had separated on top of the solution. Work-up by the same procedure as for the tosylate solvolyses gave, after solvent removal, a brown-orange tar, from which no material distilled (1 mm) up to 265°.

Trifluoroacetolysis of 2-Phenylethyl-1,1-d_2 Tosylate for One Half-Life. A solution of 1.39 g (0.0050 mol) of 2-phenylethyl-1,1-d_2 tosylate in 50 ml of buffered trifluoroacetic acid, in a 100-ml, round bottomed flask equipped with a reflux condenser and a drying tube, was heated quickly to reflux (*ca.* 72°). Boiling was maintained for 20 min (calculated half-life 17.3 min), whereupon the reaction mixture was cooled in ice water and worked up in the same way as that from complete solvolysis of the unlabeled tosylate. After solvent removal, the trifluoroacetate product was distilled from the residue (0.75 mm) and a maximum temperature of 55°, into a Dry Ice cooled receiver; yield 0.32 g (0.0015 mol, 30% of reactant). The remaining oil was triturated with pentane and cooled, resulting in crystallization of the unreacted tosylate, which was collected by filtration; yield of crude material 0.62 g (0.0026 mol, 52% of reactant). Recrystallization from pentane–ether (8:1) gave 0.45 g of colorless needles, mp 38.5–39.5°. Nmr isotope-position analysis was carried out with the neat liquid trifluoroacetate and with a 50% solution of the recovered tosylate in carbon tetrachloride. The former showed 50 ± 2% of CH_2 at C-1 and at C-2. The latter showed 5 ± 2% of CH_2 at C-1, 95% at C-2.

Stability of 2-Phenylethyl-1,1-d_2 Trifluoroacetate under Trifluoroacetolysis Conditions for the Tosylate. 2-Phenylethyl-1,1-d_2 trifluoroacetate (0.060 g, 0.27 mmol) was dissolved in 0.4 ml of buffered trifluoroacetic acid in an nmr tube, which was sealed. Heating this sample at 72 ± 2° for 4 hr produced no change in its nmr spectrum, *i.e.*, no signal for protium at C-1.

Trifluoroacetolysis of 1-Phenyl-2-propyl Tosylate. A solution of 1.452 g (0.00500 mol) of 1-phenyl-2-propyl tosylate in 50 ml of buffered trifluoroacetic acid was kept at room temperature for 5.5 hr (14 half-lives), during which time it developed a pale yellow color. The reaction mixture was worked up as in the 2-phenylethyl case, final distillation giving 1.034 g (0.00450 mol, 89%) of colorless liquid, bp 70–71° (5 mm). The infrared and nmr spectra of the product were virtually identical with those of synthetic 1-phenyl-2-propyl tosylate. Gas chromatography, however, showed the presence of a second compound, in *ca.* 0.5% abundance, with the same retention time as that of 1-phenyl-1-propyl trifluoroacetate. Further efforts were not made to identify this trace product.

Stability of 1-Phenyl-1-propyl Trifluoroacetate under Trifluoroacetolysis Conditions for 1-Phenyl-2-propyl Tosylate. A solution of 1.16 g (0.0050 mol) of 1-phenyl-1-propyl trifluoroacetate in 50 ml of buffered trifluoroacetic acid at room temperature turned dark red about 1.0 hr after preparation. After an additional 30 min a polymeric phase separated. After 5.5 hr the mixture was worked up by the same procedure as for the trifluoroacetolysis of 1-phenyl-2-propyl tosylate. The residue consisted of polymer and *ca.* 0.046 g (0.2 mmol, 4% of reactant) of 1-phenyl-1-propyl trifluoroacetate.

