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The Hydrolysis of Trimethylamine Sulfur Trioxide. Solvent Effects in Dimethyl Sulfoxide–Water

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The kinetics of the basic hydrolysis of trimethylamine sulfur trioxide, $(CH_3)_3NSO_3 + 2OH^- \rightarrow (CH_3)_3N + H_2O + SO_4^{2-}$, have been studied at 25° in dimethyl sulfoxide–water solvent mixtures. The observed rate law is $-d[(CH_3)_3NSO_3]/dt = k_1[(CH_3)_3NSO_3] + k_2[(CH_3)_3NSO_3][OH^-]$. The reaction is accelerated by decreasing water content in the solvent, an 85-fold increase in k_2 occurring over the range 0–0.800 mole fraction of dimethyl sulfoxide. In 0.500 mole fraction of dimethyl sulfoxide, $\Delta H_1^{\ddagger} = 21.1 \pm 0.5$ kcal/mole, $\Delta S_1^{\ddagger} = -8 \pm 2$ eu, and in 0.525 mole fraction of dimethyl sulfoxide, $\Delta H_2^{\ddagger} = 16.6 \pm 1.1$ kcal/mole, $\Delta S_2^{\ddagger} = -11 \pm 4$ eu. The mechanism proposed for the reaction involves a simple displacement of hydroxide ion on sulfur. The influence of other added bases suggests that the hydrolysis is sensitive to the presence of hard bases but is unaffected by polarizable bases.

Introduction

As a part of our investigation of solvent effects on inorganic nucleophilic displacement reactions,[1] we report here a kinetic study of the hydrolysis of trimethylamine sulfur trioxide.[2]

$$(CH_3)_3NSO_3 + H_2O \longrightarrow (CH_3)_3NH^+ + HSO_4^- \quad (1)$$

$$(CH_3)_3NSO_3 + 2OH^- \longrightarrow (CH_3)_3N + H_2O + SO_4^{2-} \quad (2)$$

The hydrolysis is accelerated by bases but is unaffected by acids. The reaction has been described previously in aqueous solution[3,4] and was of interest to us because it presumably involves the simple attack of hydroxide on sulfur. The present studies have been carried out in dimethyl sulfoxide (DMSO)–water solvent mixtures. This system allows a continuous change from the polar, hydrogen-bond character of water to the solvent characteristics of polar aprotic DMSO. Hard-base nucleophiles may be expected to become highly reactive in aprotic solvents owing to lack of hydrogen-bond stabilization.[5] The trimethylamine sulfur trioxide system appears to be a useful one for examining such kinetic solvation effects.

Experimental Section

Solvent.—Commercial grade DMSO (Van Waters and Rogers) was purified by slowly heating a mixture containing 1.0 g of potassium hydroxide/l. of DMSO up to 125° over a period of 1 hr. The resulting yellow solution was distilled at approximately 72° (10 mm) through a 16-in. column packed with glass helices, the center 70% being retained for use. Solvent mixtures were prepared on a weight basis by slow addition of distilled water to a partially frozen quantity of DMSO.

Reagents.—Trimethylamine sulfur trioxide was prepared by the method of Baumgarten.[6] Pyridine sulfur trioxide was synthesized by dropwise addition of practial grade chlorosulfonic acid to reagent grade pyridine in chloroform. Addition of the pyridine sulfur trioxide to an equivalent amount of reagent grade 10% aqueous trimethylamine resulted in the precipitation of trimethylamine sulfur trioxide. The crude product was recrystallized from water (55°) and then vacuum dried over phosphorus pentoxide. The melting point (240°) and ir spectrum agree closely with previous reports.[2,6] *Anal.* Calcd for $C_3H_9NO_3S$: C, 25.9; H, 6.52. Found: C, 25.7; H, 6.35.

Eastman 10% aqueous tetraethylammonium hydroxide solutions variously contained about 0.03 M CO_3^{2-} (Winkler titration). Addition of reagent grade barium hydroxide in amounts equal to 80% of theoretical values resulted in precipitation of barium carbonate which was filtered off. The resulting solutions, which contained less then 0.01 M CO_3^{2-}, were stored under nitrogen. Tetraethylammonium perchlorate was precipitated from aqueous solutions of sodium perchlorate and tetraethylammonium bromide, followed by recrystallization from water and drying over phosphorus pentoxide. Solutions of tetraethylammonium sulfate were prepared by neutralizing tetraethylammonium hydroxide with sulfuric acid directly in DMSO–water solvents of appropriate composition. All potassium salts, tetraethylammonium chloride, triphenylphosphine, and dimethyl sulfide were reagent grade and were used as received.

