Toluene-*p*-sulfonic Acid-catalysed Reaction of But-1-ene with Trifluoroacetic Acid: Return and Elimination from the Intimate Ion Pair

Dan Fărcaşiu

Department of Chemical and Petroleum Engineering, University of Pittsburgh, 1249 Benedum Hall, Pittsburgh, PA 15261, USA

At short times, reaction of but-1-ene with toluene-*p*-sulfonic acid in trifluoroacetic acid gives 2-butyl tosylate **1**, 2-butyl trifluoroacetate **2** and but-2-ene **3** in ratios of ($\geqslant$) 2.3 : 1 : ($\geqslant$) 0.41; thus internal return is the major pathway and elimination is important for the tight 2-butyl cation–tosylate anion pair.

Three groups have studied the reaction of 2-butyl sulfonates in solvents of low nucleophilicity. One study of trifluoroacetolysis of the tosylate **1** observed the absence of multiple hydrogen shifts in the trifluoroacetate product **2** and concluded that the process involves a 2,3-hydrogen bridged cation as intermediate.[1] A steady concentration of but-2-ene **3** which was seen was considered not to intervene along the solvolysis reaction path, but to be formed by reaction with trifluoroacetate anions (presumably E2); addition of toluene-*p*-sulfonic acid (TsOH) regenerates the reactant **1**.[1] Another study in the same solvent found racemization with 7% inversion in **2** and some racemization in the tosylate **1**, and concluded that 2-butyl cation (non-bridged)–tosylate ion pairs **4** are the main intermediate, and some internal return from these occurs.[2] The intermediacy of a hydrogen-bridged ion[1,3] could not give a simple prediction of the results.[2] Finally, in a third report, the ^{18}O-labelled bromobenzenesulfonate in trifluoroethanol was shown to undergo oxygen scrambling without racemization. A sigmatropic rearrangement without ionization was favoured as the mechanism, but a very short-lived ion pair, in which the anion rotates but the cation does not, was also considered possible.[4]

In a recent study, we found that trifluoroacetolysis of a homologue, 3-methyl-2-butyl tosylate **5**, involves reversible dissociation to an ion pair, in which hydrogen shift, elimination and methyl shift occur in competition in the rate-determining step.[5] We decided to study the conversion of the tight ion pairs **4**, to help elucidate the contradictions between previous reports.

Intimate alkyl toluene-*p*-sulfonate ion pairs can be generated by reaction of an alkene with toluene-*p*-sulfonic acid (TsOH) in trifluoroacetic acid (TFA).[5,6] The mechanistic purity of the reaction is unquestionable in view of the observation that even uncatalysed addition of TFA to mono- or 1,2-di-substituted double bonds is an entirely ionic process.[7]

The reaction of but-1-ene **6** (1 mol), added as a mixture with chloroform (1.14 mol), with TFA (26 mol) containing TsOH (0.74 mol) was conducted inside the NMR probe at 22.5 °C.† The ^{1}H NMR analysis showed the presence of **1**, **2** and **3** as well as unreacted **6** and TsOH in the solution.‡ The first spectrum was recorded 18 min after mixing and showed molar ratios **1**:**2**, 2.3:1; **2**:**3**, 1:0.4; **1**:TsOH, 4.85:1. All **6** had reacted after 70 min and **3** after 160 min. Thus, **6** reacted rapidly with TsOH upon mixing, after which the reaction slowed down, mainly because of depletion of TsOH. (Uncatalysed addition of TFA to **6** under the same conditions had a rate constant of 4.2×10^{-5} s^{-1}.)[8] Measurement of the disappearance of **1** after 160 min gave a solvolysis rate constant of 7.4×10^{-5} s^{-1}, which is in line with the value obtained by UV (1.12×10^{-4} s^{-1} at 25 °C).[2]

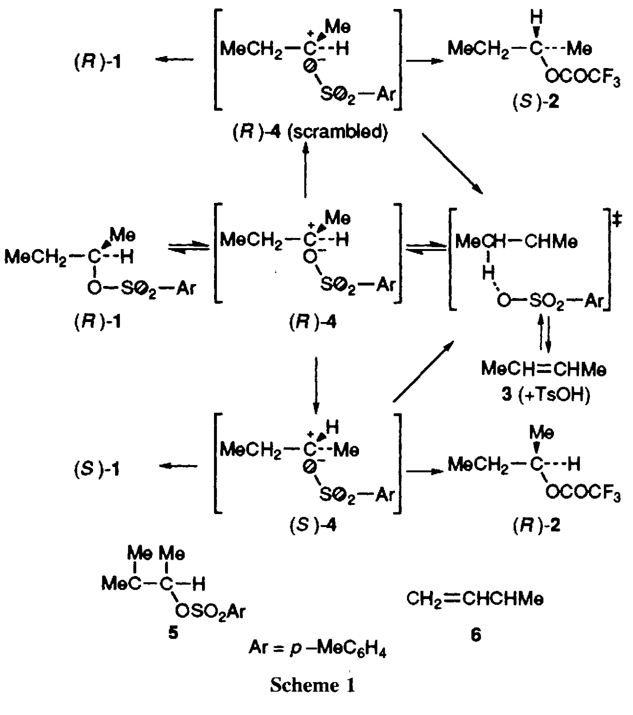
The ratio **1** : (**2** + **3**) is a measure of the internal return from **4**. The actual value is greater than the one measured at 18 min (2.3 : [1 + 0.4] = 1.64); the plot of **1** : **2** values *vs.* *t* extrapolates to a value of 3 at $t = 0$, but extrapolation is too crude an approach to be trusted quantitatively. In any event, the actual return ratio appears greater than the ratio between the polarimetric and spectrophotometric rate constants.[2] The difference includes the ion pairs which scramble the oxygen in the anion but do not racemize;[4] therefore, a sigmatropic rearrangement is unlikely as the mechanism for the latter process. The ion pairs which do not racemize are also responsible for the small excess of inversion observed in solvolysis.[2]

