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Solvolytic Reactivity of 1-Trifluoromethyl-1-phenylethyl Tosylate. Formation of a Highly Destabilized Carbonium Ion[1]

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Abstract: The solvolytic rate constants of 1-trifluoromethyl-1-phenylethyl tosylate (**2**) in solvents of widely different ionizing power and nucleophilicity are linearly related with slope $m_{\mathrm{OTs}} = 1.01$ to the rates of 2-adamantyl tosylate in the same solvents. The rate ratio $k(\mathrm{PhCHMeOTs})/k(\mathbf{2})$ is 2×10^5 in 100% EtOH. Added salts cause modest increases in the rate of solvolysis of **2** in 80% EtOH independent of the nucleophilicity or basicity of the salts. The isotope effect $k(\mathrm{CH_3})/k(\mathrm{CD_3})$ on the rate of solvolysis of **2** ranges from values around 1.6 in the less ionizing solvents to values around 1.3 in more ionizing solvents. The product from **2** is mainly that of substitution in all solvents studied, with increasing amounts of elimination in the less ionizing solvents. These results are interpreted in terms of rate-limiting ionization of **2** to form a carbonium ion intermediate.

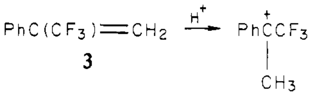
The influence of strongly electron-withdrawing substituents on the formation of carbonium ion intermediates has recently become an area of very intense activity. Particular interest has focused on reactivity studies involving the groups $\mathrm{CF_3}$,[1-5] CN,[6,7] RC=O,[8,9] and RCHOTs.[10] There have also been theoretical studies designed to illuminate the experimental studies.[6c,11]

Studies in our laboratory have concentrated on the influence of the $\mathrm{CF_3}$ substituent.[1,2] Thus it was found that $\mathrm{CF_3CMe_2OTf}$ (**1**) underwent solvolysis in a process in which formation of a carbonium ion intermediate was not solely rate limiting. The results were interpreted in terms of preliminary formation of an ion pair which then underwent rate-limiting elimination assisted by solvent or added salt to form the product alkene (eq 1). The

$$\underset{\mathbf{1}}{\mathrm{CF_3CMe_2OTf}} \rightleftharpoons \mathrm{CF_3CMe_2{}^+\ OTf^-} \xrightarrow{\text{slow}} \mathrm{CF_3CMe{=}CH_2} \quad (1)$$

evidence for this included the fact that the rates of **1** as a function of solvent were not correlated with the rates of 2-adamantyl tosylate (2-AdOTs) solvolysis (a process that does involve rate-limiting carbonium ion formation), large rate accelerations by added salts contrary to what is observed with 2-AdOTs, rate ratios $k(i\text{-PrOTf})/k(\mathbf{1})$ of 1.5×10^4 to 4×10^6 in different solvents indicating electron-withdrawing substituent effects of $\mathrm{CF_3}$ on a carbonium ion intermediate, and nonadditive $\mathrm{CH_3/CD_3}$ isotope effects. All of these results were consistent with the mechanism of eq 1 in which carbonium ion formation *and* elimination are involved before or during the rate-limiting step.

The present report deals with studies of the solvolysis of 1-trifluoromethyl-1-phenylethyl tosylate ($\mathrm{PhCCF_3MeOTs}$, **2**), which has been independently and simultaneously studied by Liu and co-workers.[3] Their studies are being pursued along lines different from ours.[3b,12] Our own work began with studies of the hydration of α-trifluoromethylstyrene (**3**) which was found to undergo rate-limiting protonation to a carbonium ion **4** at a rate actually lower than that of ethylene (eq 2).[2b] This result was predictable



$$\underset{\mathbf{3}}{\mathrm{PhC(CF_3){=}CH_2}} \xrightarrow{\mathrm{H^+}} \underset{\mathbf{4}}{\mathrm{Ph}\underset{\underset{\mathrm{CH_3}}{|}}{\overset{+}{\mathrm{C}}}\mathrm{CF_3}} \quad (2)$$

3

4

from our previously introduced correlation (eq 3) of substituent

$$\log k_{\mathrm{H^+}} = -10.5\textstyle\sum\sigma_{\mathrm{p}}{}^+ - 8.92 \quad (3)$$

effects on the rates of hydration of alkenes using the $\sigma_{\mathrm{p}}{}^+$ constants for the substituents on the alkene.

