a view of the matrix as a random collection of reactant configurations. The high content of α-truxillate and β-truxinate in the products rather indicates a strong preference for two specific site configurations. The reason why these contact geometries are important in the solid, we believe, is the tendency of the cooling liquid to optimize its molecular packing. The point is illustrated in Figure 4 which shows molecular models of the ground-state-pair configurations corresponding to the principal cyclodimers. Clearly, the α and β configurations are the most compact and will be favored as the packing density of the liquid increases.

In ethyl cinnamate glasses a reactant conversion of up to 90% can be achieved. In that case the product distribution presents a fairly complete account of the site geometries present in the matrix. In ethyl cinnamate the experimental data reveal thus the existence of a type of molecular organization which is short range and inexact, and yet clearly distinct from a random ensemble of configurations. The driving forces which bring about this intermolecular correlation are the dipolar interactions which in favorable circumstances lead to liquid crystal behavior.[37] The potentially mesogenic nature of the cinnamoyl grouping is illustrated, e.g., by 4-methoxycinnamic acid[38] which forms a nematic mesophase between 171 °C and 189 °C.

In summary, by virtue of the rich stereochemistry of the cyclobutane ring, photocycloaddition can act as an effective probe into the micromorphology of a photoreactive solid. In ethyl cinnamate glasses the high content of α-truxillate and β-truxinate in the photoproducts indicates a preference for the two contact geometries which correspond to the most compact reactant pair configurations in the ground state. The predominance of these site geometries in the matrix reveals a considerable degree of intermolecular correlation.

Photocycloaddition as a structural probe is particularly useful in the study of some photoreactive polymers where local morphology determines the chemical, and the photographic, properties of the material. We have reported on that aspect in earlier communications.[39,40]

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Solvolysis of 2-(Trifluoromethyl)-2-propyl Trifluoromethanesulfonate. Solvent, Salt, and β-Deuterium Isotope Effects. Substituent Effect of a Strongly Deactivating Group and Rate-Limiting Solvent-Assisted Elimination[1]

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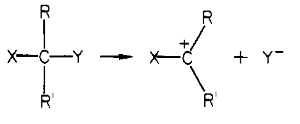
Abstract: Solvolysis rates of 2-(trifluoromethyl)-2-propyl trifluoromethanesulfonate (**2c**) in a variety of solvents did not show a correlation with rates for 2-adamantyl tosylate in the same solvents. The effect of added salts on the rates of **2c** and 2-propyl tosylate in 80% EtOH was very similar, with significant rate increases for nucleophilic/basic salts. Methyl CD_3 isotope effects on the rate of **2c** in three solvents showed average values $k(d_0)/k(d_3) = 1.78$ and $k(d_0)/k(d_6) = 3.80$. The initial observed product from **2c** was $CF_3C(CH_3){=}CH_2$ (**4**) in all cases. The rate ratio $k(i\text{-PrOTf})/k(\mathbf{2c})$ ranges from a high of 4×10^6 in TFA to a low of 1.5×10^4 in EtOH and shows a high degree of destabilization of a cationic transition state by the CF_3 group. The results are interpreted in terms of rate-limiting solvent or salt attack on an intimate ion pair formed from **2c**. The observed average product ratio $CF_3C(CD_3){=}CH_2/CF_3C(CH_3){=}CD_2$ of 1.9 from **2c**-d_3 in CF_3CO_2D, HFIP, and CD_3CO_2D is consistent with this conclusion.

The study of substituent effects on solvolytic reactions leading to carbonium ion intermediates has historically been limited to systems as shown in eq 1, where X is hydrogen or some more



(1)

electron-donating substituent such as alkyl, aryl, vinyl or some heteroatom-substituted group such as R″S or R″O. However, quite recently there has developed a strong interest in the study of systems where X is more electron withdrawing than hydrogen[2-8] and the effects of α substituents such as CHROTs,[4] CH=O,[5] and CN[7,8] have been examined, both experimentally and theoretically.[7c,8]

Our own interest in the effect of strongly deactivating groups on solvolytic reactivity arose from studies of the rates of pro-

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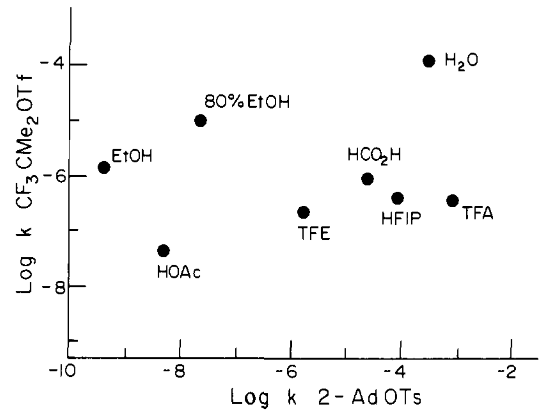


Figure 1. Comparison of solvent effects on reactivity of $CF_3C(CH_3)_2OTf$ (**2c**) and 2-adamantyl tosylate at 25 °C.

