J. Am. Chem. Soc. **1993,** *115,* 10091-10096 10091

Large Salt Effects and Ion Pairing in Trifluoroacetolysis Forming Destabilized Delocalized Benzylic Carbocations. Kinetic Analysis of the Winstein Special Salt Effect

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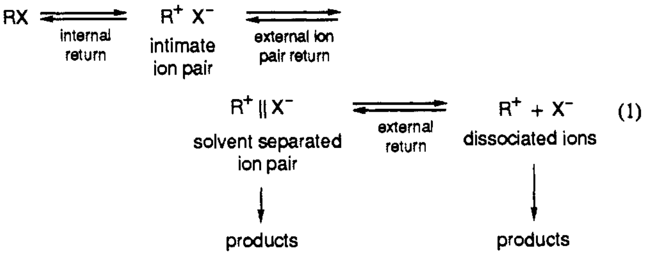
Received April 28, 1993[®]

Abstract: The trifluoroacetolysis rates of benzylic sulfonates substituted with destabilizing fluoroalkyl groups are accelerated by factors of 5.0–14.3 by the addition of 0.2 M NaO_2CCF_3, while substrates forming less delocalized carbocations show corresponding accelerations by factors of only 1.0–1.7. For $PhC(OTs)(CF_3)CH_3$ (**1**) the rates as a function of $[NaO_2CCF_3]$ or of $[KO_2CCF_3]$ show an initial sharp nonlinear increase up to 0.3 M salt, and the rate dependences on [salt] are quantitatively correlated by kinetic expressions based on the competitive capture of solvent-separated ion pairs by solvent and by salt. This behavior is consistent with the accepted interpretation of the special salt effect, with the added feature that scavenging of the ion pair by trifluoroacetate salts can lead to products either directly or through carbocation trifluoroacetate ion pairs. Even greater initial increases are observed with added $LiClO_4$, but NaOTs gives common ion rate depression. The large salt effects are particularly important in highly delocalized destablized benzylic carbocations which are resistant to solvent capture by trifluoroacetic acid but prone to ion pair return. Alkene formation from **1** is reduced by the addition of NaO_2CCF_3, and elimination in the absence of salt is proposed to occur from an ion pair, in agreement with other recent results, but contrary to a recent proposal of concerted elimination during solvolysis.

Salt effects on solvolytic reactions have been intensively examined and have usually been interpreted in terms of the Winstein ion-pair mechanism (eq 1).[1,2] Evidence for this scheme includes polarimetric rate constants k_α which exceed rates of product formation, thus indicating the presence of intimate ion pairs, and large nonlinear "special" salt effects at low [salt], implying the formation of solvent separated ion pairs which are scavenged by salt.[1,2]



There has been continuing interest in studies of salt effects in solvolysis reactions.[3] Recently, dramatic effects of added salts such as $LiClO_4$ on preparative reactions have been increasingly exploited.[4] The origins of these salt effects on synthetic reactions may differ from those in solvolysis reactions and are a matter of some debate, but they have caused a general interest in salt effects on reactivity.

Most earlier studies of kinetic salt effects[1,2,5] involved rather nucleophilic media such as acetic acid or mixed aqueous solvents. Very few studies of salt effects in trifluoroacetic acid (TFA) have appeared,[6a,b,f,g] although this medium is widely used in solvolysis

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[®] Abstract published in *Advance ACS Abstracts,* September 15, 1993.

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0002-7863/93/1515-10091$04.00/0

Table I. Salt Effects of 0.200 M CF_3CO_2Na on Solvolysis in CF_3CO_2H at 25 °C

substrate	k, s^{-1} 0.0 M CF_3CO_2Na	k, s^{-1} 0.2 M CF_3CO_2Na	ratio
$PhC(OTs)(CF_3)CH_3$ (**1**)	5.30×10^{-3}	5.74×10^{-2}	10.8
$PhC(OTs)(CF_3)CD_3$ (**2**)	3.15×10^{-3}	4.52×10^{-2}	14.3
$PhC(OTs)(CF_3)CN$ (**3**)	5.94×10^{-4}	6.53×10^{-3}	11.0
$PhC(OTs)(C_2F_5)CH_3$ (**4**)	2.25×10^{-2}	2.20×10^{-1}	9.8
$PhCH(OTf)CF_3$ (**5**)	2.22×10^{-3}	1.11×10^{-2}	5.0
2-C_2F_5-*exo*-2-NbOBs[a] (**6**)	3.05×10^{-3}	3.04×10^{-3}	1.0
2-CF_3-2-AdOTs (**7**)	4.97×10^{-4}	8.70×10^{-4}	1.7
2-BuOTs (**8**)	1.12×10^{-4}	1.64×10^{-4} [b]	1.5
2-AdOTs (**9**)	8.68×10^{-4}	1.27×10^{-3}	1.5
$ArCH(OTs)CH_3$[c] (**10**)	2.21×10^{-4}	3.48×10^{-4} [b]	1.6

[a] Reference 7g. [b] 0.125 M NaO_2CCF_3, ref 7e. [c] Ar = 3,5-$(CF_3)_2C_6H_3$.