Kinetic Measurements.—The reaction was followed over 2–3 half-lives by analyzing aliquots for acid produced in the case of the neutral reaction or for base consumed in the case of the hydroxide reaction. Samples (5–20 ml) were quenched by tenfold dilution in 10° water or in 10° solutions of standard 0.05 M HCl in the case of the hydroxide reaction. The acid present was titrated with 0.05 M NaOH using a Heath Model EUW-301 pH recording electrometer and a Beckman No. 39004 glass electrode which was stored in 10% aqueous DMSO when not in use. In a typical hydroxide run, tetraethylammonium perchlorate and trimethylamine sulfur trioxide were dissolved in the appropriate solvent and thermostated for a short time. DMSO and a calculated amount of water were added to the aqueous tetraethylammonium hydroxide in a 100-ml volumetric flask. After the reactants had equilibrated in a water bath, they were quickly mixed, initiating the hydroxide reaction. Samples were taken by rapid pipetting, a process which resulted in somewhat lower accuracy for reactions in 0.7 and 0.8 mole fractions of DMSO where half-lives were on the order of 500 sec. In runs without added hydroxide, trimethylamine sulfur trioxide was dissolved as quickly as possible in a thermostated tetraethylammonium perchlorate solution. Although reaction begins before solution is complete, the time required for complete solution was less than 2% of the half-life. Ionic strength was maintained in all runs, using tetraethylammonium perchlorate.

The stoichiometry of the neutral reaction was verified by the close agreement (±2%) between observed and calculated amounts of acid produced in the various mole fractions. The

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[1] J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966).

[2] A complete structural analysis of this crystalline adduct has not been reported. However, X-ray and ir data indicate that a normal N–S bond does exist in the molecule and that there is near tetrahedral symmetry around both the nitrogen and the sulfur: H. Z. Lecher and W. B. Hardy, *J. Am. Chem. Soc.*, **70**, 3789 (1948); F. Watari, *Z. Anorg. Allgem. Chem.*, **332**, 322 (1964).

[3] B. E. Fleischfresser and I. Lauder, *Australian J. Chem.*, **15**, 251 (1962).

[4] L. P. Bogdanova and I. G. Ryss, *Kinetika i Kataliz*, **7**, 169 (1966); *Chem. Abstr.*, **64**, 19343*a*, (1966).

[5] A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

[6] P. Baumgarten, *Chem. Ber.*, **59**, 1976 (1926).

stoichiometry of the hydroxide reaction was checked in water and in 85.0% DMSO. The *net* number of moles of base consumed was determined by titration of diluted reaction mixtures which had been allowed to react for at least 10 half-lives. Moles of sulfate produced were determined by a nephelometric procedure[7] using a Turner Model 110 fluorometer. Values obtained for the ratio of moles of base consumed per mole of sulfate produced were 1.00 in water and 1.02 and 1.00 in 85.0% DMSO, in good agreement with eq 1 and 2.

Results

(A) Neutral Reaction.—The neutral hydrolysis obeys a pseudo-first-order rate law, $-d[(CH_3)_3NSO_3]/dt = k_1[(CH_3)_3NSO_3]$, over the entire solvent range from 0 to 0.98 mole fraction of DMSO. Plots of log $(V_\infty - V_t)$ *vs.* time were linear over 2–3 half-lives (V refers to the volume of titrant base required to react with HSO_4^- in each sample). V_∞ values were obtained after at least 10 half-lives, except in water and in 0.300 mole fraction of DMSO where, because of the very long half-lives involved, calculated values of V_∞ were used. Previous reports[3,4] agree with the present study concerning the first-order nature of the reaction, although a meaningful comparison of the rate constants in water is not possible because of the considerably higher temperatures involved in the earlier work. The values reported in Table I show a marked increase with increasing mole fraction of DMSO.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE NEUTRAL HYDROLYSIS OF TRIMETHYLAMINE SULFUR TRIOXIDE AT 25.1° AND 0.150 M IONIC STRENGTH

Mole fraction of DMSO	$10^2[(CH_3)_3NSO_3]_0$, M	10^5k_1, sec^{-1}
0	1.00	0.03^a
0.300	2.00	0.73
0.500	2.00	3.9
0.500	4.00	4.2
0.500	2.00	0.155^b
0.500	2.00	13.5^c
0.700	2.00	11.4
0.800	2.00	16.2
0.950	2.00	24
0.980	2.00	24

^{a} Upper limit. ^{b} At 0.0°. ^{c} At 34.6°.