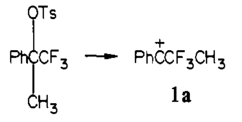
tonation of alkenes,[9] in which it was found that the reactivity of α-CF_3-substituted styrenes (eq 2) could be predicted from our

$$ArCCF_3{=}CH_2 \xrightarrow{H^+} Ar\overset{+}{C}CF_3CH_3 \quad (2)$$

$$\log k_{H^+} = -10.5\textstyle\sum\sigma_p^+(R) - 8.92 \quad (3)$$

previously introduced[9b] eq 3 by using the σ_p^+ values of the CF_3 group and of the aryl group as a whole. The rate ratio $k_{H^+}(PhCH{=}CH_2)/k_{H^+}(PhCCF_3{=}CH_2)$ was 10^7, and the ρ^+ value for the dependence of k_{H^+} on the group X for $XC_6H_4CCF_3{=}CH_2$ was −4.0, the largest magnitude of ρ^+ reported for a styrene protonation.[9a] For X = H, p-Cl, and m-Cl the styrenes were less reactive than ethylene itself by factors of 10, 10^2, and 10^3, respectively.[9a] All of these results reflect the potent destabilizing effect of the CF_3 on carbonium ion formation. Previous workers[2,3] had also shown that allylic and α-CF_3 had strong rate-retarding effects on solvolysis.

In independent and simultaneous work our group[1] and that of Liu and co-workers[10] studied the solvolysis of 1-phenyl-1(trifluoromethyl)ethyl tosylate (**1**, eq 4) and found that in 100% EtOH



$$PhC(OTs)(CF_3)CH_3 \rightarrow Ph\overset{+}{C}CF_3CH_3 \quad (4)$$

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this compound reacted with a relative rate ratio $k(PhCHOTsCH_3)/k(\mathbf{1})$ of 2×10^5 at 25 °C. The rate ratio α-CH_3/α-CD_3 in acetic acid was 1.54. Both of these facts supported rate-limiting formation of the carbonium ion **1a** and demonstrated a strong destabilizing effect of the CF_3 group. Liu and co-workers[10] also studied aryl-substituted derivatives $ArC(OTs)CF_3CH_3$ and reported a very strong dependence of the rates on the aryl substituents (ρ^+ was −6 to −9). The large magnitude of ρ^+ also illustrates the high electron demand induced by the CF_3 group.

In a preliminary communication[1] we have presented preliminary rate data for solvolysis of the 2-(trifluoromethyl)-2-propyl sulfonates **2a** and **2b**. The current report deals with the study of **2c** ($CF_3CMe_2OSO_2R$ (**2a**, R = p-Tol; **2b**, R = CH_3; **2c**, R = CF_3)).

Results

Preparation of **2** and the precursor alcohols **3**,[11] including compounds where one or both methyl groups were deuterated, was carried out as shown in Scheme I.

