric excess.

Anhydrous (−)-quinine (52.8 g, 0.163 mol, dried by vacuum dehydration at 125°, 2 mm for 4 h) and lithium aluminum hydride (6.22 g, 0.164 mol) were added sequentially to 500 ml of anhydrous ether in a 2-l. flask equipped with a sealed mechanical stirrer and reflux condenser. The mixture was heated to reflux for 3 h to form a butter yellow suspension of the complex. The mixture was cooled to room temperature, the reflux condenser was replaced with a large dry ice cold finger condenser, and 1,1,1-trifluoroacetone (18.3 g, 0.163 mol) was distilled into the flask held at room temperature (ca. 25 °C). There was no color change although the reaction mixture appeared more homogeneous. After a period of 15 h, the reaction mixture was treated successively with water (150 ml, dropwise addition) and sulfuric acid (350 ml, 20 wt %). The clear yellow aqueous layer was separated from the colorless ether layer and the ether phase was extracted successively with three 50-ml portions of cold 20% sulfuric acid and three 50-ml portions of water. The dried (sodium sulfate) ether phase was concentrated by distillation

through a vacuum jacketed Vigreux column (300 × 15 mm). The residual liquid (ca. 50 ml) was transferred to a smaller flask and fractional distillation was continued to yield a fraction bp 75–75.9 °C, 13.14 g. NMR spectra of this fraction indicated the presence of water (1 wt %), ether (6 wt %), and trifluoroacetone (4 wt %, as hemiacetal and hydrate); crude yield 62%, $\alpha^{25}D$ (neat, uncorrected) 1.990. Redistillation afforded a sample with the following properties: bp 75.8–76.2 °C (726 mm); $n^{25}D$ 1.3135; d_4^{25} 1.259; $\alpha^{25}D$ (neat) 2.165 [lit.[12] bp 77.7–77.9 °C (752 mm); $n^{25}D$ 1.3130; d_4^{25} 1.263; $\alpha^{25}D$ −7.14].

Reduction by the procedure described above at various temperatures gave the following crude yields and enantiomeric excess values: −78 °C, 26%, 9.1% ee; −10 °C, 61%, 13.3% ee; 25 °C, 62%, 30% ee.

1,1,1-Trifluoroacetone-^{18}O. 1,1,1-Trifluoroacetone (9.5 g, 85 mmol) was distilled into a cooled 50-ml two-necked flask equipped with a dry ice condenser, drying tube, stir bar, and serum cap. Water (1.58 g, 50 atom % ^{18}O, 83 mmol) was added dropwise via a syringe. The first droplets of water added solidified. These were allowed to melt to globules of water on the surface, and a mildly exothermic reaction commenced. Crystallization started after addition of about 1.0 ml of labeled water, but continued addition caused solution and gentle refluxing. The system continued to reflux for about 15 min after addition of the last portion and then rapidly solidified to a mass of prisms. The solid was warmed to room temperature and volatiles were collected in a small trap cooled in dry ice–acetone. Less than 0.1 ml of volatile material was collected during a 3-h period. A vacuum jacketed Claisen-Vigreux still was attached to the reaction flask, sulfuric acid (0.5 ml, 96 wt %) was added, and the reaction mixture was heated to reflux. Distillate (7.0 ml, 8.8 g, bp 22–24 °C) was collected in a dry ice cooled graduated receiving tube. A mass spectrum indicated ca. 25% ^{18}O incorporation.

1,1,1-Trifluoro-2-propanol-^{18}O. 1,1,1-Trifluoroacetone-^{18}O (8.59 g, 76.4 mmol, ca. 25% ^{18}O) was slowly distilled into a stirred and cooled (−40 °C) 100-ml round-bottom flask containing a suspension of lithium aluminum hydride (1.53 g, 40 mmol) in 35 ml of diglyme (freshly distilled at 20 mm from $LiAlH_4$). The reaction flask was equipped with a dry ice condenser, serum cap, and stir bar. The reaction mixture was then brought to room temperature with the dry ice condenser charged and maintained during a 3-h period. Twelve hours later, the reaction mixture was treated with 25 ml of dry diethylene glycol. A vacuum jacketed Claisen-Vigreux still was attached and the labeled alcohol was distilled directly from the quenched reaction mixture to yield 6.99 g (5.8 ml, bp 74.5–78 °C) and 1.10 g (bp 78–120 °C). NMR analysis indicated that the first fraction was 95.6 wt % alcohol (76.4% yield) with diglyme the principal impurity. Preliminary mass spectral analysis indicated ca. 25% ^{18}O incorporation.