The temperature dependence of the first-order rate constant was evaluated in 0.500 mole fraction of DMSO. Values obtained were $\Delta H_1^{\ddagger} = 21.1 \pm 0.5$ kcal/mole and $\Delta S_1^{\ddagger} = -8 \pm 2$ eu. These values may be compared with literature values in aqueous solution of $\Delta H_1^{\ddagger} = 23.1$ kcal/mole, $\Delta S_1^{\ddagger} = -22$ eu[4] and $\Delta H_1^{\ddagger} = 24.2$ kcal/mole, $\Delta S_1^{\ddagger} = -19$ eu.[3]

As pointed out in the Introduction, hydroxide ion hydrolyzes trimethylamine sulfur trioxide more rapidly than does water (part B). A number of other Lewis bases were introduced into the neutral system as potential catalysts for the hydrolysis. The results shown in Table II indicate that the soft bases dimethyl sulfide, triphenylphosphine, and bromide ion have no effect on the first-order rate constant, within experimental error. The polarizable thiophenoxide anion also failed to react with trimethylamine sulfur trioxide. In a separate experiment in 50.0 wt % methanol–water, the absorption at 260 mμ of a 6.0×10^{-5} M solution of $C_6H_5S^-$ was unchanged in the presence of trimethylamine sulfur trioxide. Chloride ion and sulfate ion (a potential autocatalyst) also were without effect on the reaction. Fluoride ion decreased the rate of production of HSO_4^-, presumably through rapid formation of the fluorosulfonate ion, as postulated by Fleischfresser and Lauder.[3] In agreement with this proposal we have found that FSO_3^- is hydrolyzed extremely slowly in 0.500 mole fraction of DMSO, even in the presence of hydroxide ion at 60°. The hard bases acetate ion and trimethylamine produce a modest acceleration. Because of the method of following the reaction, it is not feasible to make the necessary buffer studies which would have indicated whether these species act as attacking nucleophiles or merely generate small concentrations of hydroxide ion.

TABLE II

EFFECT OF ADDED BASES ON THE NEUTRAL HYDROLYSIS OF TRIMETHYLAMINE SULFUR TRIOXIDE IN 0.700 MOLE FRACTION OF DMSO AT 25.1° AND 0.150 M IONIC STRENGTH

$10^2[(CH_3)_3$-$NSO_3]_0$, M	Added base	$10^2[\text{base}]_0$, M	10^5k_1, sec^{-1}
2.00			11.4
5.00	$(CH_3)_2S$	5.00	12.4
2.00	$(C_6H_5)_3P$	2.00	11.6
10.0	Br^- (K^+)	1.00	11.3
30.0	Cl^- ($(C_2H_5)_4N^+$)	30.0	10.8
10.0	$C_2H_3O_2^-$ (K^+)	0	10.7^a
10.0	$C_2H_3O_2^-$ (K^+)	5.00	12.2^a
10.0	$C_2H_3O_2^-$ (K^+)	10.0	15.6^a
2.00	$(CH_3)_3N$	1.90	11.3
2.00	$(CH_3)_3N$	2.00	11.9
2.00	$(CH_3)_3N$	3.81	10.7
5.00	$(C_2H_5)_3N$	7.5	14.0
3.00	F^- (K^+)	3.00	3.3^b
4.00	SO_4^{2-} ($(C_2H_5)_4N^+$)	4.00	4.2^b

^{a} These runs contained 0.150 M K^+ in place of $(C_2H_5)_4N^+$. ^{b} These values were obtained in 0.500 mole fraction of DMSO and should be compared with an average $k_1 = 4.0 \times 10^{-5}$ sec^{-1}.