In another approach to the understanding of the effects of substituents in aliphatic systems, a correlation for solvolytic reactions forming carbonium ion intermediates (eq 4) of the form

$$\mathrm{RR'R''CY} \xrightarrow{-\mathrm{Y^-}} \mathrm{RR'R''C^+} \quad (4)$$

$\log k = \rho\gamma^+ + C$ has been proposed by Traylor,[13] and elaborated by Peters,[14] and by McManus and Harris.[15] The term γ^+ is a substituent constant applicable to the effect of the entire substituent R on a solvolysis reaction as shown. When R is a substituted aryl group, γ^+ is defined as the σ^+ constant of the substituent on the aryl group.[14]

Because of this great interest in extending the study of substituent effects on reactions involving carbocations to include strongly electron-withdrawing groups, and the desire to develop general correlations of substituent effects on solvolytic reactivity, we have now carried out a detailed study of the solvolysis of $\mathrm{Ph(CF_3)MeOTs}$ (**2**).

Results

The substrates $\mathrm{PhC(CF_3)(CH_3)OTs}$ (**2**) and $\mathrm{PhC(CF_3)(CD_3)OTs}$ (**2**-d_3) were prepared from the corresponding alcohols

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Table I. Solvolytic Rate Constants for 1-Trifluoromethyl-1-phenylethyl Tosylate (**2**)

solvent	*T* (°C)	k_{obsd} ($s^{-1} \times 10^{-4}$)[a]	ΔH^* (kcal/mol)	ΔS^* (eu)
TFA[b]	25.0	510	17.0	−7.5
	18.1	280		
	10.25	110		
97% HFIP	20.5	18.5		
	9.9	6.55		
	0.2	2.08		
	25.0[c]	29.5	16.6	−14.3
97% TFE	54.8	12.8		
	45.1	5.16		
	34.6	1.73		
	24.8	0.563		
	25.0[c]	0.587	19.6	−12.2
90% TFE	49.9	8.38		
	34.2	1.77		
	19.7	0.324		
	25.0[c]	0.633	19.3	−13.0
HCO_2H	39.8	23.3		
	24.6	3.56		
	9.8	0.534		
	25.0[c]	3.90[d]	21.5	−2.1
HOAc	78.7	0.737		
	77.4	0.621		
	65.0	0.119		
	61.6	0.0763		
	50.2	0.0165		
	25.0[c]	0.000300[d]	29.6	6.2
80% EtOH	85.1	10.0		
	70.5	2.27		
	54.3	0.371		
	25.0[c]	0.00865[d]	24.3	−4.9
100% EtOH[e]	115.6	9.45		
	99.1	1.91		
	82.7	0.452		
	80.1[c]	0.333		
	25.0[c]	0.000432	24.6	−9.7
100% EtOH	80.1	0.320		

[a] At least duplicate runs in each case, reproducibility ±5%, measured titrimetrically unless noted. [b] Containing 0.200 M NaO_2CCF_3, measured by UV. [c] Calculated from data at other temperatures. [d] Reference 3b reports 6.08×10^{-4} s^{-1} (HCO_2H), 4.12×10^{-8} s^{-1} (HOAc), 7.57×10^{-7} s^{-1} (80% EtOH), 1.95×10^{-6} s^{-1} (70% EtOH), 5.24×10^{-6} s^{-1} (60% EtOH). [e] Containing 6×10^{-2} M NaOAc.

Table II. Salt Effects on the Solvolysis of $PhC(CF_3)MeOTs$ in 80% EtOH-20% H_2O at 65.8 °C

salt	concn (*M*)	k_{obsd} ($s^{-1} \times 10^4$)[a]
$NaClO_4$	0.00	1.33[b]
	0.02	1.50
	0.04	1.64
	0.06	1.67
NaCl	0.00	1.33[b]
	0.02	1.43
	0.04	1.44
	0.06	1.50
NaOAc	0.00	1.33[b]
	0.02	1.34
	0.04	1.44
NaN_3	0.00	1.33[b]
	0.02	1.31
	0.04	1.45
	0.06	1.59

[a] Rates determined titrimetrically, single runs in each case. [b] The interpolated value from Table I is 1.36×10^{-4} s^{-1}.