Table II. Effect of Salts on Solvolysis of $PhC(OTs)(CF_3)CH_3$ (**1**) and $PhC(OTs)(CF_3)CD_3$ (**2**) in CF_3CO_2H at 25 °C

[salt] (M)	k(**1**), s^{-1}	k(**2**), s^{-1}	$k(CH_3)/k(CD_3)$
	NaO_2CCF_3[a]	NaO_2CCF_3[b]	
0.600	0.127	0.1029	1.23
0.419	0.0980		
0.300	0.0795	0.0589	1.35
0.252	0.0675		
0.200	0.0587	0.0452	1.30
0.150	0.0452		
0.120	0.0385	0.0295	1.31
0.0839	0.0314		
0.0600	0.0231	0.0185	1.25
0.0300	0.0155		
0.0120	0.0105		
0.0	5.26×10^{-3}	3.80×10^{-3}	1.38
	$LiClO_4$[c]	$LiClO_4$[d]	
0.0986	0.0688	0.0505	1.36
0.0789	0.0541	0.0390	1.39
0.0592	0.0411	0.0318	1.29
0.0394	0.0273	0.0233	1.17
0.0278	0.0229	0.0176	1.30
0.0197	0.0177	0.0158	1.12
0.0139	0.0141	0.0125	1.13
5.56×10^{-3}	0.0105	7.52×10^{-3}	1.40
2.78×10^{-3}	8.05×10^{-3}	6.17×10^{-3}	1.30
		NaOTs	
0.290		2.52×10^{-3}	
0.0954		2.43×10^{-3}	

[a] $k_{\text{obs}} = (3.18 \times 10^{-2})(1 + 5.0[CF_3CO_2Na])$, $r = 0.9999$ (calculated from the data for the three highest [salt]); $k^0/k^0_{\text{obs}} = 5.90$. [b] $k_{\text{obs}} = (1.59 \times 10^{-2})(1 + 9.1[CF_3CO_2Na])$, $r = 0.9999$ (calculated from the data for the three highest [salt]); $k^0/k^0_{\text{obs}} = 5.05$. [c] $k_{\text{obs}} = (0.62\ s^{-1}\ M^{-1})[LiClO_4] + (5.64 \times 10^{-3}\ s^{-1})$, $r = 0.998$. [d] $k_{\text{obs}} = (0.45\ s^{-1}\ M^{-1})[LiClO_4] + (5.31 \times 10^{-3}\ s^{-1})$, $r = 0.997$.

studies.[6,7] We now report the existence of some large effects of salts in TFA on destabilized carbocations leading to highly delocalized benzylic ions, and a kinetic analysis of these salt effects that is consistent with the accepted interpretation of the special salt effect.

Results and Discussion

The effects of 0.200 M NaO_2CCF_3 on the reactivity of the group of previously studied[7,8] substrates **1–10** were examined, and the results are given in Table I. More detailed studies of the effect of concentration of NaO_2CCF_3, KO_2CCF_3, and $LiClO_4$ on the reactivity of **1** and **2** are given in Tables II and III, and the effect of NaO_2CCF_3 on **3** is given in Table IV.

Table III. Effect of KO_2CCF_3 on Solvolysis of $PhC(OTs)(CF_3)CH_3$ (**1**) in CF_3CO_2H at 25 °C

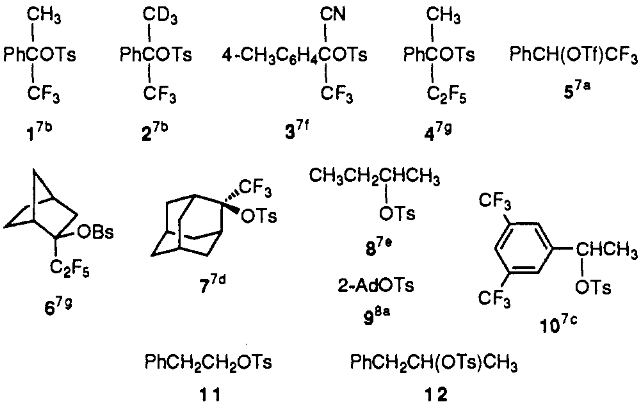
$[KO_2CCF_3]$, M	k(**1**),[a] s^{-1}	$[KO_2CCF_3]$, M	k(**1**), s^{-1}
0.595	0.101	0.208	0.0538
0.521	0.0914	0.178	0.0517
0.476	0.0870	0.119	0.0421
0.418	0.0822	0.0595	0.0271
0.357	0.0798	0.0298	0.0178
0.298	0.0770	0.0	0.00486

[a] $k_{\text{obs}} = (5.15 \times 10^{-2})(1 + 1.54[KO_2CCF_3])$, $r = 0.97$ (calculated from the data for the three highest [salt]), $k^0/k^0_{\text{obs}} = 10.6$.