(B) Hydroxide Reaction.—When hydroxide ion is added to aqueous solutions of trimethylamine sulfur trioxide, another pathway for hydrolysis is introduced which is first order in hydroxide ion. Rate data have been correlated with the rate law

$$-d[(CH_3)_3NSO_3]/dt = k_1[(CH_3)_3NSO_3] + k_2[(CH_3)_3NSO_3][OH^-] \quad (3)$$

The integrated form of this rate law is

$$(b - 2a)k_2t = \ln\left[\left(\frac{a}{a - x}\right)\left(\frac{k_1 + k_2(b - 2x)}{k_1 + bk_2}\right)\right] - k_1t \quad (4)$$

where a and b denote initial concentrations of $(CH_3)_3$-NSO_3 and OH^-, respectively, and x is the decrease in concentration of $(CH_3)_3NSO_3$ after time t. In practice it was found that 95% or more of the hydrolysis proceeds *via* the second path under the conditions of this study. The k_1 term is nearly negligible, and, indeed, plots of ln $[(b - 2x)/(a - x)]$ *vs.* time are nearly linear.

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(7) G. W. Ewing, "Instrumental Methods of Chemical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 410.

An iterative computer program was used to obtain best fit values of k_2. Trial values of k_2 were taken from the slopes of the second-order plots as indicated above. For each (x, t) pair in a run, values of a, b, x, t, k_1, and the trial k_2 were substituted into the right-hand side of eq 4, thereby allowing calculation of an improved k_2 value. The k_1 input was simply the first-order constant obtained in the corresponding solvent in the absence of hydroxide.

Table III contains k_2 values for individual runs in the various solvent mixtures as well as the average value for each solvent. As in the case of the k_1 values, there is a rather large increase in k_2 on going from water to 0.800 mole fraction of DMSO. It should be noted that, within experimental uncertainty, the k_2 values are independent of $[(CH_3)_3NSO_3]_0$ in the range 0.01–0.05 M and independent of $[OH^-]_0$ in the range 0.03–0.10 M.

TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE BASIC HYDROLYSIS OF TRIMETHYLAMINE SULFUR TRIOXIDE IN DMSO–WATER SOLVENTS

Mole fraction of DMSO	$10^2[(CH_3)_3NSO_3]_0$, M	$10^2[OH^-]_0$, M	10^2k_2,[a] M^{-1} sec^{-1}
0	1.00	5.00	0.20 ± 0.02 Av of 5 runs
0.311	2.00	5.00– 10.0	0.48 ± 0.04 Av of 6 runs
0.311	2.00	4.95	0.91 $[Na^+] = 0.050$ M
0.311	2.00	5.00	1.2 $[Na^+] = 0.150$ M
0.325	2.00	5.00	0.53
0.325	2.00	4.93	0.93 $[(CH_3)_3N] = 0.020$ M
0.325	2.00	4.93	1.7 $[(CH_3)_3N] = 0.088$ M
0.325	2.00	4.93	1.5 $[(CH_3)_3N] = 0.100$ M
0.511	1.00– 5.00	3.00– 10.0	2.2 ± 0.2 Av of 10 runs
0.511	2.00	4.97	2.4 $[Ba^{2+}] = 0.00050$ M
0.511	2.00	5.00	2.6 $[Ba^{2+}] = 0.0030$ M
0.525	2.00	5.00	0.13 (0.0°)
0.525	2.00	5.00	0.57 (12.1°)
0.525	2.00	5.00	3.0 (29.7°)
0.525	2.00	5.00	4.7 (34.6°)
0.700	2.00	3.00– 5.00	8.7 ± 0.8 Av of 5 runs
0.800	1.50– 3.43	4.00	17 ± 2 Av of 2 runs

[a] Except as noted in the table, these values were obtained at 25.1° and at an ionic strength of 0.150 M with $(C_2H_5)_4N^+$ as the only cation present.

Except as noted in Table III, $(C_2H_5)_4N^+$ was the only cation present in the reaction mixture. There is no change in rate with a change in ionic strength from 0.05 to 0.30 M. Addition of Na^+ causes a distinct increase in rate and Ba^{2+} also appears to accelerate hydrolysis. Since it is unlikely that ion pairing with hydroxide increases the rate, this acceleration probably arises through a secondary interaction of the cation with the oxygen atoms of trimethylamine sulfur trioxide.