Scheme I

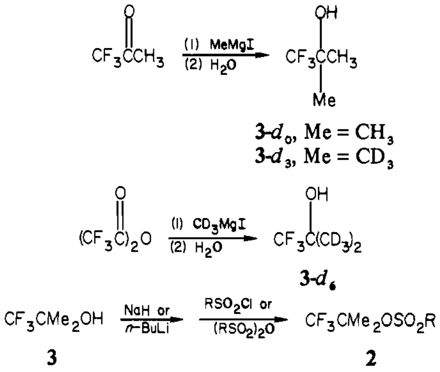

Table I. Solvolytic Rate Constants for 2-(Trifluoromethyl)-2-propyl Triflate

solvent	T, °C	10^5k_{obsd},[a] s^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
TFA	90.2	70.0		
	74.0	14.5		
	60.0	3.01		
	25.0[b]	0.0364	24.4	−6.3
97% HFIP	100.1	90.0		
	83.9	22.9		
	70.4	6.42		
	25.0[b]	0.0428	21.9	−14.3
97% TFE	99.8	79.2		
	84.5	19.7		
	70.3	4.85		
	25.0[b]	0.0227	23.4	−10.3
HCO_2H	74.3	75.0		
	58.3	9.30		
	43.7	1.51		
	25.0[b]	0.0897	27.3	5.3
HOAc	106.0	54.1		
	90.2	11.6		
	74.2	2.21		
	25.0[b]	0.00418	25.6	−6.5
80% EtOH	64.9	78.5		
	49.6	16.7		
	35.2	3.26		
	25.0[b]	0.950	21.6	−9.2
100% EtOH	84.9	73.9		
	70.5	18.9		
	54.0	3.78		
	25.0[b]	0.134	21.6	−12.8
100% EtOH (0.06 M NaOAc)	74.2	174		
	60.1	48.7		
	47.0	10.8		
	25.0[b]	0.818	21.9	−8.2

[a] Determined titrimetrically with at least two runs at each temperature, reproducibility ±5%. [b] Extrapolated.

Rates of solvolysis of **2a**[13] and **2b** were reported previously.[1] However, these derivatives reacted at inconveniently high temperatures, so in the present study resort was made to the much more reactive trifluoromethanesulfonate (triflate) **2c**.[14] Rates for **2c**-d_0 were measured titrimetrically in various solvents and are reported in Table I, along with derived activation parameters. A rate for **2c**-d_0 in H_2O at 25 °C was calculated from the previously reported[1] rate for **2a** and a $k(Tf)/k(Ts)$ ratio[14] of 7×10^4. The effects of the added salts NaN_3, NaCl, $NaClO_4$, and NaOAc on the rate of **2c** in 80% EtOH were measured at 54.6 °C and are reported in Table II along with comparative measurements for i-PrOTs under the same conditions. The effect of 0.06 M NaOAc on the rate of **2c** in 100% EtOH was also measured and is reported in Table I.

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Table II. Salt Effects on the Solvolysis of $RCMe_2OY$ in 80% Aqueous Ethanol at 54.6 °C

		10^5k_{obsd},[a] s^{-1}	
salt	concn, M	Me_2CHOTs	CF_3CMe_2OTf (2c)
$NaClO_4$	0.00	9.35[b]	28.3
	0.02	9.27	29.6
	0.04	9.59	27.9
	0.06	9.10	31.2
NaCl	0.00	9.35	28.3
	0.02	10.26	34.4
	0.04	10.17	37.5
	0.06	12.30	42.1
NaOAc	0.00	9.35	28.3
	0.02		41.7
	0.04		50.5
	0.06		64.6
NaN_3	0.00	9.35[c]	28.3[d]
	0.02	12.6[c]	41.8[d]
	0.04	20.3[c]	67.1[d]
	0.06	26.9[c]	81.4[d]

[a] Determined titrimetrically. Rates for **2c** and NaN_3 or NaCl are averages of duplicate runs; other points are single runs. [b] Lit.[17a] $8.96 \times 10^{-5}\ s^{-1}$ (interpolated). [c] Infinity titers were 96, 68, 46, and 36% of the theoretical values for 0.00, 0.02, 0.04, and 0.06 M NaN_3, respectively. [d] Infinity titers were 105, 93, 85, and 90% of the theoretical values for 0.00, 0.02, 0.04, and 0.06 M NaN_3, respectively.

Solvolysis for **2c**-d_3 and **2c**-d_6 were measured by conductivity in several solvents as reported in Table III. Rate determinations on the deuterated substrates were interspersed with measurements on **2c**-d_0 by using the same conductivity cell and the same batch of solvent to ensure the reliability of the calculated $k(d_0)/k(d_3)$ and $k(d_0)/k(d_6)$ ratios. The conductimetric rate constants for **2c**-d_0 agreed with the values interpolated from the titrimetric rates, as indicated in Table III.

Product studies were carried out by sealing a sample of **2c** in an NMR tube in the appropriate solvent and heating the tube for 10 half-lives for solvolysis. Observation of the NMR spectrum of the product in the reaction medium showed signals corresponding to 2-(trifluoromethyl)propene (**4**) as the only initial product in all of the reaction media studied, namely, TFA, HFIP, CD_3CO_2D, CD_3CD_2OD, 80% CD_3CD_2OD–20% D_2O, and 80% CD_3D_2OD–20% D_2O containing an equivalent amount of NaN_3. The detection limit for substitution products under these conditions was estimated as 5%. As **4** is a gas at 25 °C, there was probably some vapor pressure of this material in the NMR tube but no substitution products were detected in any case. Thus elimination was the observed reaction path in all the systems studied (eq 5).