Table IV. Effect of NaO_2CCF_3 on Solvolysis of 4-$CH_3C_6H_4C(OTs)(CF_3)CN$ (**3**) in CF_3CO_2H at 25 °C

$[NaO_2CCF_3]$, M	k, s^{-1}	$[NaO_2CCF_3]$, M	k, s^{-1}
0.600	1.06×10^{-2}	0.120	5.13×10^{-3}
0.503	9.95×10^{-3}	0.0600	3.69×10^{-3}
0.420	9.25×10^{-3}	0.0300	2.66×10^{-3}
0.300	7.66×10^{-3}	0.000	5.94×10^{-4}
0.201	6.53×10^{-3}		

Chart I



For substrates **1–5** there are large effects of 0.2 M NaO_2CCF_3 on the reactivity, with accelerations by factors of 5.0–14.3. By contrast, the substrates **6–10** show much smaller effects, with accelerations by factors of only 1.0–1.7, and similar accelerations of 1.7 and 1.5 have been reported[7g] for 1-pentafluoroethyl-*exo*-2-norbornyl and 2-pentafluoroethyl-*endo*-2-norbornyl brosylates, respectively. The effect of $LiClO_4$ on the reactivity of **1** and **2** is even greater, with 0.0986 M salt increasing the rate of **1** by a factor of 12.8. Higher concentrations of $LiClO_4$ could not be used for solubility reasons, and this precludes a test of whether a nonlinear dependence of k_{obs} on [salt] would be observed at higher [salt].

The effects of NaO_2CCF_3 on the reactivities of **1–3**, and of KO_2CCF_3 on **1**, show curved relationships between 0.0 and 0.3 M salt but approach linearity between 0.3 and 0.6 M salt. This qualitatively resembles the behavior reported by Reich, Diaz, and Winstein for trifluoroacetolysis of **11** and **12**.[6a,f]

For the analysis of salt effects Winstein and co-workers,[1] as well as other investigators,[5] have used the Winstein eq 2, for which the portion of the plot at higher [salt] is assumed to be linear and where k^0 is the rate constant for the linear portion of the plot extrapolated to zero salt concentration and b is a measure of the salt effect on the linear portion. A plot of the data for the effect of NaO_2CCF_3 on the reactivity of **1** with use of this method is shown in Figure 1. Similar behavior is found for **1** with KO_2CCF_3 and **2** and **3** with NaO_2CCF_3. The steeply ascending portion of such plots at lower [salt] has been ascribed[1,5,6a] to a manifestation of the special salt effect, in which the added salt was scavenging the solvent separated ion pairs and preventing

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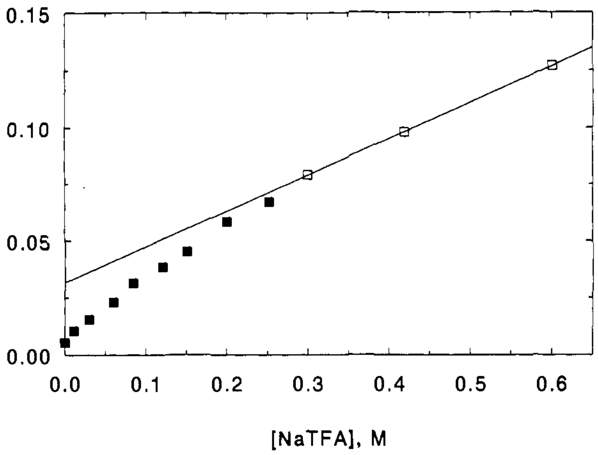

Figure 1. Effect of [NaO_2CCF_3] on the reactivity of **1** at 25 °C.

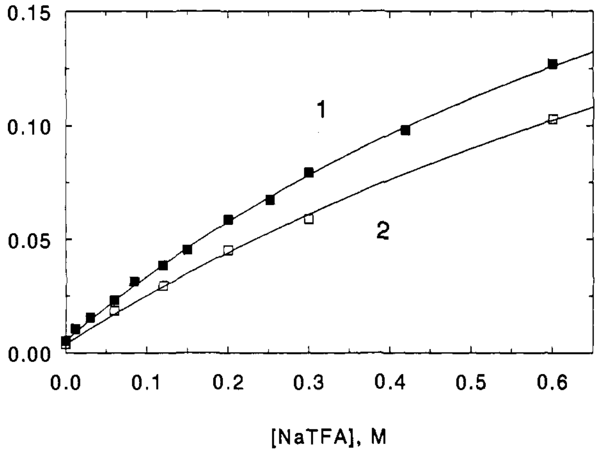

Figure 2. Effect of [NaO_2CCF_3] on the reactivity of **1** and **2** at 25 °C. Curves drawn with use of eq 7 and the parameters in Table V.

ion pair return to intimate ion pairs.

$$k_{obs} = k^0(1 + b[\text{salt}]) \tag{2}$$

The data for **1** give by this treatment $b = 5.0$ and $k^0 = 3.18 \times 10^{-2}$ s^{-1}, and combined with k^0_{obs} at 0.0 M salt the data give $k^0/k^0_{obs} = 5.9$, which is significantly larger than the corresponding ratios of 1.85 and 1.59 observed for **11** and **12**.[6a] The ratio observed for **1** is also significantly larger than those of 1.5–3.1 typically observed for other substrates which show special salt effects.[1,5a–c] Analysis of the data for **3** according to eq 2 gave $b = 2.2$, $k^0 = 4.52 \times 10^{-3}$ s^{-1}, and $k^0/k^0_{obs} = 8.2$ The latter ratio is even larger than for **1** and **2**, while the b value is less.

