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NUCLEOPHILIC PARTICIPATION IN THE SOLVOLYSIS OF THE *t*-BUTYLDIMETHYLSULFONIUM ION[1]

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Abstract: Studies with the *t*-butyldimethylsulfonium ion give evidence for nucleophilic participation in the solvolyses of *t*-butyl compounds but electrophilic assistance would be the dominant factor for *t*-butyl chloride solvolysis.

For unimolecular reactions of RX^+ species, such as the *t*-butyldimethylsulfonium ion, the Hughes-Ingold theory of solvent effects upon the rates of nucleophilic substitution reactions[2] predicts that a dispersal of charge at the transition state (eq. 1) will be accompanied by a small decrease in the rate when the solvent polarity is increased. An effect of this type has been demonstrated for variations in the composition of aqueous-ethanol,[3,4] aqueous-methanol,[4] and aqueous-acetone[4] mixtures. These data can be combined to give a reasonably linear plot[4,5] (slope of -0.09) when plotted against Grunwald-Winstein *Y* values.[6,7] It was proposed[4] that the major factor was the cation-solvating power and that an increase should retard reaction due to a greater stabilization of the ground state. However, use of solvent-nucleophilicity values[5,8,9] indicates that the faster reactions are in the solvents of higher nucleophilicity.

$$\underline{t}\text{-Bu}\overset{+}{\text{S}}\text{Me}_2 \longrightarrow [\underline{t}\text{-}\overset{\delta+}{\text{Bu}}\text{---}\overset{\delta+}{\text{S}}\text{Me}_2] \longrightarrow \underline{t}\text{-Bu}^+ + :\text{SMe}_2 \qquad (1)$$

Rate data which we have obtained for the solvolysis of *t*-butyldimethylsulfonium trifluoro-

TABLE I

Specific Rates of Solvolysis of *ca.* 0.01 *M* *t*-Butyldimethylsulfonium Trifluoromethanesulfonate at 50.0°C

Dioxane-H_2O		TFE-H_2O		Pure Solvents	
% Dioxane[a]	10^6 k (sec^{-1})[b]	% TFE[c]	10^6 k (sec^{-1})[b]	Solvent	10^6 k (sec^{-1})[b]
90	12.10[d]	97	2.88	TFE	2.86
80	10.30[d]	90	3.15	H_2O	6.09[e]
70	9.78[d]	70	4.16	*i*-PrOH	14.77
60	9.37[d]	50	5.05	*t*-BuOH	17.51
40	8.29[d]	30	5.97	CH_3COOH	8.10[f]
20	6.08	20	6.25	HCOOH	6.78

[a] On volume-volume basis at 25.0°. [b] All runs performed in duplicate with procedures paralleling those of ref. 5; standard deviations for combined runs less than 3%, except for a value of 11% for formolysis. [c] On a weight-weight basis. [d] With hexafluoroantimonate as the gegenion. [e] At 50.4°, a value of 6.52 x 10^{-6} sec^{-1} has been reported for the chloride salt (ref. 4). [f] At 50.4°, a value of 8.33 x 10^{-6} sec^{-1} has been reported for the chloride salt (ref. 4).

methanesulfonate are reported in Table I and data for the solvolysis of this substrate in 2,2,2-trifluoroethanol (TFE)-ethanol mixtures are reported elsewhere.[10] These specific solvolysis rates, and also available data[4] for the corresponding chloride salt, have been correlated with solvent ionizing power and solvent nucleophilicity values (Table II).

It has recently been demonstrated[11] that the ability of the solvent to solvate the developing chloride ion is the major factor controlling variation of rate with solvent composition in the solvolysis of _t_-butyl chloride. It is, therefore, at first sight, surprising that the associated _Y_-value scale can correlate data for RX^+ solvolyses, where only cationic species are involved. However, nature has played a cruel trick, in that, over wide composition ranges for the commonly used mixed solvents, the solvent nucleophilicities increase approximately linearly with decrease in solvent ionizing power and, for these solvents, what appears to be a decrease in rate due to increasing solvent ionizing power could actually be a decrease in rate due to decreasing solvent nucleophilicity. Indeed, for RX^+-type substrates, the reduced contributions to linear free energy relationships from the leaving-group solvation component should provide an enhanced opportunity to observe effects due to nucleophilic solvation of a developing _t_-butyl carbocation,[12,13,14] if such effects do exist.[11]

In support of nucleophilic interaction by the solvent in the rate-determining step for the solvolysis of the _t_-butyldimethylsulfonium ion, we offer the following observations:

(1) The TFE-H_2O system[15] can be used to distinguish between a dominant dependence on solvent polarity (ionizing power) and solvent nucleophilicity. For TFE-H_2O, both _Y_ and _N_ values increase as the water content is increased.[5,16] It is found that the specific rates (Table I) _increase_ with the water content, contrary to the Hughes-Ingold theory but consistent with an effect due to nucleophilic assistance at the developing _t_-butyl carbocation.

(2) Acetic and formic acids have _Y_ values that differ by 3.7 units[7] but very similar solvent nucleophilicities.[5,8,17] The specific solvolysis rates (Table I) differ only by 20%, with the faster rate in the slightly more nucleophilic[5] acetic acid.