Table III. Isotope Effects $k(CH_3)/k(CD_3)$ for $PhC(CF_3)MeOTs$

solvent	*T* (°C)	k_{obsd} ($s^{-1} \times 10^5$)[a] CH_3[d]	CD_3	$k(CH_3)/k(CD_3)$
TFA[b]	25.0	5100	3980	1.28
	18.1	2800	2230	1.26
97% HFIP	25.0	333	250	1.33
97% TFE	25.0	5.67	4.24	1.34
HCO_2H	56.2	2090	1710	1.22
	24.8	63.1	50.5	1.25
HOAc[c,f]	90.7	30.0[e]	16.9	1.77
	77.4	6.21	4.00	1.57
	61.6	0.763	0.498	1.54
80% EtOH	55.7	4.74	2.90	1.63

[a] Monitored by the decrease in the absorption at 262 nm unless indicated. All rates obtained in duplicate, with a reproducibility of at least ±5%. [b] No trifluoroacetic anhydride was added in the solvent purification. [c] Measured by titration. [d] For comparison, rates interpolated from the data in Table I are HFIP (25.0 °C), 295; TFE (25.0 °C), 5.87; HCO_2H (56.2 °C), 1340; (24.8 °C), 38.1; 80% EtOH (55.7 °C), 4.38. [e] Extrapolated from Table I. [f] $\Delta H^* = 28.7$ kcal/mol, $\Delta S^* = 2.7$ eu for the CD_3 derivative.

Table IV. Products from the Reaction of **2** in Various Solvents[a]

solvent	*T* (°C)	% **5** (substn)	% **3** (alkene)
TFA	25	85	15
97% HFIP-d_2/D_2O	25	92	8
CD_3CO_2D	75	65	35
80% C_2D_6O/D_2O	80	81	19
95% C_2D_6O/D_2O	80	70	30

[a] Determined by NMR; estimated ±5%.

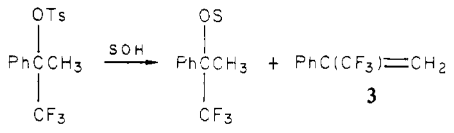
obtained by reaction of $PhCOCF_3$ with CH_3MgI or CD_3MgI, respectively.

The kinetics of reaction of **2** in a series of solvents were followed either titrimetrically or by UV[16] as reported in Tables I and III. Good agreement between these two methods and with independent measurements by Liu and co-workers[3] was found, with the exception of HCO_2H (see footnotes *d* in Tables I and III). These workers first reported[3a] a rate constant in HCO_2H at 25 °C of 4.80×10^{-4} s^{-1}, but more recently[3b] this value is given as 6.08×10^{-4} s^{-1}. The latter value agrees well with our spectrophotometric rate of 6.31×10^{-4} s^{-1} at 24.8 °C and we believe this is the preferred value.

The effects of added salts on the reactivity of **2** in 80% EtOH at 65.8 °C were measured titrimetrically and are summarized in Table II.

For measurements of the isotope effect, $k(CH_3)/k(CD_3)$ rates for all solvents but acetic acid were measured by continuous observation of the decrease in the UV absorption at 262 nm using a thermostated cell compartment in the spectrophotometer. This method was adapted from that of Shiner et al.[16c] Rates for **2** and **2**-d_3 were run in pairs using the same batches of solvents. Isotope effects in HOAc were obtained from titrimetric rates. All of the measured isotope effects are reported in Table III.

Products from the reaction of **2** in several solvents were determined by NMR as reported in Table IV. In all cases after 10 half-lives for reaction only products of substitution by solvent (**5**) and elimination (**3**) were observed. Somewhat more alkene tended to form in the less ionizing solvents. In the case of buffered TFA the further conversion of **5** (S = CF_3CO) to **3** could be observed by NMR and was found to follow first-order kinetics. Rate constants (measured in duplicate) for alkene formation were 4.19×10^{-6} s^{-1} (59.7 °C), 1.95×10^{-5} s^{-1} (75.8 °C), and 7.54×10^{-5} s^{-1} (89.4 °C) with $\Delta H^* = 22.5$ kcal/mol and $\Delta S^* = -15.8$



$$\underset{\mathbf{2}}{PhC(OTs)(CF_3)CH_3} \xrightarrow{SOH} \underset{\mathbf{5}}{PhC(OS)(CF_3)CH_3} + \underset{\mathbf{3}}{PhC(CF_3){=}CH_2}$$