For kinetic analysis of the nonlinear salt effect data the full scheme shown in eq 1 may be abbreviated as shown in eqs 3 and 4. This scheme shows ionization to a solvent separated ion pair which forms products by capture of the carbocations by solvent (k_s) or by added salt (k_t[salt]). For trifluoroacetate salts the step shown in eq 4 can involve either formation of products in a single step or formation of a trifluoroacetate ion pair which then forms products. This is in contrast to perchlorates, which must undergo a further displacement by solvent to form the final substitution product.

$$\mathrm{RX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{R^+\|X^-} \xrightarrow{k_s} \text{products} \tag{3}$$

$$\mathrm{R^+\|X^-} \xrightarrow{k_t[\text{salt}]} \text{products} \tag{4}$$

This scheme does not preclude intervention of intimate ion pairs as shown in eq 1, but the current experimental study does not address this question, which is the subject of a continuing investigation, using other techniques. The kinetic expression for eqs 3 and 4, derived using the steady state assumption for the ion pair, is given in eqs 5–9, where k_o (eq 8) is the rate constant at [salt] = 0 and K_{app} (eq 9) is a ratio of rate constants. The kinetic expressions derived by Winstein et al.[1a] for the special salt effect based on the full kinetic scheme (eq 1) have the same form as eq 7. These treatments assume that the salt effects on the rate constants in eq 3 do not obscure the analysis. Related kinetic analyses have recently been reported by others,[3b,f] but this analysis has not previously been applied to test the effect of [salt] on a solvolysis reaction over the entire range of [salt]. Thus Winstein et al.[1a] omitted data for [$LiClO_4$] above 0.0151 M from their test of this expression.

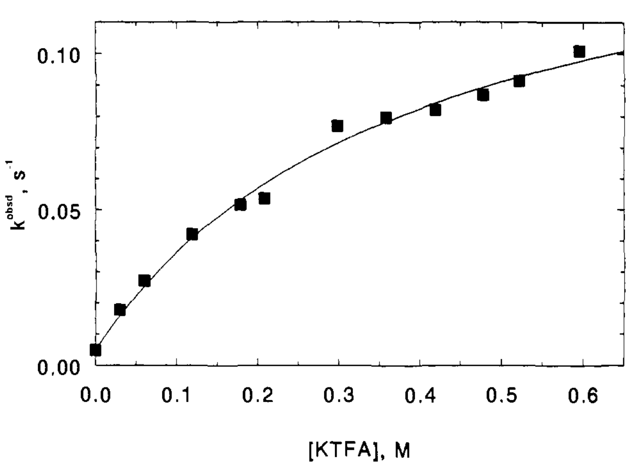

Figure 3. Effect of [KO_2CCF_3] on the reactivity of **1** at 25 °C. Curve drawn with use of eq 7 and the parameters in Table V.

$$k^{obs} = \frac{k_1(k_s + k_t[\text{salt}])}{(k_{-1} + k_s + k_t[\text{salt}])} \tag{5}$$

$$= \frac{(k_1k_s/k_t) + k_1[\text{salt}]}{((k_{-1} + k_s)/k_t + [\text{salt}])} \tag{6}$$

$$= \frac{(k_0K_{app} + k_1[\text{salt}])}{(K_{app} + [\text{salt}])} \tag{7}$$

$$k_0 = k_1k_s/(k_{-1} + k_s) \tag{8}$$

$$K_{app} = (k_{-1} + k_s)/k_t \tag{9}$$

At high [salt], when $k_t[\text{salt}] \gg (k_{-1} + k_s)$, values of k^{obs} level off at k_1, corresponding to rate-limiting ionization, and all of the carbocations are captured by salt and external ion pair return is no longer significant. Equation 7 gives a good fit of the data in Tables II–IV for the effect of NaO_2CCF_3 and KO_2CCF_3 on **1**–**3** as shown in Figures 2–4, with k_1 and K_{app} treated as parameters, and with k_o fixed at the experimental values. These constants are collected in Table V, together with the derived quantity $R = k_{-1}/k_s = (k_1 - k_o)/k_o$ (from eq 8) which measures the rate of return relative to solvent capture. Equation 10, which includes a term in [salt],^{2} provides a better fit of the data for **3** (Figure 4) than does eq 7.

$$k^{obs} = \frac{(k_0K_{app} + k_1[\text{salt}] + k_2[\text{salt}]^2)}{(K_{app} + [\text{salt}])} \tag{10}$$

We defer detailed discussion of eq 10 to a later time but note that it has the ability to describe the classic combination of special and normal salt effects, observed by Winstein and many others.[1,2,5] Thus, at high [salt], eq 10 simplifies to the following equation, $k^{obs} = k_1 + k_2[\text{salt}]$, which is equivalent to the more traditional equation (eq 2), with $k^0 = k_1$ and $b = k_2/k_1$. The reactivity of **1** and **2** is linear in [$LiClO_4$] within the accessible range of [salt] limited by the solubility (Table II), as shown in Figure 5.