Kinetics Procedure. The method of Peterson, *et al.*,[16c] was used. For the reactions above 25°, the tosylate (1.250 mmol) was placed in a 25-ml volumetric flask and dissolved in buffered or unbuffered trifluoroacetic acid, up to the mark. Up to 15 1.5-ml portions of this solution were sealed in 5-ml glass ampoules, which were placed together in a thermostatic bath at the desired temperature (±0.02°). The first tube was withdrawn when the bath regained the set temperature (*ca.* 45 sec), and was quenched in ice–water, as were successive samples. Each was warmed to room temperature and opened, and 1.00 ml of the solution was pipetted into *ca.* 48 ml of 95% ethanol in a 50-ml volumetric flask, followed by 95% ethanol up to the mark. The absorbance of the resulting solution was measured at the maximum near 273 mμ, using a Cary 15 spectrophotometer. All of the ethanol solutions were found not to change in absorbance for at least twice the time necessary to make the measurements. The theoretical infinity absorbance for each reaction was determined from a solution of 0.0500 *M* β-arylalkyl trifluoroacetate product in trifluoroacetic acid, diluted in 95% ethanol as above. Good first-order behavior was observed to at least 40% completion in all reactions except those of ethyl tosylate in buffered medium, at 115, 125, and 135°. In these cases after *ca.* 15% reaction the absorption curves in the region used for the kinetics showed a new component characterized by a long tail toward the visible, which increased in intensity with time. The side-reaction responsible for this complication was not investigated. It has been reported, however, that in ethylene glycol trifluoroacetate ion undergoes decomposition with formation of difluorocarbene at an appreciable rate at these temperatures.[19]

Kinetics and Isotope Effects in Solvolyses of Ethyl Trifluoromethanesulfonate[1]

A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received August 30, 1967*

Abstract: Acetolysis of ethyl trifluoromethanesulfonate ("triflate") is 30,000 times faster than that of ethyl tosylate at 25°. Solvent effects and α- and β-deuterium isotope effects show that acetolysis and formolysis of ethyl triflate has little carbonium ion character and much nucleophilic solvent displacement or N character.

Trifluoromethanesulfonic acid is one of the strongest known monobasic acids.[2-4] The corollary that the trifluoromethanesulfonate ion should be a facile leaving group in solvolytic displacement reactions is borne out by the chemistry of alkyl esters. Several such esters are known and have been shown to be effective alkylating agents and esterification promoters. The ethyl ester alkylates benzene, pyridine, and even ethyl ether under mild conditions.[5,6] In the only reported kinetic study of such reactions, Hansen[7] found that methyl trifluoromethanesulfonate undergoes acetolysis 10^4 faster than methyl *p*-toluenesulfonate. Such high reactivity suggests that further kinetic studies could provide important new understanding of solvolytic displacement mechanisms. In particular, such studies could provide an important bridge between the displacement reactions of halides and ordinary sulfonates and compounds not amenable to kinetic study such as the alkyldiazonium ions.

In our initial study we concentrated on the acetolysis of ethyl trifluoromethanesulfonate ("triflate") and its

(1) This work was supported by Grants GP 1594 and GP 6125X from the National Science Foundation.

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secondary deuterium isotope effects, but some comparison results in other solvents are included.

Results and Discussion

Kinetics. Ethyl triflate was prepared from ethyl iodide and silver trifluoromethanesulfonate as described by Gramstad and Haszeldine.[8] Acetolysis kinetics were followed conveniently in the usual titrimetric manner even at 25°. Note that temperatures of 100° and more are commonly used for following conveniently the acetolysis of primary alkyl arylsulfonates. Formolysis was followed titrimetrically at 25°, but solvolysis in ethanol and 80% ethanol was followed by nmr. Details are given in the Experimental Section and the kinetic results are summarized in Table I.

Table I. Kinetic Data for Solvolysis of Ethyl Trifluoromethanesulfonate

Solvent	Temp, °C	$k_1 \times 10^4$ sec^{-1}	n[a]
HOAc[b,c]	25.0	0.527 ± 0.005	9
	40.0	2.32 ± 0.04	2
	50.0	5.84 ± 0.02	3
	50.0	7.84[c,d]	1
HCO_2H[e]	25.0	6.11 ± 0.13	7
100% EtOH[f]	5 ± 1	6.9 ± 1.7	1
	25 ± 1	36.7 ± 9.0	3
80% EtOH[f]	5 ± 1	13.4 ± 1.8	1
	25[g]	71	

[a] Number of separate kinetic determinations which were averaged to give the reported standard deviation and rate constant. [b] Activation parameters are $\Delta H^* = 17.4 \pm 0.8$ kcal/mol and $\Delta S^* = -19.7 \pm 0.3$ eu. [c] About 0.02 M in ester. [d] In the presence of added (0.062 M) sodium acetate. [e] About 0.08 M in ester. [f] About 1–2 M in ester. [g] This rate was estimated from the rate ratio of the 100 and 80% ethanol runs at 5°.