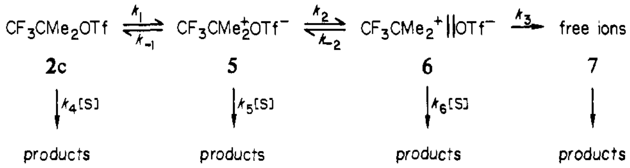
$$\underset{\mathbf{2c}}{CF_3C(OTf)(CH_3)_2} \rightarrow \underset{\mathbf{4}}{CF_3C(CH_3){=}CH_2} \qquad (5)$$

The infinity titers in 80% CH_3CH_2OH containing 0.00, 0.02, 0.04, and 0.06 M NaN_3 were 105, 93, 85, and 90% of the theoretical values, respectively. The formation of covalent azide product would have resulted in a proportional decrease in these infinity titers, so these results confirm that no more than 15% of such a product is formed.

The product ratio $CF_3C(CD_3){=}CH_2/CF_3C(CH_3){=}CD_2$ from **2c**-d_3 in HFIP-d_2, CF_3CO_2D, and CD_3CO_2D was measured by the same NMR method by integration of the CH_2 (near δ 5.30 and 5.60) and CH_3 (near δ 1.90) resonances and found to be δ 1.9 (±0.1) in each. The same ratio in CD_3OD was found to be 3.0 (±0.4), but this ratio was harder to measure because the OH peak in the product overlapped the vinyl resonance. Interestingly the CH_3 signal of **4**-d_2 overlaps that of its precursor **2c**-d_3 in all the solvents studied, although the former is somewhat sharper. After 4 days in CF_3CO_2D at 80 °C (75 half-lives) the product from **2c**-d_3 showed conversion to the extent of 30% to a mixture of $CD_2{=}C(CH_3)CO_2D$ and $CH_2{=}C(CD_3)CO_2D$, as evidenced by the appearance of sharp resonances at δ 1.96 (CH_3) and 5.90 and 6.40 ($C{=}CH_2$). The conversion of **4** to methacrylic acid under solvolytic conditions was observed by us previously,[9a] and the sharp signals in the methacrylic acid are consistent with the reduced allylic couplings in these deuterated acids. Successive solvolysis of the fluorines of **4** as previously proposed[9a] according to the stoichiometry below fits the current result.

$$4CF_3CO_2D + \underset{\mathbf{4}}{CH_2{=}CMeCF_3} \rightarrow 2(CF_3CO)_2O + CH_2{=}CMeCO_2D + 3DF$$

Scheme II



Discussion

The details of the steps involved during the solvolysis of sulfonate esters have been a long standing subject of mechanistic study, and there has been a continuing increase in the level of understanding of these reactions.[15] Many different techniques have been developed for elucidating the details of these processes, and those that were applied in the present study were the effect of variation in solvent,[16] salt effects,[17] and structural β-deuterium isotope effects.[18]

The solvolysis of **2c** by the generally accepted[15] ion-pair mechanism is shown in Scheme II in which the substrate CF_3CMe_2OTf (**2c**) ionizes to an intimate ion pair **5** which dissociates to solvent-separated ion pair **6** and then to free ions **7**. Product formation can be considered to occur from any of the compounds **2c** and **5**–**7** by attack of solvent or other species (such as added salt) present in the solution to give products of either nucleophilic substitution or elimination.

In the case of **2c** it is immediately apparent from the results that one of the steps, k_4 to k_6, involving solvent assistance must be rate determining. This follows from the absence of a dependence of the observed rates upon the solvent-ionizing power and is supported by the effect of added salts upon the rates and the β-deuterium isotope effects. If formation of the ion pair or **5** or dissociation to **6** or **7** were rate limiting, then a correlation of the rate with solvent ionizing power would be expected, as was observed in the case of 1-aryl-1-(trifluoromethyl)ethyl sulfonates.[1,10] The fact that the rates for **2c** are faster in the relatively poorly ionizing but strongly nucleophilic solvents 80% EtOH and EtOH than in TFA, TFE, and HFIP shows that direct involvement of the solvent in the rate-limiting transition state is important.