(3) Plots of log (k/k_0) against solvent nucleophilicity values based on triethyloxonium ion solvolysis[5] (eq. 2) give reasonably linear correlations over wide ranges of the mixed

$$\log (k/k_0) = \underline{\ell}\, \underline{N}_{KL} \qquad (2)$$

solvent systems (Table II) but with dispersal of the type familiar for Grunwald-Winstein plots.[6,7] Of course, any comprehensive treatment would have to include effects due to solvent polarity, ion-pairing,[18,19] and resolvation of the sulfur during the change from a sulfonium ion to a dimethyl sulfide molecule. Nonetheless, for five of the six solvent systems studied, the $\underline{\ell}$ values lie in the range of 0.32 to 0.48, intermediate between the 0.5 calculated for isopropyl _p_-toluenesulfonate and the 0.25 calculated for cyclopentyl _p_-toluenesulfonate.[5] For the aqueous-acetone system, where the range of $\underline{N}_{KL}$ values is extremely narrow (-0.26 to -0.52), the $\underline{\ell}$ values vary considerably with the counterion and with the range of solvent composition.

(4) If Hughes-Ingold-type effects dominate, a similar solvolysis behavior would be expected for _t_-butyl- and 1-adamantyl- dimethylsulfonium cations. However, these species differ in that the cage structure prevents rear-side attack during solvolysis of the 1-adamantyldimethylsulfonium cation. Major differences in solvolytic behavior have been found to exist, and indeed

TABLE II

Correlation of the Specific Rates of Solvolysis of the *t*-Butyldimethylsulfonium Ion, as the Chloride Salt at 50.4°C[a] or the Trifluoromethanesulfonate Salt at 50.0°C

			Grunwald-Winstein		Equation 2	
Anion	Solvent System[b]	n^c	m^d	r^e	ℓ^f	r^e
Cl	100-40% EtOH-H_2O	6	-0.087	0.977	+0.354	0.988
Cl	100-70% MeOH-H_2O	2	-0.091		+0.343	
Cl	90-50% Acetone-H_2O	4	-0.106	0.999	+1.19	0.954
OTf	90-50% Acetone-H_2O	4^g	-0.072	0.986	+0.780	0.907
OTf	80-50% Acetone-H_2O	3^g	-0.058	0.994	+0.521	0.993
OTf	80-20% Dioxane-H_2O	5	-0.057	0.932	+0.420	0.957
OTf	90-20% TFE-H_2O	5	+0.172	0.975	+0.324	0.990
OTf	90- 0% TFE-EtOH	9	-0.252	0.995	+0.477	0.992

[a] Rate data from ref. 4. [b] Volume percentage of first mentioned component, except for TFE-H_2O which is on a weight percentage basis. [c] Number of solvent compositions considered. [d] Using *Y* values from refs. 7, 15, and 16. [e] Correlation coefficient. [f] Using N_{KL} values from refs. 5 and 10. [g] Specific rates (10^6 k, sec^{-1}) are as follows: 90% acetone, 16.1; 80% acetone, 12.1; 70% acetone, 11.2; 50% acetone, 9.2.

the 1-adamantyldimethylsulfonium trifluoromethanesulfonate usually gives a variation in solvolytic specific rate with solvent composition that is contrary to the Hughes-Ingold theory. For example, with varying aqueous-ethanol compositions at 70.0°C, the specific solvolysis rate *increases* as one increases the water content (from 2.1×10^{-6} sec^{-1} in ethanol to 4.1×10^{-6} sec^{-1} in water). Further, the EtOH > H_2O > TFE ordering of reactivities for the *t*-butyldimethylsulfonium ion is reversed for the 1-adamantyldimethylsulfonium ion.

The specific solvolysis rate of the *t*-butyldimethylsulfonium ion in pure TFE (2.86×10^{-6} sec^{-1}) is faster than one would predict based upon its mixed solvent systems (an extrapolated value of 0.91×10^{-6} sec^{-1} is obtained by applying eq. 2 to TFE-EtOH mixtures). This may reflect the incursion of a dominant non-nucleophilically-assisted pathway when the solvent nucleophilicity becomes very low.

Abraham[20] has estimated that for *t*-butyl chloride solvolysis in protic solvents the activated complex is very product like with 0.8-0.9 charge development. If the transition state is similarly situated for the sulfonium ion solvolysis, it can be viewed as a situation where the charge is 80-90% transferred from the sulfur to the *t*-butyl group. For such a situation, the ground-state to transition-state variation is perhaps better viewed in terms of *transfer* rather than dispersal of charge. The Hughes-Ingold theory would apply best when the charge is about one-half transferred and it would become increasingly less relevant as one moved to earlier or later transition states. Hence, for the *t*-butyldimethylsulfonium ion solvolysis, it is reasonable to assume that a major factor, in most cases a dominant factor, would be the ability to solvate the almost fully developed carbocation.

If the solvolyses of *t*-butyl chloride involve a similar extent of nucleophilic solvation, we can estimate the influence on the *Y* values. Using aqueous ethanol[5] as an example, the N_{KL} and *Y* values are interrelated by eq. 3 and, substituting in the four parameter Grunwald-

$$N_{KL} = -0.24\ Y \qquad (3)$$

Winstein equation,[5,8,9] one can write eq. 4, where Y^{true} would be the value in the absence of

$$Y = \ell\ N_{KL} + Y^{true} \qquad (4)$$

nucleophilic assistance. Substituting within eq. 4 from eq. 3 and Table II,

$$Y^{true} = Y + 0.35 \times 0.24\ Y = 1.09\ Y.$$

For aqueous-ethanol mixtures the corrected values would differ by less than 10% from those in the literature and it is possible to agree both with the position that nucleophilic assistance does exist[12,13,14] and with the position that it does not make an appreciable contribution to linear free energy relationships.[11]

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