The present study confirms the conclusions of Hansen[7] regarding the relative reactivity of perfluoroalkanesulfonate esters. We find, for example, that the acetolysis of ethyl trifluoromethanesulfonate proceeds about 30,000 times faster than the acetolysis of ethyl tosylate[9] and 5000 times faster than that of ethyl brosylate[10] at 25°. Its ethanolysis in 100% ethanol at that temperature is about 450,000 times faster than that of ethyl iodide[12] and 30,000 times faster than that of ethyl benzenesulfonate.[13] In 80% aqueous ethanol it solvolyzes 150,000 times faster than ethyl bromide.[14] Clearly, the triflate leaving group is far more reactive than those usually used in solvolytic displacement reactions.

The relatively high reactivity of ethyl triflate in solvolytic reactions poses the question of the degree of ethyl cation character in the transition states of such solvolyses. Solvolyses of primary alkyl systems are known to be generally far from limiting[15] (*Lim* character), and to have a high degree of solvent nucleophilic or **N** character. Evidence comes from stereochemical studies and from effects on rate of solvent change, added salts, lyate ion, and isotopic substitution.[16] We have applied some of these criteria to the present solvolyses in the discussions which follow.

Solvent Effects. Winstein, *et al.*,[15] have perceptively analyzed the effect of solvent on solvolysis rates in terms of solvent "ionizing power," **Y**, and nucleophilic character, **N**. The original definition[17] of **Y** of a solvent as the logarithm of the rate of solvolysis of *t*-butyl chloride at 25° relative to that in 80% aqueous ethanol[16] retains much of its usefulness despite the more recent recognition of the importance of solvation of the leaving group with hydrogen bonds[18] and of internal return.[19] Other definitions of ionizing power, such as Kosower's **Z** values,[20] have been shown to be proportional to **Y** values.[21]

The solvolysis rates of ethyl triflate in ethanol and 80% aqueous ethanol correspond to $m = 0.15 \pm 0.06$, a small value that reflects little dependence on solvent ionizing power. For comparison, m values in aqueous ethanol solvents for other substrates are:[16] ethyl benzenesulfonate, 0.28; *n*-butyl *p*-bromobenzenesulfonate, 0.32; ethyl bromide, 0.34; allyl chloride, 0.40.

The acetolysis and formolysis rates give the sensitivity to ionizing power at a lower level of solvent nucleophilicity. The corresponding "apparent" m value for ethyl triflate is 0.29, a value larger than that for the alcoholic solvents but still only comparable or lower than that for other leaving groups; for example,[16] ethyl tosylate, 0.44; *n*-butyl *p*-bromobenzenesulfonate, 0.38.

These relatively low m values suggest that the ethyl triflate solvolyses have no more carbonium ion character than those with less reactive leaving groups. Although this conclusion is moderated by possible lowered requirements for hydrogen bonding demand by the triflate ion, there is clearly no qualitative difference discernible with this leaving group.

The effect of solvent nucleophilicity is determined as the relative solvolysis rates in acetic acid and in aqueous ethanol of the same **Y**; *i.e.* $(k_{\text{aq alc}}/k_{\text{AcOH}})_Y$. This quantity is about 79 for ethyl triflate and is clearly comparable to the value, 80, given for ethyl tosylate.[16] The higher rate in the alcoholic solvent clearly shows the importance of an **N** component in these solvolyses.