It is worthy of note that solvent participation in the nucleophilic media in the rate-limiting step is implied for **2c** even though the only product observed in any of these solvents is that of elimination

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Table III. Structural β-Deuterium Isotope Effects in Solvolysis of $CF_3CMeMe'OTf$

solvent	T, °C	10^5k_{obsd},[a] s^{-1} Me, Me′ = CH_3	Me = CH_3, Me′ = CD_3	Me, Me′ = CD_3	k_H/k_{d_3}	k_H/k_{d_6}
97% TFE	64.3	2.42[b]	1.29	0.650	1.87	3.73
100% EtOH	70.5	18.9[b]		5.07		3.73
100% EtOH	64.0	11.1[b]	6.42	2.80	1.73	3.97
80% EtOH	54.8	28.8[b]	16.6	7.62	1.73	3.78

[a] Determined conductimetrically. Duplicate runs in all cases, with agreement between runs of +5%. [b] Interpolated values from Table I are 2.58, 19.5, 10.5, and 28.6, respectively.

and not nucleophilic substitution. However it is known[17b] that there is some correspondence between the ability of salts to promote elimination and their nucleophilicity, and it is not unreasonable that similar behavior is observed for solvent effects.

The dependence of the rates in 80% ethanol on the presence of added salts (Table II) is also consistent with rate-limiting attack of solvent or salt. Thus for the nonnucleophilic, nonbasic $NaClO_4$ very little effect on the rate of either *i*-PrOTs or **2c** is observed.[19] For the highly nucleophilic NaN_3 there is a strong dependence of both substrates on the concentration of added salt, and coincidently the rate increase is by the same factor (2.9) for the comparison of 0.06–0 M salt concentration for both. In the case of isopropyl tosylate the rate acceleration is due to the formation of covalently bonded isopropyl azide and is quantitatively correlated with the decrease in infinity titers.[17a] For **2c** no formation of covalent azide product could be detected either by NMR analysis of the product or by change in the infinity titers (the detection limit is estimated as 10%). This equality of the rate acceleration of azide by nucleophilic attack on isopropyl tosylate and by salt-induced elimination on **2c** is consistent with the known[17b] correspondence of these properties already noted. The effect of NaOAc on the rate of solvolysis of **2c** in 80% EtOH is almost as great as the effect of NaN_3, and even NaCl makes a significant contribution to the reactivity of both substrates (the acceleration by 0.06 M NaCl is by a factor of 1.32 for *i*-PrOTs and 1.49 for **2c**).

Thus the effect of the change of solvents and the effect of salts on the rate of **2c** both indicate that the rate-limiting step is one involving participation by the medium. The isotope effect on the rate confirms that elimination is rate limiting and is consistent with the intervention of ion pairs.

In Table III data are presented for the influence of both one and two CD_3 groups on the rate of reaction in several solvents. The isotope effects are seen to be largely unaffected by changes in solvent and temperature so the origin of the observed effects is a general one for the solvents studied. The most consistent explanation of this behavior is that there is an equilibrium formation of the intimate ion pair, which undergoes elimination in the rate-determining step of the reaction.[20a] Thus the reactions that would be involved for the d_0, d_3, and d_6 substrates and the corresponding rate laws for each are as shown in eq 6–12 (Scheme III). In eq 10 there is a primary isotope effect r'_5 for loss of deuterium and a secondary isotope effect r_5 of a CD_3 group for loss of a proton from CH_3. The factor $^1/_2$ is in eq 10 because there are only half the number of equivalent methyl groups in this compound as there are in the other two substrates. From these equations the values of the calculated isotope effects are as given in eq 13 and 14.[20a] Values of the parameters $r_1 = 1/1.46$ and

$$k(d_0)/k(d_3) = 2/r_1(r_5 + r'_5) \qquad (13)$$

$$k(d_0)/k(d_6) = 1/r_1^2r_5r'_5 \qquad (14)$$

$r'_5 = 1/1.90$ are available[18c] in 80% EtOH at 25 °C. From eq 9 the ratio alkene-d_3/alkene-d_2 equals r_5/r'_5 so from the observed average alkene ratio of 1.9 for HFIP, CF_3CO_2D, and CD_3CO_2D r_5 is calculated as 1.0. This result is not inconsistent with known[20b] secondary deuterium isotope effects on elimination in cyclopentyl systems. By eq 13 and 14 these give values $k(d_0)/k(d_3) = 1.91$ and $k(d_0)/k(d_6) = 4.05$, in reasonable agreement with the average measured values of 1.78 and 3.80, respectively.

