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SOLVENT EFFECTS ON INTIMATE ION PAIRS; THE TRIFLUOROETHANOLYSIS OF 5-METHOXY-1-PENTYL TOSYLATE

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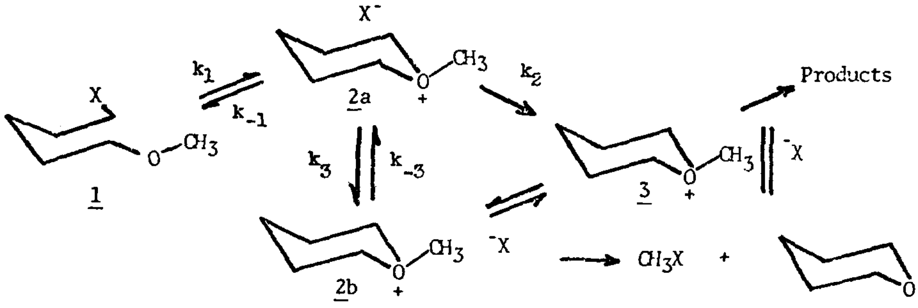
We wish to report our preliminary findings on the trifluoroethanolysis of 5-methoxy-1-pentyl tosylate (1-OTs) which may have a bearing on the number and nature of ion pair intermediates in solvolysis reactions.[1] The previously reported[2] kinetic and product study data indicate that the acetolysis of (1-OBs) proceeds by the MeO-6 assisted pathway via the cyclic methoxonium ion. Rearrangement to methyl brosylate and the fact that added salts (e.g., $LiClO_4$) completely eliminate rearrangement required that the mechanistic interpretation include two internal (2a and 2b) and an external ion pair (3), with no direct interconversion between 2a and 2b ($k_2 \gg k_3$).[2]



The same intermediates undoubtedly intervene in the trifluoroethanolysis of **1**-OTs since the neighboring group rate acceleration is *ca*. 530 (relative to n-octyl tosylate; see Table) and since rearrangement to methyl tosylate to the extent of 28.5% was observed.

Table. Summary of Kinetic Data in Trifluoroethanol at 69.90°.

Compound	CF_3CH_2ONa, M	k ($sec.^{-1}$)	Rel. Rate
n-octyl tosylate	-	3×10^{-7}	1.0
1-OTs	-	$1.59 \pm 0.03 \times 10^{4}$	530
1-OTs	0.056	$2.04 \pm 0.02 \times 10^{-4}$	680

In trifluoroethanol, however, it was found that it was not possible to suppress the rearrangement by the addition of either lithium perchlorate or sodium trifluoroethoxide. In the presence of lithium perchlorate (*ca*. 0.0125 M) only 81% of the theoretical amount of p-toluenesulfonic acid was liberated after 20 half-lives. Thus $LiClO_4$ is able to eliminate only about one-third of the rearrangement. In CF_3CH_2ONa/CF_3CH_2OH the theoretical amount (100 ±1%) of acid was formed (base consumed), but the instantaneous first order rate constant drifted upward during a kinetic run. This result again indicates MeOTs formation and its subsequent bimolecular displacement by trifluoroethoxide ion, the upward drift in the rate constant being due to the fact that the rate of S_N2 attack on MeOTs by CF_3CH_2ONa is comparable to the rate of solvolysis of the starting material.[3] From the linear plot of the instantaneous rate constant versus percent reaction the solvolysis rate constant for **1**-OTs in 0.056 M CF_3CH_2ONa/CF_3CH_2OH was obtained by extrapolation to zero percent reaction (see Table). In absolute methanol steady first order kinetics ($k = 2.08 \pm 0.02 \times 10^{-5}$ $sec.^{-1}$ at 59.85°), a 97.5% infinity titer, and an MeO-6 rate acceleration of 2.72 (compared to 2.84 for the brosylate in EtOH at 75°)[4] were observed.

The fact that added salts fail to eliminate rearrangement implies (within the framework of the Winstein ionization-dissociation scheme)[5] that either 1) the external ion pair **3** is not appreciably scavenged by added salts in trifluoroethanol, or 2) rearrangement occurs largely via non-capturable intermediates, i.e., via direct interconversion of internal (intimate) ion pairs without passing through the external ion pair stage. In either case this behavior is in marked contrast with that of **1** and a variety of other systems in acetic acid solvent,[2,4,6] where the interception of external ion pairs and the return rearrangement is a remarkably efficient process. The apparent generality of the facile capturability of ion pairs even in solvents other than acetic acid[7,8,9] and the fact that some (*ca*. 33%) of the rearrangement is prevented by $LiClO_4$ render the second explanation more likely than the first (*vide supra*).

Thus in trifluoroethanol the original mechanistic scheme must be amended to include the direct interconversion $\underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}}$ between the intimate ion pairs 2a and 2b. This result is obviously due to the sensitivity of the ion pair chemistry to the differences in the solvent properties of acetic acid and trifluoroethanol. The difference in ion pair chemistry in going from acetic acid to trifluoroethanol merely reflects the difference in the k_2/k_3 ratio for the two solvents: in trifluoroethanol $k_3 \sim k_2$, while in acetic acid $k_3 << k_2$.

However, the direct interconversion of 2a and 2b in trifluoroethanol but not in acetic acid has mechanistic implications that require further comment. It should first be noted that trifluoroethanol is a considerably more ionizing solvent than acetic acid, and approaches formic acid in ionizing power. This is evident from the greater MeO-6 rate acceleration in the trifluoroethanolysis (530) than in the acetolysis (123)[4] of 1. Also, in more quantitative terms, the Y values for acetic acid (-1.63) and trifluoroethanol (+0.94)[10] indicate the much greater ionizing power of the latter. The Y value for formic acid is +2.08. It is also well known that increasing the ionizing power of the solvent increasingly favors the further dissociation of intimate ion pairs to the external ion pair (and free ion) stage at the expense of internal return. It would similarly be expected that the k_2/k_3 ratio in the above scheme should also increase with increasing solvent ionizing power. This expectation is based on the fact that while k_2 is a dissociation step, k_3 is not. The k_3 step is merely a (non-interceptible) migration of X^- within the intimate ion pair solvent shell.

Thus it is clear from the above result that $k_2 \sim k_3$ in the more ionizing solvent trifluoroethanol while $k_2 >> k_3$ in the less ionizing acetic acid is not in accord with the expected increase in k_2/k_3 in going to a more ionizing solvent. This fact suggests as a possible explanation that the intimate ion pairs themselves can have differing degrees of dissociation depending on the ionizing power of the solvent, though still remaining intimate in the sense that they are not interceptible by added salts. Thus the results may be explained by the reasonable assumption that the intimate ion pair 2a in trifluoroethanol (but not in acetic acid) is sufficiently dissociated ("loose") to allow facile migration of the anion from the O-methylene carbon to the back side of the O-methyl group (k_3) but sufficiently tight to prevent interception by added $LiClO_4$ or CF_3CH_2ONa. It would otherwise be difficult to explain why k_3 increases relative to k_2 in going to a more ionizing solvent. This unique behavior in trifluoroethanol is observed neither in the less ionizing acetic acid (where k_3 is unimportant because of the tightness of the intimate ion pair) nor in the more ionizing formic acid (where the greater solvent power allows k_2 to dominate)[2] and would seem to represent a further calibration point in the ionization-dissociation phenomenon. The results at least suggest that further elucidation of mechanism is needed and also that trifluoroethanol may prove to be a particularly useful solvent for the continuing study of carbonium ion pair reactions.

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