Non-limiting Solvolysis of a 2-Propyl Sulphonate in Trifluoroacetic Acid. A Redetermination of Deuterium Kinetic Isotope Effects

Hiroshi Yamataka,*[a] Shinich Tamura,[a] Terukiyo Hanafusa,[a] and Takashi Ando*[b]

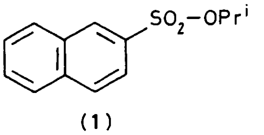
[a] *Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan*
[b] *Department of Chemistry, Shiga University of Medical Science, Otsu, Shiga 520–21, Japan*

Contrary to an earlier report, the α-deuterium isotope effect (k_H/k_D) for the trifluoroacetolysis of a 2-propyl arenesulphonate is smaller than 1.22 at 25 °C, suggesting that the reaction does not proceed *via* the limiting S_N1 mechanism.

The trifluoroacetolysis of simple secondary alkyl substrates has often been assumed to be limiting k_c (S_N1), and the mechanisms of secondary substrates in other solvents are discussed based on this assumption. We present here a piece of evidence which indicates that this assumption may be incorrect.

The mechanism of 2-propyl ester solvolysis is known to have borderline characteristics and to be sensitive to subtle changes in solvent properties.[1] The reaction is subject to nucleophilic attack by solvent molecules; the degree of solvent assistance depends on the nucleophilicity of the solvent. In 1969, Streitwieser *et al.* measured the α- and β-deuterium kinetic isotope effects in the trifluoroacetolysis of 2-propyl toluene-*p*-sulphonate and found large α-D_1 (k_H/k_D = 1.22 ± 0.02) and β-D_6 (k_H/k_D = 2.12 ± 0.1) isotope effects at 25 °C.[2] These results have been regarded as evidence for the limiting S_N1 mechanism of the reaction. Recently, Bentley *et al.* have claimed that based on the α-Me/H rate ratio and the ρ* correlation, the solvolysis of 2-propyl toluene-*p*-sulphonate is nucleophilically assisted by solvent molecules even in trifluoroacetic acid (TFA) and hexafluoropropan-2-ol.[3]

In the course of our recent study on solvolysis mechanisms,[4] it became necessary for us to determine kinetic isotope effects for all the constituent atoms of a simple secondary substrate in the limiting S_N1 solvolysis. We first of all measured α- and β-deuterium isotope effects for the trifluoroacetolysis of 2-propyl naphthalene-β-sulphonate (1) at 25 and 45 °C, expecting the limiting values as in the case of 2-propyl toluene-*p*-sulphonate reported in the literature.[2] However, we actually observed somewhat different results as listed in Table 1. It is apparent that both α- and β-deuterium isotope effects are smaller than those reported by Streitwieser *et al.*[2] It is unlikely that these differences come from the difference in the leaving group.



(1)

It has been recognized that TFA is difficult to purify to a constant state. In fact, Schleyer *et al.* have shown that trifluoroacetolysis rate constants can vary to a great extent depending on the method of purification,[5] which could explain the present discrepancy between our results and the literature values. Our TFA was purified by duplicate distillation and freshly distilled trifluoroacetic anhydride was added, while TFA in the literature was purified by distillation from H_2SO_4.[2] The amount of the buffer salt was also different for the two solvent systems. To check this, we also measured isotope effects in TFA which was prepared according to the Streitwieser method. As shown in Table 1, the difference in the solvent seems to cause a small change in the isotope effects in the expected direction; the α-deuterium isotope effect became barely within the rather large uncertainty of the reported value. Hence, the mechanism of the trifluoroacetolysis of the 2-propyl ester is not limiting (S_N1) according to the α-deuterium isotope effect probe. This is consistent with the conclusion based on the α-Me/H rate ratio probe.[3]