If the effect of sodium acetate on the acetolysis rate is described in terms of a normal salt effect, eq 1,[22] the

$$k = k^0(1 + b[\text{salt}]) \quad (1)$$

data in Table I correspond to $b = 5.5$ l./mol. This value is only somewhat higher than the values often found for the effect of added alkali acetates on sulfonate acetolyses; *e.g.*, 4.5 l./mol for cyclohexyl tosylate with potassium acetate at 75°,[23] 2.6–4.1 l./mol for 3-phenyl-2-butyl tosylate with sodium acetate at 75°,[23]

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1.1 l./mol for neophyl *p*-bromobenzenesulfonate with lithium acetate at 50°,[24] and 2 ± 2 l./mol for β-(*p*-anisyl)ethyl tosylate with potassium acetate at 75°.[25]

The activation parameters for acetolysis of ethyl triflate are: $\Delta H^* = 17.4 \pm 0.8$ kcal/mol and $\Delta S^* = -19.7 \pm 0.3$ eu. Comparison of these values with the activation parameters for acetolysis of ethyl tosylate, $\Delta H^* = 24.4$ kcal/mol, $\Delta S^* = -16.7$ eu,[9] and ethyl brosylate, $\Delta H^* = 22.6$ kcal/mol, $\Delta S^* = -19.3$ eu,[26] shows that the enhanced reactivity of the triflate comes almost entirely from the enthalpy of activation. The similarity of the entropies of activation also suggest a basic similarity of reaction mechanism.

Secondary Deuterium Isotope Effects. The secondary isotope effects resulting from deuterium substitution in the α and β positions have been found to be useful probes of solvolytic transition states. The data must be used with care since the effects are comparatively small and it is clear that only gross changes rather than small variations are significant. In general, the β effect is a measure of the carbonium ion character of the transition state and the α effect is a measure of the geometric structure of the transition state,[16,27] at least when oxygen is the leaving atom.

Ethyl-1,1-d_2 and ethyl-2,2,2-d_3 triflates were prepared and solvolyzed in acetic and formic acids with the results summarized in Table II.

Table II. Secondary Deuterium Isotope Effects for Solvolysis of Ethyl Trifluoromethanesulfonates at 25°

d substn	Solvent	$10^5 k_1$, sec^{-1}	*n*[a]	k_H/k_D	$\Delta\Delta F^*$ per D, cal/mol
1,1-d_2	AcOH	4.70 ± 0.14	2	1.12 ± 0.04	34
	HCOOH	56.2 ± 1.4	3	1.09 ± 0.04	26
2,2,2-d_3	AcOH	4.75 ± 0.08	2	1.11 ± 0.02	21
	HCOOH	52.7 ± 1.1	3	1.16 ± 0.03	29

[a] Number of determinations.

The β effect is larger than that for ethyl-2,2,2-d_3 brosylate in acetic acid at 117°, $k_H/k_D = 1.01$ ($\Delta\Delta F^* = 3$ cal/mol per D),[11] and indicates somewhat more carbonium ion character at the transition state, but the effect is substantially smaller than the values found for secondary alkyl sulfonates ($\Delta\Delta F^* \cong 100$ cal/mol per D). The increased isotope effect in the formolysis is consistent with additional carbonium ion character in the more ionizing solvent—but the effect is rather small.

The α effect is about the same as that reported for acetolysis of ethyl-1,1-d_2 brosylate at 100°, $k_H/k_D = 1.09$ ($\Delta\Delta F^* = 32$ cal/mol per D).[11] These values are much smaller than those found for the more limiting acetolyses of *sec*-alkyl sulfonates ($k_H/k_D \cong 1.15$ or ~90 cal/mol per D), and points up again the displacement or N character of these solvolyses.

Conclusion

The solvent effects and secondary deuterium isotope effects agree in demonstrating for solvolyses of ethyl triflate a transition state with comparatively little positive charge and substantial bonding to a nucleophilic solvent molecule. Despite the comparatively high reactivity of this ester, the mechanism of solvolysis is substantially the same as that for ethyl arenesulfonates. The importance of nucleophilic displacement even for such a "good" leaving group as the triflate ion suggests strongly that nucleophilic displacement will still be important even with better leaving groups, for example, nitrogen.

Note that the 7-kcal/mol reduction in activation energy from ethyl tosylate acetolysis to that for ethyl triflate represents a substantial fraction of the total change to reaction of ethyldiazonium ion whose activation energy for acetolysis is probably of the order of 5–10 kcal/mol.