2 **5** **3**

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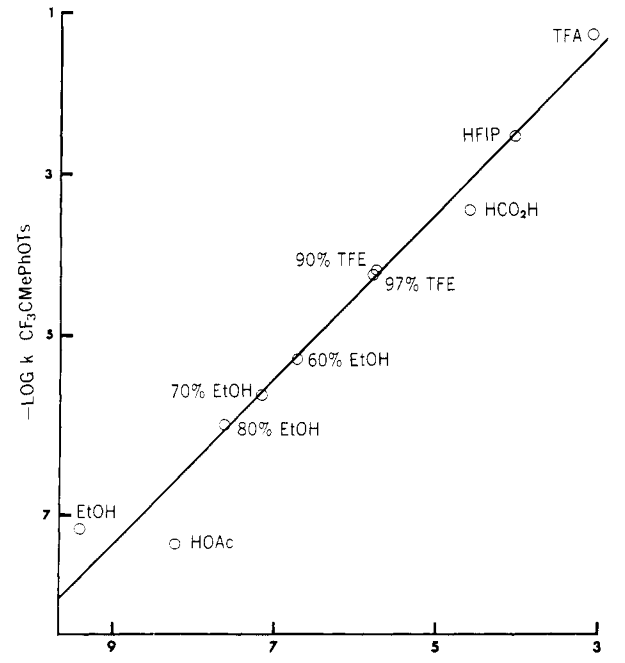
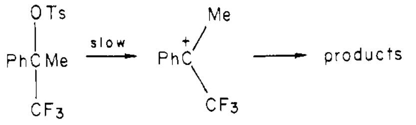


Figure 1. Comparison of solvent effects on reactivity of $CF_3CPhMeOTs$ (**2**) and 2-adamantyl tosylate at 25 °C.

cal/(° mol). The extrapolated rate for the formation of **3** from **5**-$COCF_3$ in TFA at 25 °C is 7.0×10^{-8} s^{-1} or only 10^{-6} times the rate of formation of **5** from **2** at that temperature.

Discussion

The effect of solvent on the rate of reaction of a substrate has proved to be an extremely useful criterion of the reaction mechanism.[2a,17-19] In Figure 1 log k for **2** in various solvents[3c] is compared to log k for 2-AdOTs in the same solvents.[18a,b] A reasonable linear correlation is found with a slope $m_{OTs} = 1.01$ and correlation coefficient 0.986. It is well established that 2-AdOTs reacts by the k_c route of rate-limiting carbonium ion formation,[17-19] and on the basis of the correlation illustrated this mechanism (eq 5) can be assigned to **2** as well.



$$\mathrm{Ph}\overset{\mathrm{OTs}}{\underset{\mathrm{CF_3}}{\mathrm{C}}}\mathrm{Me} \xrightarrow{\text{slow}} \mathrm{Ph}\overset{+}{\mathrm{C}}(\mathrm{Me})\mathrm{CF_3} \longrightarrow \text{products} \qquad (5)$$

2 **4**

Even though the ionization of **2** is rate determining as indicated by eq 5, several intermediates are presumably involved, as formed in the usual ion-pair mechanism for solvolysis (eq 6). In this

$$\underset{\mathbf{6}}{\mathrm{ROTs}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{7}}{\mathrm{R^+OTs^-}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathbf{8}}{\mathrm{R^+||OTs^-}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\mathbf{9}}{\mathrm{R^+}} \qquad (6)$$

scheme product formation can occur by attack on any of the species **6**–**9** to give substitution or elimination products. In the case of CF_3CMe_2OTf (**1**) as mentioned above (eq 1), the dependence of the rate on solvent and other data led to the interpretation that the formation of the initial ion pair **7** was reversible, and that solvent-assisted elimination from this ion pair was rate determining, although direct elimination concerted with ionization could not be rigorously excluded.[2a] The particular paths followed by **1** and **2** depend on several rate constants, but the relative stability of the ion $PhC^+(CF_3)Me$ (**4**) is indicated by its direct observation by NMR,[20] whereas $CF_3C^+Me_2$ has not been observed, and could not be generated by protonation of $CF_3CMe{=}CH_2$.[2b]