Trifluoroacetolysis of **1** is mechanistically similar to that of the homologue **6**.[5] It involves reversible ionization to a tight ion pair **4**. There is no hydrogen participation: any hydrogen shift competes with attack by solvent and elimination in the subsequent rate-determining step(s). Thus, it is the mechanism of Allen, Ambidge and Tidwell[2] which is substantiated in its main lines by these results.

The amount of alkene **3** (30% of the mixture **2** + **3**) formed from **4** is close to, but somewhat smaller than, the extent of deuteriation of **2** formed from **1** in F_3CO_2D (40%), which is as expected, because further reaction of deuteriated **1** leads to some dideuteriated **2**. Thus, elimination occurs *along the reaction path*. In the possible movements of the ions in the pair, rotation of the anion produces oxygen scrambling upon recombination, and rotation of the cation produces racemization. If during these movements the anion moves closer to a β hydrogen, elimination takes place. The observation of accumulation of **3** when solvolysis of **1** was conducted in the presence of CF_3CO_2Na[1] can be assigned to neutralization of TsOH, which in the mechanism replaced the fast readdition of TsOH by the slow addition of TFA.

The mechanism of trifluoroacetolysis of **1** to the stage of tight ion pairs **4** is shown in Scheme 1. Further evolution to solvent-separated ion pairs and, possibly, free ions should occur in the normal manner.[9]

This work was supported by a grant (CTS-9121454) from



Scheme 1

NSF. Dr Tonis Pehk is thanked for help with the NMR spectra.

Received, 19th August 1994; Com. 4/05103C

Footnotes

† TsOH·H$_2$O was dissolved in 99% TFA and enough trifluoroacetic anhydride was added to remove all water (exothermic reaction upon mixing) and leave some unreacted anhydride (1.5% equiv. with respect to TFA) for any water brought by the other reactant or entering the system during reaction. The solution was cooled to −10 °C and a **5**–CHCl$_3$ mixture precooled to −10 °C was added. A sample was placed in an NMR tube and inserted into the magnet.

‡ Spectra: 300.13 MHz, 8 k points for 5000 Hz width, 9 μs pulses, 2 s delay, phase cycling, transformed with zero filling to 32 k and exponential multiplication (line broadening 0.3 Hz), baseline correction for integration with spline function. The chemical shifts (δ) were as follows (appropriate relative intensities and splitting were observed): **1**, *7.87 (CH)*, 7.45 (CH), *4.76 (CH)*, 2.48 (CH$_3$), 1.68 (CH$_2$), 1.33 (CH$_3$), 0.87 (CH$_3$); **2**, *5.19 (CH)*, 1.79 (CH$_2$), 1.41 (CH$_3$), 1.00 (CH$_3$); **3**, *5.52 (CH)*, 1.60 (CH$_3$); **5**, *5.91 (CH)*, 5.03–4.88 (=CH$_2$), 2.07 (CH$_2$), 1.00 (CH$_3$); TsOH, *8.02 (CH)*, 7.49 (CH), 2.51 (CH$_3$); CHCl$_3$, *7.24* (standard). The italicised signals were integrated.

References

1 J. J. Dannenberg, B. J. Goldberg, J. K. Barton, K. Dill, D. H. Weinwurzel and M. O. Longas, *J. Am. Chem. Soc.*, 1981, **103**, 7764.

2 A. D. Allen, C. Ambidge and T. T. Tidwell, *J. Org. Chem.*, 1983, **48**, 4527.

3 J. J. Dannenberg, J. K. Barton, B. Bunch, B. J. Goldberg and T. Kowalski, *J. Org. Chem.*, 1983, **48**, 4524.

4 P. E. Dietze and M. Wojciechowski, *J. Am. Chem. Soc.*, 1990, **112**, 5240.

5 D. Fărcaşiu, G. Marino, J. M. Harris, B. A. Hovanes and C. S. Hsu, *J. Org. Chem.*, 1994, **59**, 154.

6 V. J. Shiner, Jr. and W. Dowd, *J. Am. Chem. Soc.*, 1969, **91**, 6528.

7 D. Fărcaşiu, G. Marino and C. S. Hsu, *J. Org. Chem.*, 1994, **59**, 163.

8 A. D. Allen and T. T. Tidwell, *J. Am. Chem. Soc.*, 1982, **104**, 3145, give a value of 8.06×10^{-5} at 25 °C.

9 S. Winstein, B. Appel, R. Baker and A. Diaz, *Organic Reaction Mechanism*, Special Publication No. 19, The Chemical Society, London, 1965, p. 109. Other reviews are listed in ref. 5.