It was suggested a decade ago that nucleophilic displacement is an important component in reaction of primary alkyldiazonium ions;[28] this interpretation is reinforced by the present results.

Experimental Section

Materials. Barium trifluoromethanesulfonate was obtained as a white crystalline solid from the Minnesota Mining & Manufacturing Co.[29] and was used without further purification. Acetic-d_3 acid-*d* (Lot A-38, 99.5% *d*) and ethyl-1,1-d_2 iodide (Lot A-175, 99% 1-*d*) were purchased from Merck Sharp and Dohme of Canada, Ltd. and were used without further purification. Matheson Coleman and Bell propionic acid (Assay 99%) and formic acid (97–100%) were used without further purification. Glacial acetic acid (reagent grade) was dried by adding 10% by volume acetic anhydride and 1 g of concentrated sulfuric acid per liter of this mixture and allowing the solution to reflux for 2 days. At the end of this time, a forerun was distilled and dry acetic acid, bp 117.5–118°, was collected. Commercial Solvents Corp. "Gold Shield" absolute ethanol was dried by adding calcium hydride, heating under reflux overnight, then distilling off dry ethanol. Aqueous ethanol (80% ethanol–20% water, v/v at 25°) was prepared by adding the correct weight of water to a known weight of the dry ethanol.

Silver trifluoromethanesulfonate was prepared from the barium salt by conversion of the salt to the acid, neutralization of the water solution of the acid with silver carbonate, and evaporation of the resulting solution in the manner of Gramstad and Haszeldine.[8] Yields were 90–95%.

Ethyl trifluoromethanesulfonate was prepared by the reaction of ethyl iodide with silver trifluoromethanesulfonate using the method of Gramstad and Haszeldine.[8] Yields were consistently 50%.

Ethyl-1,1-d_2 trifluoromethanesulfonate was prepared by the reaction of ethyl-1,1-d_2 iodide as above except that pentane was used as solvent for the reaction instead of ethyl ether. The product ester showed no detectable methylene resonances in its nmr. The methyl resonance appeared as a broad singlet.

Ethyl-2,2,2-d_3 Trifluoromethanesulfonate. Acetic-d_3 acid-*d* was reduced with lithium aluminum hydride in ether to give ethanol-2,2,2-d_3. This was then converted to the tosylate and heated with potassium iodide in ethylene glycol to give ethyl-2,2,2-d_3 iodide.[30] The product iodide showed no methyl resonance in its nmr spectrum. The desired ester was then prepared by reaction of this iodide with silver trifluoromethanesulfonate in pentane as before. The ester showed no methyl resonance in its nmr spectrum.

Kinetic Measurements. A. Acetic Acid. In a typical run, *ca.* 100 ml of dry acetic acid was placed in a volumetric flask and the flask was placed in a constant temperature bath which was maintained at 25.00 ± 0.02°. After allowing the solvent to equilibrate for 15 to 30 min, about 0.4 g of the ethyl trifluoromethanesulfonate was added and the solution was allowed to equilibrate an additional 5 to 15 min after being shaken thoroughly. At various intervals, 10-ml aliquots of the reaction mixture were withdrawn and titrated potentiometrically with 0.0625 *N* sodium acetate solution in acetic

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acid, using a Potentiograph E 336 (Metrohm AG, Herisau, Switzerland) automatic titrator. The time of each sample was taken as the time the end point was reached. Generally 8–12 points were taken per run.

B. Formic Acid. In the formic acid runs, *ca.* 25 ml of formic acid was allowed to equilibrate in the constant temperature bath at 25.00 ± 0.02°. Approximately 0.4 g of ethyl trifluoromethanesulfonate was added, and after about 5 min, 2-ml aliquots were withdrawn at intervals and quenched in 8-ml portions of ice-cold propionic acid. The times were taken as the time when half the aliquot had drained into the quenching solution. The quenched propionic acid solutions were then titrated as in the acetic acid case with standard sodium acetate solution in acetic acid.