Scheme III

d_0 Case

$$\text{ROTf} \xrightleftharpoons{K_1} \text{R}^+\text{OTf}^- \xrightarrow{k_5} \text{alkene-}d_0 \qquad (6)$$

$$\text{rate} = k_5K_1[\text{ROTf}] \qquad (7)$$

d_3 Case

$$\text{ROTf} \xrightleftharpoons{r_1K_1} \text{R}^+\text{OTf}^- \qquad (8)$$

$$\text{alkene-}d_2 \xleftarrow{r'_5k_5} \text{R}^+\text{OTf}^- \xrightarrow{r_5k_5} \text{alkene-}d_3 \qquad (9)$$

$$\text{rate} = r_1K_1(r_5 + r'_5)^1/_2k_5[\text{ROTf}] \qquad (10)$$

d_6 Case

$$\text{ROTf} \xrightleftharpoons{r_1^2K_1} \text{R}^+\text{OTf}^- \xrightarrow{r_5r'_5k_5} \text{alkene-}d_5 \qquad (11)$$

$$\text{rate} = r_1^2K_1r_5r'_5k_5[\text{ROTf}] \qquad (12)$$

This agreement between the measured isotope effects and the expectations for rate-limiting elimination from the intimate ion pair gives support to this mechanism. In particular the observation that the d_6 isotope effect is greater than the square of the d_3 isotope effect argues strongly for rate-limiting elimination. It is highly unlikely that a solvent-separated ion pair could be formed reversibly in this case; this occurs only with very stable carbonium ion intermediates,[21] and $CF_3CMe_2^+$ is strongly destabilized by the CF_3 group.[22] Attempts to prepare this ion by protonation of $CF_3CMe{=}CH_2$ were unsuccessful.[9a]

Other precedent for the involvement of ion pairs in solvolytic reactions comes from studies of other methyl-substituted tertiary substrates which were interpreted in terms of equilibrium formation of intimate ion pairs,[18c] and studies by Bunnett and coworkers[23] of ^{18}O scrambling in solvolysis of secondary benzenesulfonates which implicate reversible formation of ion pairs. Other studies have also suggested the generality of ion-pair formation in solvolysis.[17e,24]

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(19) the magnitudes of "normal" salt effects are known to be quite specific for different salts and depend upon both R and X in solvolysis of RX as well as the solvent and temperature: Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2763–7.

(20) (a) This assumption of an equilibrium of **2c** and the intimate ion pair follows the treatment of: Humski, K.; Sendijarevič, V.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 7722–7728. An alternative approach uses a steady-state treatment for cumyl derivatives, including d_0, d_3, and d_6 compounds: Smith, S. G.; Goon, D. J. W. *J. Org. Chem.* **1969**, *34*, 3127–3131. Our consideration of product formation from **2c**-d_3 is analogous to that of these earlier authors but assumes that the contribution of external ion OTf^- on the elimination is negligible. The slight effects of added $NaClO_4$ on the rates suggest this assumption is reasonable. For a recent related study on isotope effects in alkene formation from a carbonium ion see: Lomas, J. S. *J. Org. Chem.* **1981**, *46*, 412–415. (b) Shiner, V. J.; Nollen, D. A.; Humski, K. *J. Org. Chem.* **1979**, *44*, 2108–15. (c) For a report of almost cumulative effects in an elimination see: Thorne, M. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 716–8.

(21) For references and a recently reported example see: Miller, L. S.; Zazzaron, D.; Dannenberg, J. J.; Metra, R.; Gillard, M. *J. Org. Chem.* **1980**, *45*, 641–4.

(22) Comparison of the heats of the reactions $CF_3CH_3 \rightarrow CF_3CH_2^+$ and $CH_3CH_3 \rightarrow CH_3CH_2^+$ indicates the formation of the trifluoroethyl cation is 53 kcal/mol less favorable: Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 58–67; **1977**, *99*, 7432–9.

(23) Paradisi, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 946–8.

It has however recently been suggested by Jencks[25] that solvolysis reactions that would lead to intermediates no more stable than secondary carbonium ions in the presence of "reasonably good nucleophiles" do not actually form intimate ion pairs but instead react through essentially concerted processes. As the cation $CF_3CMe_2^+$ is significantly less stable[22] than secondary cations such as Me_2CH^+, this interpretation suggests that k_4 (Scheme II) would be rate determining. Jencks' view even presupposes[25] that ^{18}O scrambling in labeled substrates occurs by sigmatropic rearrangement and not ionization, so this experiment cannot be used as a definitive test. The evidence at hand for **2c** does not rigorously exclude k_4 as being rate determining, and resolution of this mechanistic ambiguity must await the results of further study.