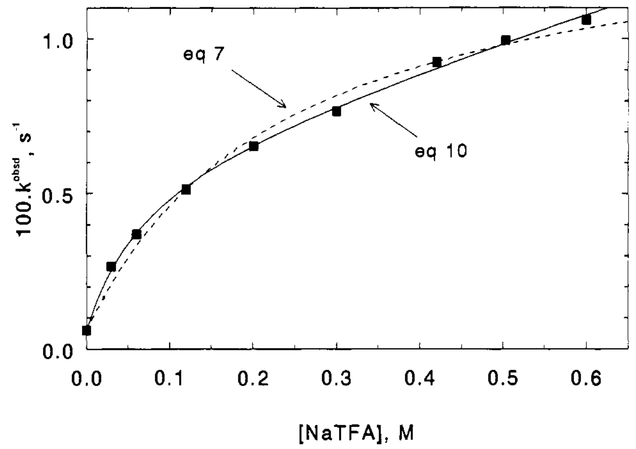

Figure 4. Effect of [NaO_2CCF_3] on the reactivity of **3** at 25 °C. Curves drawn with use of eqs 7 and 10 and the parameters in Table V.

As a further example and test of eq 7 this was applied to published rate data[5d] for the effects of salts on the solvolysis of 4-methoxybenzyl chloride (**13**) in aqueous dioxane (Table V), which had shown a pronounced curved plot of rate vs [salt] characteristic of the special salt effect. A good fit is obtained (Figure 6), and the use of eq 10 is not required.

$4\text{-}MeOC_6H_4CHCl_2$
13

As seen in Table V there is a large amount of external ion pair return in the absence of added salt for **1–3** and **13**, as quantitatively expressed in the values of R of 10–94. Rather large salt concentrations (0.2–1.0 M) are required to significantly reduce the amount of external return whereas in previous studies, usually using the much more nucleophilic NaOAc in HOAc,[1,5] efficient scavenging of the solvent separated ion pairs occurs at much lower [salt].

Assuming that 10^{10} M^{-1} s^{-1} is an upper limit for a diffusion-controlled value of the rate constant k_t for salt capture then $(k_{-1} + k_s) \sim 5 \times 10^9$ s^{-1}, indicating lifetimes of $\sim 2 \times 10^{-8}$ s for the carbocations, and relatively slow maximum rate constants for solvent capture of the cations by TFA. This is consistent with the low nucleophilicity of TFA, as measured by its N_{OTs} value of -5.56, which is significantly less than those of -3.0 and -4.27 for CF_3CH_2OH and 97% $(CF_3)_2CHOH$, respectively.[8b] In solvents much more nucleophilic than TFA, such as 80% EtOH (N_{OTs} = 0.00), k_s is much greater than k_t for salt capture, and so only normal salt effects are detected.[7b]

In contrast to **1–3**, in the trifluoroacetolysis of 2-phenylethyl tosylate (**11**),[6a] the special salt effect is observed at lower [NaO_2CCF_3] (*ca.* 0.02 M), and the total increase due to this effect is rather small (*ca.* 1.9). These facts indicate that the phenonium ion derived from **11** is much more liable to attack by both salt and solvent, and so external return is much less important.

In the case of **11** confirmatory evidence for a special salt effect was found by the addition of NaOTs.[6a] This substrate showed a significant rate depression, attributed to common ion rate depression due to the reformation of the substrate from the solvent separated ion pair.[6a] For **2** the addition of NaOTs also gave reduced rate constants of 2.43×10^{-3} s^{-1} (0.0954 M) and 2.52×10^{-3} s^{-1} (0.290 M). The occurrence of this common ion rate depression is additional strong evidence that the rate accelerations due to other salts are caused by scavenging of ion pairs, and that the initial curved rate acceleration is due to a special salt effect.

Comparison of the effects of the apparent special salts to the common ion salt for **2** can be made from the values of the ratio $k(\text{salt})/k_o$ of 0.77, 6.2, and 12.3 for NaOTs, NaO_2CCF_3, and $LiClO_4$ respectively, at 0.0954 M salt. At 0.290 M salt the same ratio is 0.80 (NaOTs) and 18.3 (NaO_2CCF_3). For **11** the same ratio was 0.39 and 1.54 at 0.954 M $n\text{-}Bu_4NOTs$ and NaO_2CCF_3, respectively, and 0.30 and 1.7 at 0.290 M salt.[6a] These may be compared together by the ratio $k(NaO_2CCF_3)/k(MOTs)$, which is 8.0 (0.0954 M) and 22.9 (0.290 M) in our study and 3.9 and 5.7, respectively, for **11**.[6a] Thus the contrast between the common ion and the presumed special salt effect is even more marked in **2** than for **11**.

