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SOLVOLYSES IN FLUOROALCOHOLS. II. ANOMALOUS BEHAVIOR OF tert-BUTYL CHLORIDE AND 7-METHYL-7-NORBORNYL TOSYLATE IN HEXAFLUOROISOPROPANOL-WATER MIXTURES

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Recently[1] we reported the relative insensitivity of solvolysis rates of 7-methyl-7-norbornyl tosylate (MNBOTs) in trifluoroethanol (TFE) towards changes in the Grunwald-Winstein Y value[2]. In this communication we report the anomalous behavior of solvolysis rates of t-butyl chloride and MNBOTs in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)*.

t-Butyl chloride was solvolyzed in HFIP-water mixtures at 25° and the reaction rates were determined by continuous potentiometric titration of the liberated acid using the previously described technique[3]. The rate data and the derived Y values are presented in Table 1. As can be seen, contrary to the behavior in other solvent systems[5], the rates do not change monotonously with the increase of the water content, but manifest a minimum at 66.7 mole % of water. In view of the unusual behavior of MNBOTs in TFE[1] we also determined the solvolysis rates of this compound in HFIP-water mixtures. The rate data for both t-BuCl and MNBOTs in different

Table 1. Rate of t-BuCl Solvolysis in HFIP-H_2O Mixtures and Y Values[a], 25°

Wt % HFIP	Mole % H_2O	$k \times 10^4 sec^{-1}$	Y
97	22.4	26.9 ±0.50	2.458
90	50.8	9.12±0.05	1.987
82.3	66.7	6.87±0.05	1.864
80	70.1	6.82±0.05	1.862
75.6	75.0	7.18±0.05	1.885
70	80.0	7.75±0.03	1.917
60	86.2	9.75±0.13	2.017
50	90.3	12.8 ±0.04	2.135

[a] Y values based on k value of 9.376×10^{-6} for 80% vol EtOH - 20% vol H_2O.[4]

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* We wish to thank Professor V. J. Shiner, Jr. for drawing our attention to this solvent.

HFIP-water mixtures are illustrated in Figure 1. The anomalous behavior of MNBOTs is again evident. The solvolysis rates decreased with increasing water content but showed a sharp inflection (see Figure 1.). The position of the inflection coincides with the minimum of the t-BuCl solvolysis rate. These results imply that hexafluoroisopropanol forms a dihydrate and that mixtures of this dihydrate with either water or HFIP have to be considered as two different binary solvent systems*. This is even more evident if log k for t-BuCl is plotted against the mole % of the dihydrate in dihydrate-water and dihydrate-HFIP mixtures, respectively (Figure 2.). For comparison Shiner's data[10] for t-BuCl in TFE-water mixtures are also included.

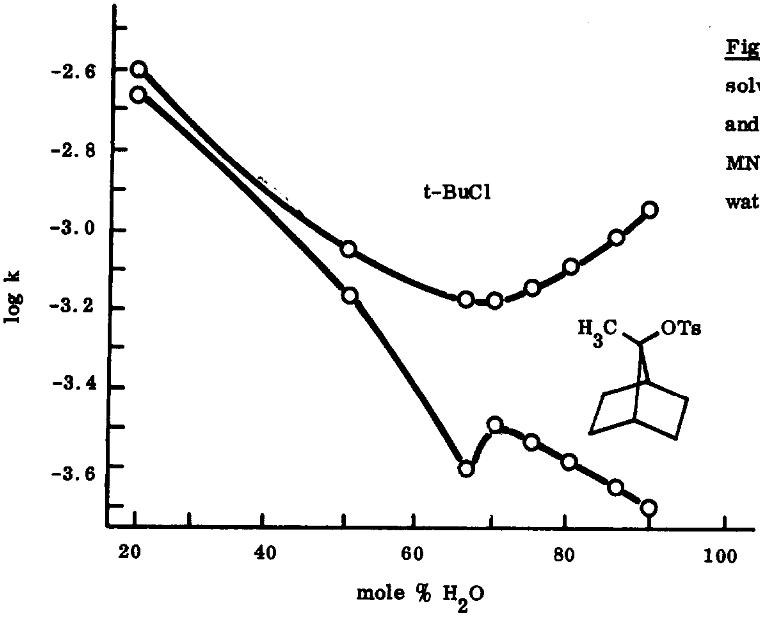

Figure 1. Plot of log k for solvolysis of t-BuCl at 25° and for solvolysis of MNBOTs at 5°, *vs*. mole % water in HFIP-water mixtures.