A quantitative measure of the degree of solvent participation in a solvent has been proposed[15a] as $[k(\text{ROTs})/k(\text{2-AdOTs})]_{\text{solvent}}/[k(\text{ROTs})/k(\text{2-AdOTs})]_{\text{TFA}}$. For **2c** this expression yields values for the solvent participation of 1030, 11, 340, 84, 1.8×10^4, 9.7×10^5, and 7.7×10^6 in H_2O,[26a] HFIP, TFE, HCO_2H, HOAc,[26a] 80% EtOH, and EtOH, respectively. These values are greater than those of *i*-PrOTs[15a] in every case, and the indicated degree of solvent assistance even in 97% TFE and HFIP is quite remarkable.

Rate ratios $k(i\text{-PrOTf})/k(\mathbf{2c})$ were calculated[26b] and range from a high of 4×10^6 in TFA to a low of 1.5×10^4 in EtOH. The larger value is comparable to the k_H/k_{CF_3} ratio for PhCRMeOTs[1,27] which apparently involves carbonium ion formation. The lower values in the more nucleophilic solvents are consistent with solvent participation being more important for **2c** than for *i*-PrOTs.

An interesting comparison can be made between **2c** and $NCCMe_2OTf$.[7] This cyanotosylate undergoes solvolysis to give the elimination product methacrylonitrile as the only observed product in 100% TFE, with a rate slower than that of $HCMe_2OTf$ by 4×10^3. It was proposed that this process occurs by rate-limiting ionization via a transition state that contained an incipient carbonium ion center. The strongest piece of evidence for this conclusion was the isotope effect $NCC(CH_3)_2OTf/NCC(CD_3)_2OTf = 2.19$, which was felt to be appropriate for such a process but not for a rate-limiting elimination or nucleophilic solvent displacement. At that time we had reported no isotope effects for **2c** for comparison, but the values in Table III give strong confirmation that **2c** and $NCCMe_2OTf$ do react by different mechanisms. Thus the larger isotope effect for **2c** is consistent with rate-limiting elimination, whereas the smaller effect found for $NCCMe_2OTf$ is in agreement with rate-limiting ionization, as proposed by Gassman and co-workers.[7]

Experimental Section

Elemental analyses were by Galbraith Laboratories, Knoxville, TN. Melting points and boiling points are uncorrected. NMR spectra were measured by using a Varian T-60 instrument with tetramethylsilane as an internal standard.

Commercial reagents included iodomethane-d_3 (>99.5% *d*) from Merck, Sharp, and Dohme (Canada), hexafluoro-2-propanol (HFIP) from Eastman; 2-(trifluoromethyl)propene (**4**) from PCR, and 1,1,1-trifluoroacetone, trifluoroacetic anhydride, trifluoroacetic acid, sodium trifluoroacetate, trifluoromethanesulfonyl chloride, trifluoromethanesulfonic anhydride, and trifluoroethanol (TFE) from Aldrich.

2-(Trifluoromethyl)-2-propanol (**3**)[11] was prepared from addition of trifluoroacetone (5.6 g, 0.05 mol) in 25 mL of ether to a stirred solution of methylmagnesium iodide (0.05 mol) in ether under N_2 at 0 °C. After being stirred 4 h while being warmed to room temperature, the solution was cooled again in ice and a saturated solution of NH_4Cl was slowly added with stirring. The ether layer was separated and the aqueous layer extracted with ether. The combined ether layers were washed with saturated NaCl and dried over Drierite. The ether was slowly distilled away and the residue fractionated at atmospheric pressure through a 20-cm column containing a metal spiral to give 4.5 g (0.035 mol, 70%) of **3**: bp 78–80 °C; NMR (CCl_4) δ 1.42 (s, 6, Me_2) 2.00 (s, 1, OH). The preparations of **3**-d_6 were carried out in a similar fashion by using CD_3MgI (prepared from CD_3I) instead of CH_3I and substituting[11] $(CF_3CO)_2O$ for trifluoroacetone in the latter case.