In a study of the effect of [NaO_2CCF_3] on the reactivity of MeOTs, EtOTs, and n-PrOTs in TFA it was found that the rates were linearly dependent on [NaO_2CCF_3], with k_2 values of 6.1×10^{-5}, 4.9×10^{-5}, and 4.2×10^{-5} M^{-1} s^{-1}, respectively, at 100 °C.[6g] Evidently these reactions involve direct displacement of tosylate by trifluoroacetate. However, such behavior is ruled out for **1–5**.[7,9] The substrates have been shown to react without solvent participation, as evidenced by a number of criteria, of which the large effects of aryl substituents on the rate of reaction, measured by the ρ^+ values, are perhaps the most convincing. Substrates **1–4** are also tertiary, and bear α-fluorinated substituents which strongly hinder nucleophilic displacement. Substrates **11** and **12** also have been shown to react by aryl participation, thereby ruling out nucleophilic assistance.[6a]

The fact that substrates **1–5**, **11**, and **12** display the behavior associated with special salt effects for the presence of NaO_2CCF_3 in TFA whereas **6–10** do not, shows that this behavior is substrate dependent, and that it is not a general medium effect. Furthermore, the magnitude of the effect, as measured by k^0/k^0_{obs} and b values, is highly substrate dependent, most notably for the much larger k^0/k^0_{obs} value for **1–3** compared to **11** and **12**.

A distinguishing feature of substrates **1–5** is that all contain destabilizing α-fluoroalkyl groups and α-aryl groups, and as a result the carbocations produced from them are highly delocalized. Evidence for such delocalization in benzylic systems bearing fluorinated substituents includes large ρ^+ values, measuring the effect of ring substituents, fairly modest effects of the solvent polarity on the rates of the reaction, and the occurrence of *ipso* solvent attack directly on the aromatic rings.[7,9]

Substrates **6–9** do not possess aromatic groups which can delocalize the positive charge away from the CF_3 groups. Substrates **11** and **12** react in CF_3CO_2H by k_Δ pathways giving bridged phenonium ions that are also extensively delocalized, but give less external ion pair return than **1–5**, probably because of the ease of attack on the ethylene bridge. Thus it appears that the manifestations of the special salt effect are particularly prevalent in ions that are extensively delocalized and also hindered to attack by nucleophiles, and therefore react slowly with solvents and give extensive external ion pair return. In the presence of added salts the ion solvent separated pairs are scavenged by salts and external ion pair return is prevented, thus causing the large observed rate increases.

The trifluoroacetolysis of optically active **10** gives k_α/k_{prod} of 1.4, showing modest detection of ion pair return.[7c] In confirmation of this there is only a small acceleration of 1.6 of the rate due to 0.200 M CF_3CO_2Na (Table I). For optically active 2-BuOTs (**8**) k_α was unaffected by added NaO_2CCF_3, while the rate of product formation increased, so that k_α/k_{prod} decreased from 1.55 at [salt] = 0 to 1.05 at [salt] = 0.125 M.[7e] These results are consistent with racemization occurring in an intimate ion pair unaffected by salt, while product formation from subsequent intermediates is enhanced by added salt (eq 1).

It is relevant that association constants K_a of (25.1 and 4.56) $\times 10^5$ M^{-1} for NaO_2CCF_3 and KO_2CCF_3 in CF_3CO_2H have been measured using conductivity methods over the concentration range of $[\text{salt}]_{\text{initial}}$ of (0.0248 to 0.1670) $\times 10^{-3}$ M for NaO_2CCF_3, and

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(9) (a) Allen, A. D.; Tidwell, T. T. *Adv. Carbocation Chem.* **1989**, *1*, 1–44. (b) Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279–285. (c) Creary, X. *Chem. Rev.* **1991**, *91*, 1625–1678. (d) Richard, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 6735–6744. (e) Richard, J. P.; Amyes, T. L.; Vontor, T. *J. Am. Chem. Soc.* **1992**, *114*, 5626–5634.

Table V. Derived Kinetic Parameters for Equations 7 and 10[a]

substrate	salt	k_0, s^{-1}	k_1, s^{-1}	K_{app}, M	r	eq	k_2, $M^{-1}\,s^{-1}$	$R = k_{-1}/k_s$
1	NaO_2CCF_3	5.26×10^{-3}	3.51×10^{-1}	1.12	0.9995	7		66
2	NaO_2CCF_3	3.80×10^{-3}	3.60×10^{-1}	1.57	0.9993	7		94
1	KO_2CCF_3	4.86×10^{-3}	1.58×10^{-1}	0.387	0.9959	7		32
3	NaO_2CCF_3	5.94×10^{-4}	7.00×10^{-3}	0.0722	0.9994	10	8.32×10^{-3}	23
13	$LiClO_4$	8.96×10^{-5}	6.17×10^{-3}	0.347	0.9992	7		68
13	Bu_4NClO_4	8.96×10^{-5}	1.02×10^{-3}	0.251	0.9996	7		10

[a] For solvolysis of compounds **1–3** in CF_3CO_2H. Data for compound **13** in 85% (v/v) aqueous dioxane.[5d] The fits for **1**, **2**, and **13** are not significantly better with eq 10. The quantity r is the correlation coefficient in the nonlinear least-squares fitting.