The salt effects (Table II) on the reactivity of **2** in 80% EtOH are similar for the different salts and show a modest (13 to 25%) increase in rate on changing from 0.0 to 0.06 M salt. In the solvolysis of 1-adamantyl bromide and 2-adamantyl tosylate in 80% EtOH at 75 °C the presence of 0.06 M NaN_3 caused rate enhancements of 13 and 16%, respectively.[21] These results are suggestive that **2** and the adamantyl derivatives react by the same mechanism, namely, rate-limiting ionization, and are in strong contrast to the results for CF_3CMe_2OTf (**1**), which showed rate enhancements of 120 to 190% with 0.06 M NaOAc and NaN_3, respectively.[2a] The results for **1** were similar to those for the isopropyl tosylate[2a] and indicate both of these substrates are subject to rate-enhancing direct participation by salts and solvent. One test (Table I) showed the effect of NaOAc on the reaction rate of **2** in 100% EtOH was also rather small.

There is a noticeable difference in the methyl isotope effect[22-25] $k(CH_3)/k(CD_3)$ for **2** as a function of solvent (Table III). In particular, for the solvents of higher ionizing strength lower values (1.22 to 1.34) are observed, whereas for the more nucleophilic solvents larger values (1.54 to 1.77) are found. A straightforward explanation of this solvent dependence is that in the more polar solvents there is more stabilization of the developing carbonium ion center by solvent and hence a reduced demand for hyperconjugative stabilization by methyl and a lower isotope effect.

The isotope effects for the different solvents were not measured at the same temperature, but in three cases the temperature dependence of the isotope effect was measured and does not appear to be the major contributor to the observed variations.

Our isotope effect study may be compared with that of aryl-substituted 1-phenylethyl chlorides ArCHClMe.[24] For substrates in this group reacting by a k_c process (eq 7), there was a decrease

$$\mathrm{ArCHClMe} \xrightarrow{\text{-Hal}} \mathrm{Ar}\overset{+}{\mathrm{C}}\mathrm{HMe} \qquad (7)$$

in $k(CH_3)/k(CD_3)$ with increasing carbonium ion stabilizing power of the aryl substituent. For poor electron-donating substituents (m-Br, p-NO_2), low isotope effects were attributed to the incursion of nucleophilic solvent participation. The decrease in rate of **2** induced by solvent change from TFA to 80% EtOH is 6×10^4 and the isotope effect increases by a factor of 2.4 for these solvents, while in the phenylethyl chlorides the rate change induced by the substituents is 1×10^6 and the isotope effect increases by a factor of 2.0. Thus the increase in isotope effect with the decrease in reactivity in these two systems is quite comparable.

In a study of solvolysis of $ArCCl_2Me$ in aqueous dioxane the isotope effect $k(CH_2)/k(CD_3)$ was also found to decrease with increasing solvent polarity.[25] However, this change was attributed to the intervention of rate-limiting elimination in the less polar solvents. In cumyl derivatives a change in leaving group from p-nitrobenzoate to thionbenzoate gave an increase in reactivity

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of 3×10^3 and an increase in $k(d_0)/k(d_6)$ from 1.46 to 1.94.[22d] This effect was interpreted to possibly implicate intervention of rate-limiting elimination giving the larger isotope effects. In cyclopentyl brosylate an increase in the isotope effect $k(\mathrm{H})/k(\beta\text{-}d_4)$ with increasing solvent ionizing power was also ascribed to rate-limiting elimination in the more polar solvent.[16c,26] The argument was made[16c] in this latter study that for the ionization steps "very similar isotope effects for each step apply in all these solvents". We believe, however, on the basis of the foregoing discussion that this latter argument is not applicable to **2**.

It may also be noted that a general linear relationship was proposed between methyl isotope effects and the stability of incipient carbonium ions in solvolysis for widely different carbon structures.[22c] However, this proposal has been recently criticized[18d] and requires further critical examination.

Thus the results obtained for **2** provide convincing evidence that ionization as in eq 5 is rate limiting. Another recent analysis[27] of our preliminary data[1] reaches the same conclusion.

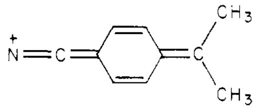
In an independent study of substrates $\mathrm{ArCCF_3MeOTs}$ Liu and co-workers have most recently[3b] concluded that rate-limiting ionization occurs for all the aryl groups and solvents studied. Linear plots of log *k* vs. σ^+ for aryl substituents and of log *k* vs. mY_{OTs} for the Ph and $m\text{-ClC}_6\mathrm{H}_4$ derivatives were particularly convincing evidence for this interpretation.