C. Ethanol. Both the 100% and the 80% ethanol solvolysis rates were determined in the same manner. About 0.4 ml of the solvent in an nmr tube was inserted in the Varian variable-temperature probe of a Varian A-60 nuclear magnetic resonance spectrometer. The desired temperature setting was made and the solvent was allowed to equilibrate. After temperature equilibration was complete, 160–300 mg of ethyl trifluoromethanesulfonate was added; the tube was shaken thoroughly and replaced in the probe. Another few minutes were allowed for reequilibration and then the methylene proton quartet of the ester was repeatedly integrated at intervals and the time of each integration was recorded. This quartet is easily identifiable since it appears at approximately 1 ppm lower field than the ethanol quartet. The true sample temperature was obtained by measuring the separation of the methanol hydroxyl and methyl peaks in a sample of methanol at the same temperature setting immediately before and after each run.

Calculation of Rate Constants. All rate constants were computed by the nonlinear least-squares method on an IBM 7090-94 computer using a modification of the LSKIN1 program of DeTar.[31]

(31) We are indebted to Professor D. F. DeTar for a copy of his program and to H. A. Hammond for appropriate modifications.

The Mechanism of the Formation and Hydrolysis of Phenyl Ether in the Basic Hydrolysis of Chlorobenzene[1]

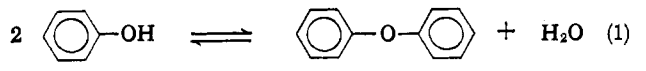
Gary W. Dalman and Fred W. Neumann

Contribution from the Benzene Research Laboratory of The Dow Chemical Company, Midland, Michigan 48640. *Received April 10, 1967*

Abstract: The mechanism of the formation and hydrolysis of diaryl ethers has been studied by carbon-14 tracer technique using phenyl ether and also by the hydrolysis of *p*-ditolyl ether. These studies have shown that phenyl ether is formed by the reaction of phenolate ion with benzyne. However, the hydrolysis of phenyl ether does not go through the benzyne intermediate. It has also been demonstrated that the loss of chloride by the chlorophenyl anion to form benzyne is a reversible reaction which can lead to carbon-14 activity distributed around the benzene ring.

The hydrolysis of chlorobenzene to phenol produces many by-products; the major one is phenyl ether, and in some instances its formation may account for 30% of the chlorobenzene.[2]

Earlier studies of the formation and hydrolysis of phenyl ether in the basic hydrolysis of chlorobenzene are summarized by Hale and Britton.[3] The mechanism was not discussed; however, the formation was depicted as a double decomposition reaction of chlorobenzene and sodium phenolate. Hale and Britton also proposed the existence of an equilibrium as shown in eq 1. This equilibrium was also proposed as occurring during the



(1)

manufacture of phenol from chlorobenzene.[2]

We have found no evidence for equilibrium 1 under the conditions employed in our work. No phenol could be detected when phenyl ether was heated with excess water at 400°, and no phenyl ether was formed when phenol was heated at 400° in the presence of excess 4 *N* aqueous sodium hydroxide. Claes and Jungers have studied the kinetics of the above equilibrium in the presence of a thoria catalyst.[4]

Lüttringhaus and Sääf studied the cleavage of alkyl aryl ethers by alkalies and found the main products to be phenolates and unsaturated hydrocarbons.[5] The reaction of 2,4-dinitrophenyl phenyl ether with bases (usually weak bases such as piperidine) has been studied in detail.[6–9] However, the nitro group is involved in the mechanism of the reaction and the same mechanism would not hold for the hydrolysis of phenyl ether. The formation of phenyl ethers has been studied under conditions of the Ullman condensation,[10] but the conclusions regarding the mechanism are considered applicable only in the presence of a copper catalyst.

Lüttringhaus and Ambros proposed that benzyne was an intermediate both in the formation of phenyl ether from chlorobenzene and alkali and in the hydrolysis of phenyl ether to phenol.[11] They base their conclusions on comparison to the reaction of phenyl ether with phenylsodium in which they obtained phenol, *o*-phenylphenol, diphenylphenols, and biphenyl phenyl ethers. These are some of the same by-products that

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