The temperature dependence of k_2 was evaluated in 0.525 mole fraction of DMSO. Values obtained were $\Delta H_2^{\ddagger} = 16.6 \pm 1.1$ kcal/mole and $\Delta S_2^{\ddagger} = -11 \pm 4$ eu. Values of $\Delta H_2^{\ddagger} = 17.7$ kcal/mole and $\Delta S_2^{\ddagger} = -11$ eu have been reported recently for aqueous solution.[4]

Discussion

In a general way, reactions 1 and 2 may be described by a limiting SN1 dissociative process, an SN2 process, or a blend of these two, depending on the degree of bond making in the transition state. The observed rate law is consistent with an SN2 step and, with certain restrictions, would result from a dissociative process, also. As discussed below, the SN2 process is preferred. A dissociative mechanism cannot be ruled out in neutral solution. However, in the basic solutions, the dissociative mechanism would require an inverse dependence on the concentrations of added trimethylamine and of hydroxide ion. The data in 0.511 mole fraction of DMSO (Table III) show that within an experimental uncertainty of ±10%, the observed second-order constant is independent of the initial concentration of hydroxide. Data in 0.325 mole fraction of DMSO indicate an increase, rather than a decrease, in the second-order constant in the presence of added trimethylamine. Prior dissociation of $(CH_3)_3NSO_3$, therefore, does not constitute an important path for basic hydrolysis in these solvents.

The SN2 description is further supported by the rather negative entropies of activation observed, $\Delta S_1^{\ddagger} = -8$ eu and $\Delta S_2^{\ddagger} = -11$ eu. $\Delta S^{\ddagger}$ values in the range -5 to -25 eu are usually associated with A2 mechanisms in aqueous solution.[8] In 0.51 mole fraction of DMSO, Tommila and Murto[9] reported $\Delta S_2^{\ddagger} = -21$ eu for the basic hydrolysis of ethyl acetate, an SN2 process. For the particular case of nitrogen–sulfur bond cleavage, Wilkins and Candlin[10] found positive activation entropies for several aqueous hydroxylamine sulfonate hydrolyses, processes which have A1 characteristics. $\Delta S^{\ddagger} = 1$ eu for the hydrolysis of sulfamic acid, $H_3N^+SO_3^-$, which is closely related to $(CH_3)_3NSO_3$.[11] Although the $\Delta S^{\ddagger}$ values obtained in this study do not demand an SN2 description for $(CH_3)_3NSO_3$, they clearly indicate that its hydrolysis involves considerably more bond making than the hydrolysis reactions referred to above.

The neutral hydrolysis is accelerated by a factor of 22 on going from 0.300 to 0.800 mole fraction of DMSO. The 0–0.800 mole fraction range involves an acceleration greater than 500-fold. Similar though smaller increases have been reported in acetone–water.[3] The reorganization of the solvent structure and the increased basicity of water in the presence of DMSO contribute to this acceleration. Hydrogen-bond interaction with DMSO should increase the nucleophilicity of oxygen in a water molecule, $(CH_3)_2SO\cdots{}^{\delta+}H^{\delta-}OH$.

The basic hydrolysis also shows a very significant increase in rate as the water content of the solvent decreases (Table III). The acceleration is somewhat larger than that observed for several ester hydrolyses,[9,12] although it is considerably smaller than that expected for a reaction of hydroxide ion in DMSO.[5] Within the

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(8) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 1 (1963).
(9) E. Tommila and M. Murto, *Acta Chem. Scand.*, **17**, 1947 (1963).
(10) J. P. Candlin and R. G. Wilkins, *J. Am. Chem. Soc.*, **87**, 1490 (1965).
(11) J. P. Candlin and R. G. Wilkins, *J. Chem. Soc.*, 4236 (1960).
(12) D. D. Roberts, *J. Org. Chem.*, **30**, 3516 (1965).

framework of an SN2 description lie two kinetically indistinguishable processes. The incoming nucleophile may either attack $(CH_3)_3NSO_3$ directly or act as a general base in the sense that it diffuses to the solvent shell of the adduct and converts a molecule of water to a hydroxide ion which then reacts with $(CH_3)_3NSO_3$. For example, the modest acceleration noted for acetate ion (Table II) may arise from hydrolysis to form OH^- or from direct attack to give $CH_3CO{-}OSO_3^-$, an intermediate which would rapidly hydrolyze to the final products. There is reason for preferring the direct attack, in addition to the fact that it is conceptually simpler. Fluoride ion decreases the rate of production of HSO_4^-,[3] a behavior which almost certainly arises from rapid and direct attack of fluoride on sulfur to give FSO_3^-, which in turn hydrolyzes slowly. In a related reaction in aqueous solution, the hydrolysis of *p*-nitrophenylsulfate ion, amine adducts of the type R_2NSO_3 have been identified as intermediates.[13] These intermediates arise from direct attack on sulfur of added secondary amine.