The preparations of **2a**[13] and **2b** were carried out by reaction of **3** with *n*-butyllithium in ether followed by the appropriate sulfonyl chloride: **2a** bp 84 °C (0.2 mm); **2b** bp 84 °C (30 mm), mp 21 °C; NMR (CCl_4) δ 1.78 (s, 6, CF_3CMe_2) and 3.02 (s, 3, $MeSO_2$). Anal. Calcd for $C_5H_9F_3O_3S$ (mol wt. 206.18) C, 29.13; H, 4.40. Found: C, 28.73, 28.44; H, 4.14, 4.39.

For preparation of 2-(trifluoromethyl)-2-propyl trifluoromethanesulfonate (**2c**) 6.5 g (0.051 mol) of **3** in 20 mL of ether was added to 0.51 mmol of NaH (pentane washed) in 100 mL of ether stirred in an ice bath. Then 8.6 mL (14.4 g, 0.071 mol) of trifluoromethanesulfonic anhydride was added slowly through a syringe, and the solution was stirred overnight while being warmed to room temperature. The reaction mixture was filtered and the ether removed by rotary evaporation and distilled to give 3.9 g (0.015 mol, 29%) of **2c**: bp 75 °C (50 mm); NMR (CCl_4) δ 1.78 (br s).

Solvent Purification. Glacial acetic acid (Fisher) was refluxed with triacetyl borate (2 g 100 mL) and distilled at atmospheric pressure.[28a] Formic acid (BDH 97%) was treated with B_2O_3 for 3 days at room temperature, decanted, and distilled from fresh B_2O_3 at reduced pressure.[28b] Trifluoroacetic acid (Aldrich) was distilled at 71–72 °C, and 1% trifluoroacetic anhydride and 0.2 M NaO_2CCF_3 were added to the distillate.[28c] Trifluoroethanol (Aldrich) was distilled from P_2O_5 (1.5 g/100 mL) at 73–75 °C, and 3% (w/w) H_2O was added.[18c] Hexafluoro-2-propanol was kept over 3A molecular sieves 2 days, decanted, distilled from fresh molecular sieves, and 3% (w/w) H_2O was added.[28d] Absolute ethanol (60 mL) was refluxed with 5 g of Mg turnings and a few drops of $CHCl_3$. When the Mg metal had completely reacted, and additional 900 mL of absolute ethanol was added, refluxed and distilled.[28a] Ethanol (80%) was prepared from 400 mL of absolute ethanol and 100 mL of distilled H_2O.

Kinetics. Titrimetric rates were carried out by the ampule procedure of Winstein et al.[28b] with 0.01–0.05 M solutions. Aliquots (2 mL) in sealed tubes were quenched in 15 mL of reagent grade acetone and titrated at 0 °C with 0.02 M NaOH with bromothymol blue indicator. Hydrolysis of **2b** was measured by using 5-mL aliquots of an 0.012 M solution, and the results were reported previously.[1]

Salt effects in 80% EtOH were measured[17a] by using 4.5-mL samples of 0.01 M solutions of **2c** containing the specified salt concentrations. Ampules were removed from the constant-temperature bath at appropriate intervals and quickly cooled, and 4-mL aliquots were titrated by using 0.02 M NaOH and bromthymol blue indicator.

Trifluoroacetolysis rates were followed by NMR with 0.18 M **2c** and 0.2 M added NaO_2CCF_3. Aliquots were sealed in ampules which were withdrawn periodically from the constant-temperature bath and cooled, the cold solutions transferred to NMR tubes, and areas of the alkyl and alkene absorptions integrated.

Conductimetric rates were measured by using $(0.5\text{–}1) \times 10^{-3}$ M solutions and a Beckman conductivity bridge.

Products. A solution of 50 mg of **2c** and 0.5 mL of solvent was sealed in an NMR tube which was placed in the constant-temperature bath. The spectrum was recorded after 1, 2, and 10 half-lives and in all cases showed conversion to $CH_3C(CF_3){=}CH_2$ (**4**) as the only observable product. A sample of $Me_2C(CF_3)O_2CCF_3$ was prepared from the alcohol and trifluoroacetic anhydride and showed no measurable conversion to **4** after 10 half-lives for the reaction of **2c** in TFA. On prolonged reaction in TFA **4** underwent conversion to methacrylic acid, as described in the Results.

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(26) (a) These values differ slightly from those reported in ref 1. (b) with use of a $k(\text{OTf})/k(\text{OTs})$ ratio of 7×10^4.[14]

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