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SOLVOLYSIS RATES OF 7-METHYL- AND 7-METHYL-d_3-7-NORBORNYL TOSYLATES IN TRIFLUOROETHANOL. A CASE OF AN APPARENT BREAKDOWN OF THE mY RELATIONSHIP

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We wish to report the unexpected solvolytic behavior of 7-methyl-7-norbornyl tosylate (MNBOTs) in 2,2,2-trifluoroethanol (TFE). When this compound was solvolyzed in TFE-water mixtures the solvolysis rates changed insignificantly within the range of 100% to 70% TFE. When log k is plotted against Y for solvolysis in TFE and ethanol, it can be seen that only when increasing the water content to 50% TFE does a significant rate increase occur (Fig. 1).

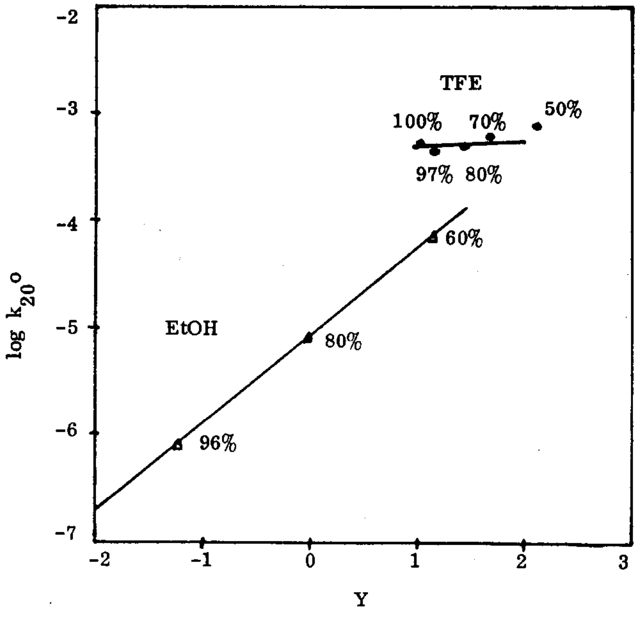

Figure 1. Plot of log k (20°) for solvolysis of 7-methyl-7-norbornyl tosylate vs. Y.

A similar, though inverse behavior was observed when methyl-d_3 isotope effects were measured. Here the β-effects show in TFE a much higher sensitivity towards changes in Y than in ethanol-water mixtures (Fig. 2).

The mechanistic evaluation of solvolysis rates as well as secondary isotope effects[1] has to take into account not only the selectivity of the substrate towards nucleophilic attack (of the solvent) but also the nucleophilicity and the ionizing power of the solvent. Trifluoroethanol, due to its low nucleophilicity and high ionizing power has been shown to be a superior solvent than either acetic acid or aqueous ethanol, the two most commonly used solvents for solvolytic reactions[2].

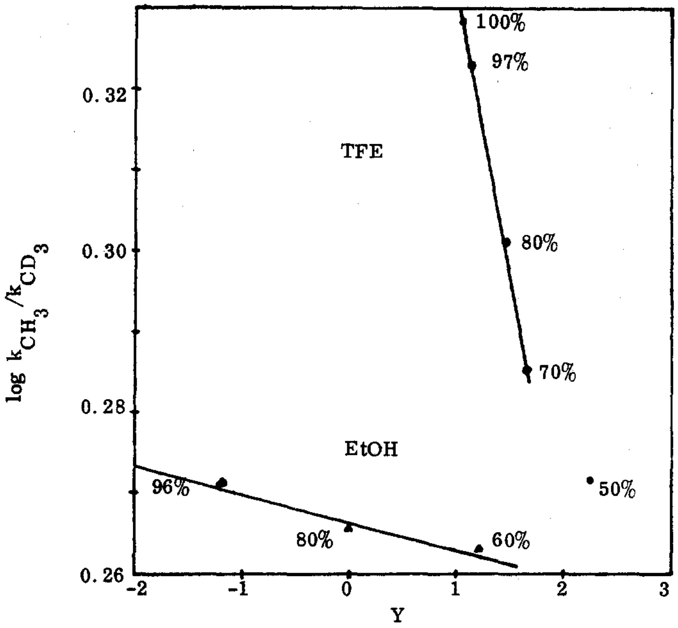

Figure 2. Plot of log k_{CH_3} - log k_{CD_3} for solvolysis of 7-methyl-7-norbornyl tosylate vs. Y.

When solvolysis rates in TFE of other substrates reported in the literature are evaluated in terms of the Winstein-Grunwald mY correlation[3], an interesting observation can be made. A number of systems of different geometry, secondary as well as tertiary, open chain and cyclic, show relatively low m values in TFE (Table 1).

Table 1. m values for solvolyses in TFE- and ethanol-water mixtures

Substrate	Solvent		References
	TFE	EtOH	
2-Adamantyl triflate	0.476		4
1-Adamantyl bromide	0.427	1.183	1b
Pinacolyl brosylate	0.280	0.727	5
7-Methyl-*anti*-7-norbornenyl p-nitrobenzoate	0.213		6
7-Methyl-7-norbornyl tosylate	0.062*	0.684	this work

*the rate in 50% TFE was not taken into account

However, the value for MNBOTs is the lowest as yet observed with tertiary substrates[1b]. Even when using Y values for TFE based on solvolysis rates of 1-adamantyl bromide[1b] rather than those based on t-BuCl, the slope of log k vs. Y does not increase significantly. From Fig. 3 it can be seen that the rate effects in TFE are almost entirely due to enthalpy changes. This pertains also for solvolysis in ethanol-water mixtures.