The chemical shift of the C-2 proton of HFIP is also solvent dependent. By increasing the water content a downfield shift was observed, which indicates an electrostatic or hydrogen bond interaction of this proton with the oxygen atom in water.

The observed high solvolysis rates in fluorinated alcohols can be ascribed to the ability of these solvents to form strong hydrogen bonds with the leaving group in the solvolysis transition state. From the inspection of molecular models a structure for the HFIP·$2H_2O$ complex can be

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*Unusual properties of HFIP have been observed by other workers. Stable 1:1 complexes with several organic compounds such as tetrahydrofuran, diethylether or pyridine are known[6,7,8]. Murto and Kivinen[9] concluded on the basis of some physical properties that a 1:1 complex with water probably also exists.

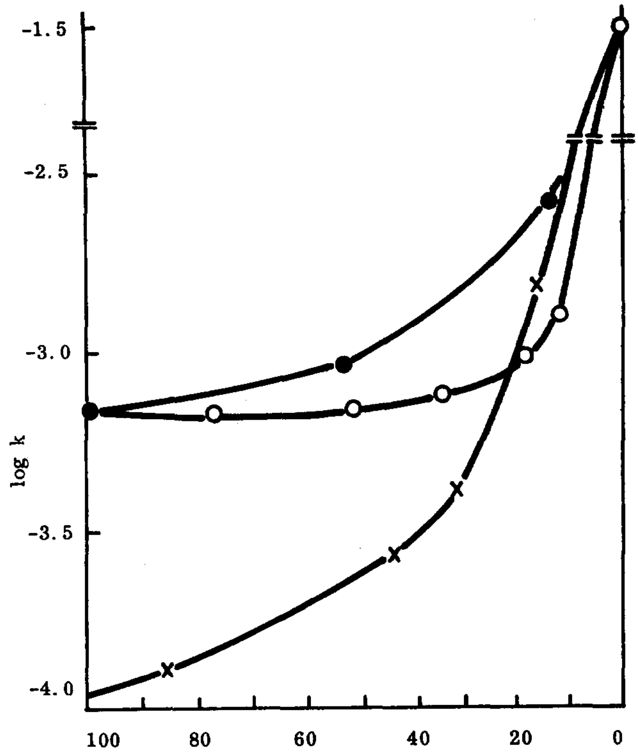

Figure 2. Solvolysis rates of t-BuCl in aqueous HFIP and TFE mixtures.
● mole % HFIP·$2H_2O$ in HFIP
o mole % HFIP·$2H_2O$ in H_2O
x mole % TFE in H_2O

proposed. Since the HFIP·$2H_2O$ complex is internally compensated, with only two fluorine atoms not hydrogen bonded to the two water molecules, it has the smallest solvating power and may be responsible for the minimum in the observed solvolysis rate for t-BuCl. The addition of either water or HFIP to this complex increases the solvating ability of the solvent mixture, and the ionizing power (greater Y values). This consequently results in increased solvolysis rates.

MNBOTs solvolyzes about six times faster than t-BuCl in both TFE[1,10] and HFIP. However in HFIP the rates are decreasing with an increasing water content (see Figure 1.), which appears to be a consequence of the structure of this substrate[1]. The methyl-d_3 isotope effects are the highest as yet observed for this compound (Table 2.). The observed decrease in the effect with the increasing nucleophilicity of the solvent parallels the behavior in the TFE-water mixtures[1]. To what extent these larger effects are caused by an increased elimination remains

Table 2. Me-d_3 Isotope Effects in the Solvolysis of 7-Methyl-7-norbornyl Tosylate at 5°

Wt % HFIP	97	80	70
k_{CH_3}/k_{CD_3}	2.33	2.27	2.22

to be investigated. It is, however, of interest to point out that with t-BuCl the solvolysis in 75.6 wt % HFIP (Y = 1.885) yields the same amount of isobutene (30.4%, determined by NMR) as in 97 wt % TFE (Y = 1.147)[10].

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