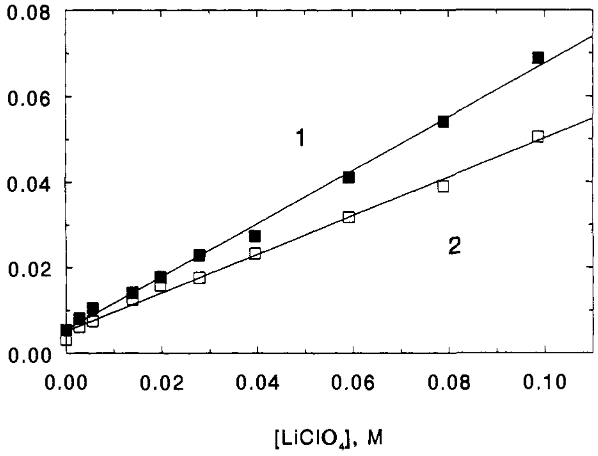

Figure 5. Effect of [$LiClO_4$] on the reactivity of **1** at 25 °C.

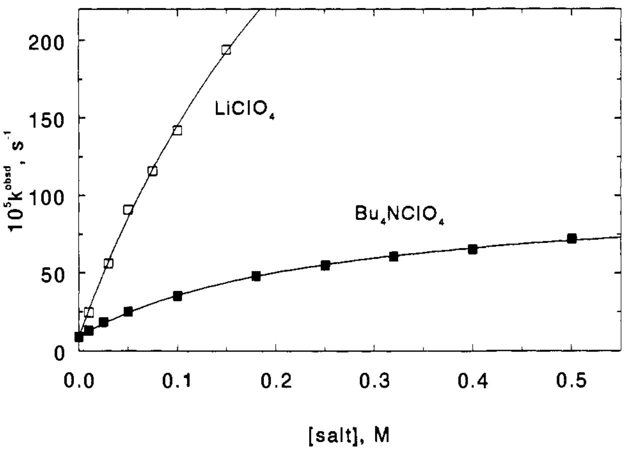

Figure 6. Effect of [salt] on the reactivity of **13**. Curves drawn with use of eq 7 and parameters in Table V.

(0.00961 to 0.1707) $\times 10^{-3}$ M for KO_2CCF_3.[10a] The concentration range for which these K_a values were measured is well below that for which the salt effects are measured in this study. If the assumption is made that these K_a values[10b] are valid for the [salt] used in this study, then the Na salt is calculated to be dissociated only to the extent of 0.0815% and 0.631% at 0.6 M and 0.01 M salt, respectively, while the corresponding values for the K salt are 0.191 and 1.48%.

It appears unlikely that it is these small concentrations of dissociated salt ions that play the major role in causing the curved dependences of rate upon [salt]. Thus although both the concentrations of dissociated ions and the rates increase with [salt], the effect of the K^+ salt on the reactivity of **1** ranges from being modestly greater (by a factor of 1.15) than Na^+ at 0.03 M to a modestly lesser effect (by a factor of 0.80) at 0.60 M. However, the K^+ salt is always more highly dissociated than the Na^+ salt, by a factor of 2.35, throughout the range studied.

It has also been concluded by Perrin and Pressing[3h] from an analysis of electrostatic dipole–dipole interactions that since most of the salt is present as ion pairs and not free ions, and also since the effects of ions and ion pairs of the salts in promoting ionization should be quite similar, that "the special salt effect cannot be attributed to acceleration by the small fraction of free ions present."

The isotope effect $k(CH_3)/k(CD_3)$ at different [salt] for **1** and **2** averages 1.26 (±0.14) (Table II) and the deviations appear random and unaffected by [salt]. For **1** the substitution/elimination ratio is increased from 79/21 to 92/8 as the [NaO_2CCF_3] is changed from 0.0 to 0.2 M. Thus NaO_2CCF_3 preferentially leads to trifluoroacetate product rather than alkene, and since neither this salt nor $LiClO_4$ affect the isotope effect it appears the role of both salts is to form a new ion pair which then partitions to products.

A decrease in the isotope effect $k(CH_3)/k(CD_3)$ for $Ph_2C(Cl)Me$ from 1.73 in pure CH_3CN to 1.34 in 20% $MeOH/CH_3CN$ was observed and attributed to the decreased contribution of elimination promoted by the chloride counterion in the ion pair in the latter solvent.[11a] The latter isotope effect and our measured value of 1.26 (±0.14) agree with the mechanistic assignment of Creary et al.[11b] that "rate-limiting ionization ... to give a tertiary benzylic cationic intermediate" would have "a normal secondary deuterium isotope effect of 1.27 per CD_3." Similarly Guo and Fry[11c] studied the acetolysis of **1** with ^{14}C labeled in the CH_3 group and concluded that the small isotope effect of 1.008 ± 0.002 was "as expected for a branching $S_N1/E1$ reaction (mostly S_N1)." Larger isotope effects $k(CH_3)/k(CD_3)$ have been ascribed to rate-limiting elimination from ion pairs for other systems.[11d,12]

Elimination from an ion pair also provides an alternative explanation to the claim by Amyes and Richard[11e] that some of the olefin formation in the solvolysis of substituted cumyl benzoates and chlorides involved "concerted pericyclic elimination". This proposal appears questionable to us because it requires the extraordinary intervention of cyclic transition states with both 6-members (for the benzoates) and 4-members (for the chlorides). Also the ρ^+ value for the process proposed to be a "concerted pericyclic elimination" is −4.6, whereas cumyl chlorides are also the substrates used to define the σ^+ scale for rate-limiting carbocation formation, and the magnitude of the former ρ^+ value is essentially the same as that of −4.54 (in a different solvent) of this defining reaction.[11f] Elimination from ion pairs would appear to provide a ready explanation for the results of Amyes and Richard.[11e] Similar conclusions have been reached by Creary et

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(10) (a) Harriss, M. G.; Milne, J. B. *Can. J. Chem.* **1971**, *49*, 1888–1894. (b) Slightly different K_a values are presented in the following: Milne, J. B. *Can. J. Chem.* **1980**, *58*, 283–286. The difference does not affect the conclusions.