The rate ratio $k(\mathrm{H})/k(\mathrm{CF_3})$ for PhCRMeOTs in 100% EtOH at 25 °C may be calculated as 2×10^5 from our data and the rate of $8.35 \times 10^{-3}\ \mathrm{s^{-1}}$ interpolated for PhCHMeOTs (**10**) from the data of Hoffmann.[28] Rates for **10** over a wide range of solvent polarity would be difficult to measure because of this compound's high reactivity. Whether or not the rate ratio of 2×10^5 is a true estimate of the rate deceleration of $\mathrm{CF_3}$ on a developing carbonium ion transition state depends on the mechanism of solvolysis of **2** and **10** in EtOH. A k_c process was suggested for 1-phenylethyl chloride in several solvents on the basis of isotope effects,[24] but when electron-withdrawing substituents are present on the aryl ring of 1-phenylethyl chlorides nucleophilic solvent displacement was suggested to become important. The reaction of 1-phenylethyl bromide in 100% EtOH at 50 °C was proposed to involve reversible formation of an ion pair,[29a] but this has been disputed.[29b] Benzyl halides were judged to react largely by a solvent participation mechanism.[17b] In a recent review[30] it was concluded that the 1-phenylethyl system could not be interpreted with confidence in the absence of more systematic study. If there is any contribution of a solvent-assisted path to the reaction of either **2** or **10** in 100% EtOH, then the observed $k(\mathrm{H})/k(\mathrm{CF_3})$ ratio of 2×10^5 would not necessarily be the ratio applicable to a limiting carbonium ion reaction in this solvent. In any event the higher calculated rate of **2** in 100% EtOH at 25 °C compared to HOAc is an artifact of the extrapolation. At 80 °C, close to the temperature of actual measurements for each solvent, the rate is 2.6 times greater in HOAc.

The $k(\mathrm{H})/k(\mathrm{CF_3})$ ratio for the system $\mathrm{Me_2CROTs}$ varied from 1.5×10^4 in EtOH to 4×10^6 in TFA.[2a] Solvent assistance is significant for both of these compounds but would be least important in TFA. The sum of the results suggests that a value of 10^5 to 10^7 is appropriate for this ratio in a carbonium ion forming reaction, and indeed the value found[2b] for styrene protonation $k(\mathrm{PhCH{=}CH_2})/k(\mathrm{PhC(CF_3){=}CH_2})$ was 2×10^7.

For comparison the rate ratio $k(\mathrm{H})/k(\mathrm{CN})$ for carbonium ion forming reactions is about 2×10^3 for a number of systems which are not especially stabilized by other strong donor groups,[6a,d] but assumes values of around 10^6 when an additional strongly stabilizing group is present.[6b] These experimental results indicate a variable electron-donating ability of the cyano group; specifically in cases of high electron demand resonance electron donation is implicated in placing positive charge on nitrogen.[6] This hypothesis

has received theoretical support,[5c,11] but there is neither theoretical nor experimental evidence for a significant electron donation by $\mathrm{CF_3}$ in similar systems. One basis for predicting the relative effects of α-cyano and $\mathrm{CF_3}$ groups on solvolysis reactions would be their $\sigma_p{}^+$ constants, which are 0.66 and 0.61, respectively.[31] These values suggest approximately equal influences of these substituents on carbonium ions, as is observed when electron donation by cyano is not enhanced by high electron demand. The $\sigma_p{}^+$ value for *p*-CN is derived from the solvolysis rate of *p*-cyanocumyl chloride,[31] and this comparison suggests that contributions of the type **11** are not important in the ion from this solvolysis.