One of the consequences of the non-limiting nature of the trifluoroacetolysis of 2-propyl esters is on the solvolysis mechanism of pinacolyl derivatives. There has been a long debate on the mechanism of pinacolyl solvolysis, neighbouring group assisted k_Δ *vs.* non-assisted k_c, and it is not fully settled yet;[1] this system plays an important role in Shiner's interpretation of the solvolysis mechanism.[6] One of the principal arguments for the k_c mechanism comes from the fact that the trifluoroacetolysis rate constants of a number of secondary alkyl toluene-*p*-sulphonates including pinacolyl toluene-*p*-sulphonate give linear plots against Σσ* of the alkyl groups.[1] By regarding the trifluoroacetolysis of simple secondary alkyl toluene-*p*-sulphonates as limiting, the mechanism of the trifluoroacetolysis of pinacolyl toluene-*p*-sulphonate was also concluded to be limiting k_c. However, if we take the

Table 1. Rate constants and deuterium isotope effects in the trifluoroacetolysis of (**1**).[a]

	25 °C		45 °C	
	10^5k_1/s^{-1}	k_H/k_D	10^4k_1/s^{-1}	k_H/k_D
(1)	2.73 ± 0.02[b]		2.43 ± 0.02[b]	
	2.80 ± 0.03[c]		2.53[c]	
(1) α-D_1	2.30 ± 0.01[b]	1.189 ± 0.002[b]	2.09 ± 0.03[b]	1.168 ± 0.007[b]
	2.35[c]	1.20[c]	2.14[c]	1.18[c]
(1) β-D_6	1.36 ± 0.02[b]	2.007 ± 0.015[b]	1.23 ± 0.05[b]	1.976 ± 0.016[b]
	1.35[c]	2.05[c]		

[a] Rate constants were determined spectrophotometrically at 325 nm, and deuterium isotope effects were calculated from pairs of runs and then averaged. Uncertainties are standard deviations for two or more determinations. [b] [Ester] = 0.036 and [$NaOCOCF_3$] = 0.0432 M. TFA was twice-distilled and freshly distilled trifluoroacetic anhydride was added. [c] [Ester] = 0.050 and [$NaOCOCF_3$] = 0.125 M. TFA was twice-distilled from H_2SO_4.

position that the trifluoroacetolysis of secondary esters is not limiting, the reported linear free energy relationship may be regarded as evidence for the assisted mechanism; the reactions of simple secondary alkyl toluene-*p*-sulphonates are nucleophilically assisted by solvent, while the reaction of pinacolyl toluene-*p*-sulphonate is assisted either by the neighbouring methyl group[7] or by solvent.[3]

Trifluoroethanolysis of (**1**) gave an even smaller α-deuterium isotope effect suggesting that there is a higher degree of solvent attachment in the transition state of the reaction.[4] We feel at present that solvolytic reactions of secondary alkyl sulphonates in any solvent should have nucleophilic solvent attachment in the transition state unless it is prohibited by steric reasons. The solvolysis mechanism of secondary alkyl substrates must be discussed on this basis.

Received, 24th October 1983; Com. 1391

References

1 J. M. Harris, in 'Progress in Physical Organic Chemistry,' vol. 11, eds. A. Streitwieser, Jr., and R. W. Taft, Wiley, New York, 1974, p. 89; T. W. Bentley and P. v. R. Schleyer, in 'Advances in Physical Organic Chemistry,' vol. 14, eds. V. Gold and D. Bethell, Academic Press, London, 1977, p. 1.

2 A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Lett.*, 1969, 1263.

3 T. W. Bentley, C. T. Bowen, W. Parker, and C. I. F. Watt, *J. Am. Chem. Soc.*, 1979, **101**, 2486; *J. Chem. Soc., Perkin Trans.* 2, 1980, 1244; T. W. Bentley, C. T. Bowen, D. H. Morten, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1981, **103**, 5466.

4 T. Ando, H. Yamataka, S. Tamura, and T. Hanafusa, *J. Am. Chem. Soc.*, 1982, **104**, 5493.

5 F. L. Schadt III, C. J. Lancelot, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1978, **100**, 2542.

6 V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *J. Am. Chem. Soc.*, 1969, **91**, 7748; T. W. Bentley, S. H. Liggero, M. A. Imhoff, and P. v. R. Schleyer, *ibid.*, 1974, **96**, 1970.

7 T. Ando and H. Morisaki, *Tetrahedron Lett.*, 1979, 121.