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(12) (a) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969. (b) Bates, D. M.; Watts, D. G. *Nonlinear Regression Analysis and its Applications*; Wiley: New York, 1988. (c) Mezei, L. M. *Practical Spreadsheet Statistics and Curve Fitting for Scientists and Engineers*; Prentice-Hall: Englewood Cliffs, New Jersey, 1990.

al.[11b] It may also be noted that according to current discussions even gas-phase ester pyrolysis may involve ion pair intermediates, and not concerted processes.[11g] The proposal of Amyes and Richard[11e] was based on arguments that a "triple ion complex" involving N_3^- was too unstable to exist as an intermediate, and therefore was a transition state leading only to substitution product. However as shown by Carpenter[11h] species that collapse with no barrier can partition between different products, and this could explain their results.

In summary: this study has revealed that large effects of salts on the rates of trifluoroacetolysis may occur, particularly in delocalized, destabilized carbocations. There is a nonlinear dependence of the rates on $[NaO_2CCF_3]$ which is similar to the behavior usually described as the "special salt effect". The effects of salts are quantitatively correlated by a kinetic treatment in which solvent separated ion pairs are competitively captured by solvent and by salt, and this same treatment also appears to fit the extensive results on perchlorate salt effects from Winstein *et al.*[1,6a] and others[5] and agrees with the accepted explanation of this phenomenon, although trifluoroacetate salts can form products directly or through trifluoroacetate ion pairs. The effects of KO_2CCF_3 and NaO_2CCF_3 on trifluoroacetolysis are rather similar, although the former salt is indicated to be significantly more highly dissociated in this medium.

This study raises many unanswered questions regarding the effect of salts on solvolysis and also possible experiments to answer some of the questions. Some of these studies are underway.

Experimental Section

Substrates **1**–**10** were described previously.[7,8] Solvents and salts were obtained from Aldrich. Trifluoroacetic acid was distilled before use, and the salts were dried at 100 °C and 0.2 Torr over P_2O_5 for 5 h prior to use.

A 0.600 M solution of NaO_2CCF_3 was prepared by dissolving NaO_2CCF_3 (2.04 g, 0.0150 mol) in 25 mL of CF_3CO_2H. Less concentrated solutions were prepared by dilution. For comparison to a 0.200 M solution prepared in this way anhydrous Na_2CO_3 (0.1066 g, 1.006 mmol) was diluted to 10 mL with CF_3CO_2H containing 140 μL (1.00 mmol) of $(CF_3CO)_2O$. Rate constants for **1** in these two solvents were 0.0587 and 0.0555 s^{-1}, respectively, and agreed within ±3%.

Kinetics were typically measured by injecting 10-μL aliquots of 0.09 M solutions of the substrate into 1.2 mL of solvent in the UV cell to give a 7×10^{-4} M solution and observing the change in the UV absorption at 262 nm with time. At least duplicate runs were measured in all cases with maximum deviations of ±5%.

For rate measurements in the presence of common ion there was added to **2** (0.086 g, 0.25 mmol) 5 mL of a solution of NaOTs in CF_3CO_2H equilibrated at 25 °C, and the solution was mixed for 50 s. At intervals 500-μL aliquots were withdrawn with a syringe and quenched with 8-mL samples of 95% EtOH. After 10 half-lives two infinity samples were taken, and all the samples were made up to 10 mL and the UV absorptions at 272 nm were measured. For the runs at 0.290 M NaOTs a solution of the salt in CF_3CO_2H was used in the compensating cell because of the significant absorption of the salt. Total absorbance changes of 0.6 unit were observed, and duplicate runs were carried out at each [NaOTs], with maximum deviations of ±3%.

For measurements of the salt effect on the product distribution 0.05 M solutions of **1** in CF_3CO_2D containing 5% $(CF_3C)_2O$ were prepared in NMR tubes, with one solution containing 0.2 M NaO_2CCF_3. After 10 half-lives for reaction the ^1H NMR signals (δ) due to the CH_3 of the trifluoroacetate product at 2.10, the CH_3 of TsOH at 2.33, the olefinic protons at 5.61 and 5.80, and the aryl protons between 7.2 and 7.7 were integrated, showing elimination/substitution ratios of 21/79 and 8/92 in the absence and presence of NaO_2CCF_3, respectively.

Nonlinear least squares fitting of eqs 7 and 10 to the data was carried out with in-house computer software based on the Marquardt algorithm.[12] The constants k_1, k_2, and K_{app} were treated as parameters, keeping k_o fixed at the experimental value (k^{obsd} at zero salt).

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.