11

A quantitative correlation of α-substituent effects by γ^+ parameters[13-15] was mentioned above. We previously calculated[1] a γ^+ value for $\mathrm{CF_3}$ of 3.0 based on the reactivity of $\mathrm{CF_3CMe_2OTs}$ in HOAc, even though solvent participation is implicated in the rate-limiting step of this reaction. To derive a γ^+ for $\mathrm{CF_3}$ from the data for **2**, the correlation $\log k/k_0 = -3.23\sigma^+$ established for 1-aryl-1-phenylethyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C can be utilized.[32] A rate for $\mathrm{CF_3CMePhOPNB}$ in this medium is calculated as $9.8 \times 10^{-19}\ \mathrm{s^{-1}}$ from the observed rate for **2** in HOAc and the relationship $k^{\mathrm{PNB}}_{80\%\ \mathrm{acetone}} = (3.27 \times 10^{-11})k^{\mathrm{Ts}}_{\mathrm{HOAc}}$.[14] Replacement of the aryl group by $\mathrm{CF_3}$ in the correlation above thus leads to a γ^+ value of 3.69 for $\mathrm{CF_3}$ in **2**. However, as has been pointed out[15] the system RCMePhOPNB is one in which steric effects are likely to be significant, and indeed use of γ^+ for Me derived from less crowded systems leads to a wide divergence in calculated and observed rate constants for R = Me in this system.[15] Crowding induced rate deceleration due to twisting of the aryl groups out of conjugation was suggested,[15] but steric acceleration due to relief of ground-state strain on ionization is also conceivable. It is clear that study of other $\mathrm{CF_3}$-substituted systems in which steric factors are less significant are needed to accurately assess the γ^+ value of this group, as well as testing this treatment of substituent effects.

In summary, there is clear evidence for rate-limiting ionization of **2** to form the ion **4**, with a strong destabilization of **4** by $\mathrm{CF_3}$. The complete understanding of the effects of electron-withdrawing α-substituents on solvolytic reactions of the type of eq 4 will require the study and assessment of a sufficient number of examples of this family to provide a representative selection of combinations of substituents, including those electron-withdrawing relative to hydrogen.

Experimental Section

1-Trifluoromethyl-1-phenylethyl tosylate (**2**) was obtained by addition of 5 g (0.026 mol) of $\mathrm{PhC(CF_3)MeOH}$[2b] in 25 mL of ether to 1.3 g (0.06 mol) of NaH stirred in 50 mL of ether at room temperature. The mixture was stirred 1 h, and then 4.75 g (0.025 mol) of *p*-TsCl in 75 mL of ether was added. After stirring 12 h the mixture was filtered and cooled, and 4 g (0.011 mol, 44%) of **2** crystallized. After recrystallization from ether, **2** had mp 101 °C; NMR ($\mathrm{CCl_4}$) δ 2.20 (s, 3, $\mathrm{CF_3CCH_3}$), 2.42 (s, 3, $\mathrm{CH_3C_6H_4}$), 7.32 (s, 5, $\mathrm{C_6H_5}$), and 7.45 (center of $\mathrm{A_2B_2}$ quartet, $\mathrm{C_6H_4}$). Anal. Calcd for $\mathrm{C_{16}H_{15}F_3O_3S}$ (mol wt 344.34): C, 55.81; H, 4.39. Found (Galbraith): C, 56.05; H, 4.47.

The preparation of **2**-d_3 was carried out by the reaction of 5.0 g (0.028 mol) of $\mathrm{PhCOCF_3}$ (Aldrich) with the Grignard reagent from 4.2 g (0.029 mol) of $\mathrm{CD_3I}$ (Stohler Isotopes) to yield 3.5 g (0.018 mol, 65%) of $\mathrm{PhC(CF_3)(CD_3)OH}$. This was converted to the tosylate as described for **2**-h_3.

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Kinetics. Solvents were prepared as described previously,[2a] except for TFA. Titrimetric rates were usually measured on 0.04 to 0.08 M solutions. The reactions in TFE and HFIP were carried out in volumetric flasks by adding solid **2** to the solvent preequilibrated to the reaction temperature. Samples (0.5 mL) were withdrawn at intervals with pipets and discharged into cold acetone and titrated with 0.02 M NaOH using methyl red indicator. For reactions in HCO_2H, aliquots were added to a 60:40 mixture of HOAc and Ac_2O and titrated with NaOAc in HOAc. Reactions in HOAc, 80% EtOH, and 100% EtOH were carried out using sealed tubes and were titrated using 0.05 M NaOAc in HOAc and bromophenol blue in the former case and 0.02 M NaOH and methyl red in the latter two cases. For salt effect measurements 0.01 M solutions of **2** were measured using the ampule technique and titration with 0.02 M NaOH and bromthymol blue indicator.