***p*-Toluenesulfonates of 1,1,1-Trifluoro-2-propanols.** The following procedure is representative. (+)-1,1,1-Trifluoro-2-propanol (10.1 g, 88 mmol, $\alpha^{25}D$ +1.101) was added slowly via a syringe to a cold (−7 °C), magnetically stirred solution of dry pyridine (60 ml) and *p*-toluenesulfonyl chloride (16.0 g, 84 mmol). The resulting mixture was stored in the freezer (−20 °C) for 2 weeks. The extent of conversion was monitored by NMR spectroscopy. The tosylate was isolated in the usual way, and purified by vacuum distillation to yield (−)-1,1,1-trifluoro-2-propyl tosylate, 13.1 g (56%), bp 97.5 °C (1 mm), $\alpha^{20}D$ −4.024, $n^{25}D$ 1.4165. Unlabeled and ^{18}O-labeled tosylates were prepared by similar means in 50 and 80% isolated yields, respectively. NMR spectra and refractive indices were identical.

Solvolysis of 1,1,1-Trifluoro-2-propyl *p*-Toluenesulfonate-*ether*-^{18}O. A sample of the ^{18}O-labeled tosylate (0.4618 g, 1.72 mmol) was transferred to a 10-ml volumetric flask and 98 wt % sulfuric acid was added to the mark. The resulting solution was double sealed and held at 25 °C until the reaction was about 80% complete. The reaction mixture was quenched by pouring it on 80 g of crushed ice with magnetic stirring and external cooling, and the resulting acidic solution was neutralized with ca. 20 ml of 50% sodium hydroxide solution by dropwise addition with stirring and cooling so that the temperature did not exceed 15 °C. The solution was adjusted to pH 9, additional water was added to dissolve precipitated sodium sulfate, and the aqueous suspension was extracted with three 10-ml portions of methylene chloride. Thirty-seven milligrams of tosylate was recovered from the methylene chloride extracts. The NMR and mass spectra were identical with those of starting material.

The aqueous solution containing sodium sulfate, sodium 1,1,1-trifluoro-2-propyl sulfate, and sodium *p*-toluenesulfonate was rotary evaporated (temperature less than 35 °C) to yield a crystalline mass that was more thoroughly dried at the oil pump (1 mm, 25 °C, 24 h). The mixture of salts was triturated with two 15-ml portions of refluxing anhydrous methanol and the methanol filtrate evaporated to yield 0.97 g of hydrated crystalline residue. The NMR spectrum (D_2O) indicated a mole ratio sodium 1,1,1-trifluoro-2-propyl sulfate:sodium *p*-toluenesulfonate of 0.95:1.0.

Samples of unlabeled and chiral 1,1,1-trifluoro-2-propyl tosylate were solvolyzed in an identical manner. Products were isolated by the procedure described with similar results. Samples of 1,1,1-trifluoro-2-propyl hydrogen sulfate were prepared by direct esterification of labeled and chiral samples of 1,1,1-trifluoro-2-propanol with 98% sulfuric acid. The alkyl hydrogen sulfate was isolated as the sodium salt and purified by the method described above.

Hydrolyses of Sodium 1,1,1-Trifluoro-2-propyl Sulfates in Moist Ether. The procedure used is based on the known method most recently discussed by Groen and Kochansky.[13] The following is representative. The mixed salts, sodium (−)-1,1,1-trifluoro-2-propyl sulfate and sodium *p*-toluenesulfonate (4.68 g, 11.4 mmol of sulfate ester), obtained via steps ABD (Scheme I) were mixed with anhydrous ether (65 ml), water (0.5 ml), and 10% sulfuric acid (0.1 ml). The mixture was heated at reflux for 60 min and then titrated with standard base; 10.4 mequiv was consumed, 91% yield. The ether layer was separated. The aqueous layer was saturated with sodium sulfate and then extracted twice with ether. The combined, dried (sodium sulfate) ether layers were concentrated by distillation and the residue was distilled with the use of a one-piece vacuum-jacketed Vigreux microstill to yield 0.625 g, bp 72–76 °C, plus 0.200 g of hold-up in the still. NMR analysis indicated that the distilled fraction was 78.7 wt % alcohol (38%), contaminated with water and some ether. Rotation measurements and density measurements were made with this sample dissolved in 95% ethanol. A calibration chart was constructed with the use of standard solutions containing known amounts of the starting alcohol 1 in 95% ethanol. The observed rotations could then be converted to comparable specific rotations.

Samples of 1-^{18}O obtained via steps ABDE and CDE were purified by GLC (Carbowax 20M) and analyzed by mass spectrometry. The intense CF_3CO^+H ion was used for these measurements.

Registry No.—(+)-1, 17628-73-8; (−)-2, 58219-97-9; (−)-3, 58219-98-0; (−)-4, 58219-99-1; *p*-toluenesulfonyl chloride, 95-59-9; sulfuric acid, 7664-93-9.

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HMO Calculation of the First Transition Energy of the Seleninium Cation and Its Benzologs[1]

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The uv spectra of the seleninium cation and its benzologs are very similar to those of their analogues in the thiapyr-