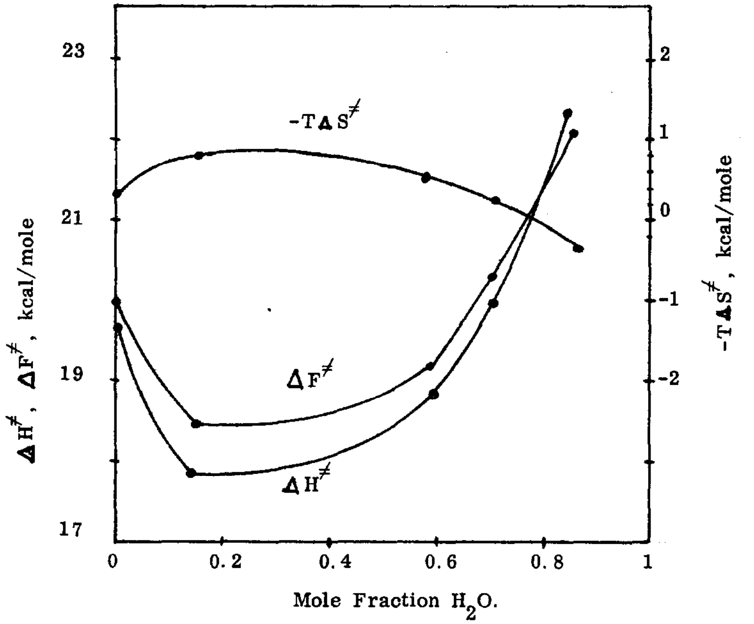

Figure 3. Plot of $\Delta H^{\neq}$, $\Delta F^{\neq}$ and $-T\Delta S^{\neq}$ vs. mole fraction H_2O for solvolysis of 7-methyl-7-norbornyl tosylate in TFE-water mixtures at 25.0°.

In order to rationalize these results it is necessary (i) to examine the apparently unique structural features of 7-methyl-7-norbornyl tosylate and (ii) to compare the properties of TFE with those of other solvents.

7-Methyl-7-norbornyl tosylate solvolyses under similar conditions $10^{8.6}$ times faster than the parent 7-norbornyl tosylate[7]. This is one of the highest CH_3/H rate ratios observed. In 2-methyl-2-adamantyl bromide[8] this ratio is $10^{7.5}$. It can therefore be assumed that in both cases solvent participation from the rear is insignificant due to the steric hindrance. For a k_c process, the Me-d_3 isotope effects should be similar in these two systems. This is however not the case. Thus, 2-methyl-2-adamantyl chloride shows a CD_3 effect in 80% ethanol[5,9] of 1.68, while the effect in 7-methyl-d_3-7-norbornyl tosylate is much higher ($k_H/k_D = 1.86$ in 80% EtOH, and 2.10 in 97% TFE respectively). Although solvolysis in 97% TFE yielded 67 (46)% of olefin[+] in addition to

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[+] values in brackets refer to products from the CD_3- derivative; the analysis was performed by v.p.c. and m.s. - the olefin had the correct mass for 7-methylenenorbornane.

10 (10)% MNB-OH and 23 (43)% MNB-trifluoroethyl ether, a rate determining elimination from the tight ion pair cannot be the main source of this large effect. When 7-methyl-d_1-7-norbornyl tosylate was solvolyzed in 97% TFE the effect was still exceptionally large (k_H/k_D 1.26±0.02) in spite of the fact that in this case hydrogen should eliminate preferentially. To what extent the angle strain at C_7 with the corresponding reduction of the C_7-CH_3 bond distance could be made responsible for the large β-effects remains to be investigated.

That TFE behaves differently from other solvents is not surprising. A substitution of fluorine for hydrogen in ethanol influences greatly the ability of this solvent to form hydrogen bonds and therefore should affect the solvation of the ground state or - what is more probable - of the solvolysis transition state. The solvation of the first formed ion pair(s) is probably unaffected by adding water up to 30%, while the solvation shell breaks down when more water is present.

REFERENCES

1. (a) For a recent review, see V. J. Shiner, Jr., "Deuterium Isotope Effects in Solvolytic Substitution at Saturated Carbon", in C. J. Collins and N.S. Bowman, Ed. "Isotope Effects in Chemical Reactions", van Nostrand Reinhold Co., New York, N.Y., 1971.
   (b) D. J. Raber, R.C. Bingham, J. M. Harris, J. L. Fry, and P. v.R. Schleyer, J. Amer. Chem. Soc., 92, 5977 (1970).
2. V. J. Shiner, Jr., W. Dowd, R.D. Fisher, S.R. Hartshorn, M.A. Kessick, L. Milakofsky and M.W. Rapp, J. Amer. Chem. Soc., 91, 4838 (1969).
3. S. Winstein, A.H. Fainberg, and E. Grunwald, J. Amer. Chem. Soc., 79, 4146 (1957), and references therein.
4. V. J. Shiner, Jr. and R.D. Fisher, J. Amer. Chem. Soc., 93, 2553 (1971).
5. V. J. Shiner, Jr., private communication.
6. I. Szele, unpublished results from this laboratory.
7. (a) M. Tomić, unpublished results from this laboratory.
   (b) S. Winstein, M. Shatavsky, C. Norton, and R.B. Woodward, J. Amer. Chem. Soc., 77, 4183 (1955).
8. J. L. Fry, J. M. Harris, R.C. Bingham, and P. v.R. Schleyer, J. Amer. Chem. Soc., 92, 2540 (1970).
9. A CH_3/CD_3 effect of 1.42 was also observed in the solvolysis of 2-methyl-2-adamantyl bromide (P. v.R. Schleyer, private communication).