Trifluoroacetic acid was distilled immediately before use. Trifluoroacetic anhydride was not added to the solution as has been done previously[2a,16a] because the strong UV absorption of the anhydride interfered with the kinetic measurements. The solvent was made 0.20 M in NaO_2CCF_3.[2a]

For measurements of the kinetics in TFA and for observing the isotope effects in TFA, HFIP, TFE, HCO_2H, and 80% EtOH, the rates were followed by injecting 4 μL of **2** (0.5 M in CH_3CN) into the solvent preequilibrated in 1-cm UV cells to give 10^{-3} M solutions and observing the decrease in absorption at 262 nm.[16a,26]

The rate of **2** in TFA with 0.125 M NaO_2CCF_3 was measured as $4.33 \times 10^{-2}\ s^{-1}$, as compared to $5.10 \times 10^{-2}\ s^{-1}$ with 0.20 M salt. The rate of *i*-PrOTs in 0.125 M NaO_2CCF_3 at 53.6 °C was measured as $4.95 \times 10^{-4}\ s^{-1}$ by UV. This compares to the value of $4.85 \times 10^{-4}\ s^{-1}$ calculated from data at other temperatures and 0.060 M salt[16a] using a correction factor of 1.16 to convert rates in 0.06 M to 0.125 M salt.[16a,b] It should be noted that the rate of *i*-PrOTs at 55.0 °C is $5.09 \times 10^{-4}\ s^{-1}$ (J. E. Norlander, private communication), and the published rate constant at 50.0 °C[16a] is a typographical error.

Products were measured by sealing 50 mg (0.145 mmol) of **2** in 0.5 mL of deuterated solvent in an NMR tube and heating for 10 half-lives, and then observing the spectrum. In TFA the product showed signals at δ 2.30 (CH_3CCF_3), 2.48 ($CH_3C_6H_4$), 5.82 and 6.00 ($C{=}CH_2$). In 95% ethanol-d_6 the chemical shift difference between the CH_3 groups was more (0.52 ppm) and between the vinyl H was less (0.14 ppm). These signals were integrated to calculate the product yields. No signals attributable to any other products were observed.

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Registry No. 2, 73572-26-6; **2**-d_3, 73572-27-7; 2-adamantyl tosylate, 25139-43-9; $PhC(CF_3)MeOH$, 426-54-0.

Solvolytic Studies of the Highly Deactivated 1-Aryl-1-(trifluoromethyl)ethyl Tosylates

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Abstract: The rates of solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates **1b–i** and 1-aryl-1-(trifluoromethyl)ethyl bromides **3a,b** in 80% ethanol, and of 1-phenyl- and 1-(3-chlorophenyl)-1-(trifluoromethyl)ethyl tosylates (**1e** and **1g**) in a variety of solvents, were measured. Linear mY_{OTs} plots with $m = 1.09$ for **1e** and $m = 1.03$ for **1g** were observed. These and the very high tosylate/bromide rate ratio, 3.94×10^4, for 1-(4-methylphenyl) derivatives **1b** vs. **3b** indicate a rate-limiting ionization process without intervention of solvent participation. The rate-retarding effect of the α-trifluoromethyl group is so large that a highly negative reaction constant, −7.46, results from a Hammett–Brown $\rho\sigma^+$ treatment of the rate data. Moreover, the 1-phenyl derivative **1e** is even less reactive than benzyl tosylate in trifluoroethanol. The rate data can also be correlated with the Yukawa–Tsuno equation, $\log (k/k_0) = \rho(\sigma + r(\sigma^+ - \sigma))$. The choice of these two treatments and possible mechanistic complexities are discussed.

The electronic effect of substituents on the reactivity of organic compounds involving the formation of carbenium ion intermediates is a theme which has received intense and continuous attention ever since the beginning of mechanistic studies on these systems.[1] Although the importance of the rate-retarding effect of strongly electron-withdrawing substituents β to cationic centers in solvolysis has been realized for more than a decade,[2] studies on the α effect of such substituents became a subject of active research only recently.[3-7] Decreases in rates on the order of 10^7 for the α-carbonyl relative to the α-methylene group,[3] and of 10^2–10^6 for the α-cyano[4] and of 10^{-4}–10^{-6} for the α-trifluoromethyl group[5-7] relative to α-hydrogen were observed, respectively.

The electron-withdrawing influence of the trifluoromethyl group on a cationic intermediate through the aromatic ring is already known.[8] The deactivating effect of this group in solvolysis has also been noted when it is at the C-1[5] and C-3[5,9] positions of allyl sulfonates. Tidwell and co-workers have studied the electrophilic addition to substituted α-trifluoromethylstyrenes[10] and the solvolysis of α-trifluoromethyl sulfonate esters.[6] From the observed

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