Assuming that direct attack occurs, the solvent acceleration is consistent with an increase in hydroxide ion reactivity as hydrogen-bonding water molecules are withdrawn from the solvent mixture. However, a consideration of the hydroxide solvation alone leads one to expect an acceleration much greater than that observed. In the assumed transition state $HO^{\delta-}\cdots{}^{\delta+}SO_3\cdots{}^{\delta-}N(CH_3)_3$ dispersal of the high negative charge density on hydroxide ion is accompanied by partial formation of the hard base, trimethylamine.[14] Even though the extended charge structure of the activated complex should be stabilized by DMSO molecules, it is evident that considerable hard-base character remains in the activated complex. Thus, acceleration arising from loss of hydrogen bonding in the ground state will be partially compensated by a corresponding, though smaller, loss of solvation in the transition state.[15]

Although the direction and magnitude of the solvent effect are consistent with the proposal of hard-base destabilization in aprotic solvents, the dielectric effect of the medium is also significant. The observed second-order rate constants appear to correlate well with the change in dielectric constant in the solvent range 0–0.800 mole fraction of DMSO, Figure 1. However, the increase in rate is too large to be explained entirely by a dielectric effect. Negative values of the activated complex radius, $r_\ddagger$, are obtained using the approximate relation[16]

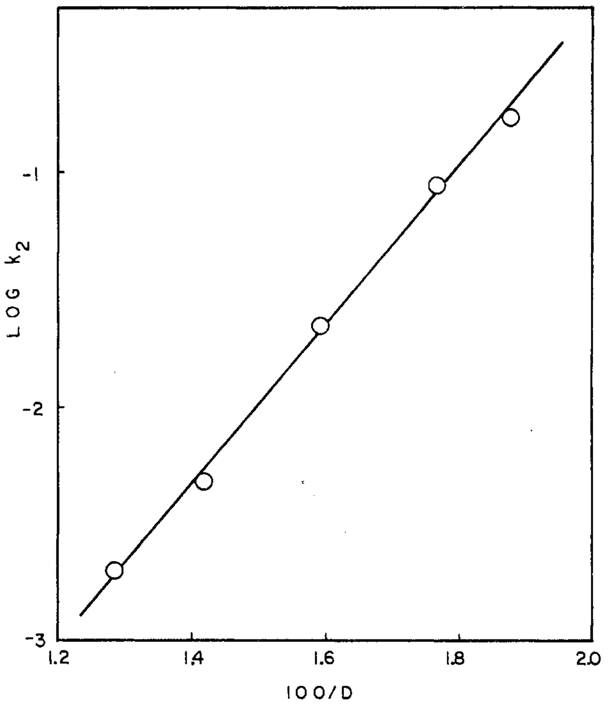

Figure 1.—The effect of dielectric constant on the second-order rate constant.

$$\log k = \frac{z_A^2 e^2}{2kT}\left(\frac{1}{r_A} - \frac{1}{r_\ddagger}\right)\left(\frac{1}{D}\right) + \text{constant} \qquad (5)$$

Similar results have been obtained for the hydrolysis of ethyl acetate in DMSO–water mixtures.[9]

The data in Table II indicate that sulfur in $(CH_3)_3NSO_3$ is susceptible to attack by hard-base nucleophiles only. Although fluoride apparently reacts with the adduct, the more polarizable chloride and bromide ions have no effect. In addition, the soft bases dimethyl sulfide and triphenylphosphine do not accelerate the neutral hydrolysis reaction. This behavior is consistent with the rather high charge density (hard-acid character) of the sulfur in $(CH_3)_3NSO_3$.[17,18]

Acknowledgment.—We are grateful to the National Science Foundation for support of this work under Grant No. GP-2968.

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[13] S. J. Benkovic and P. A. Benkovic, *J. Am. Chem. Soc.*, **88**, 5504 (1966).

[14] Apparently, the basicity of amines in DMSO is comparable to that in water: I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, **1**, 189 (1962).

[15] Similar behavior has been noted in displacement reactions at carbon; see, for example, B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *J. Chem. Soc., Sect. B*, 152 (1966).

[16] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 439.

[17] J. F. Bunnett in "Annual Review of Physical Chemistry," Vol. 13, H. Eyring, C. J. Christensen, and H. S. Johnston, Ed., Annual Reviews Inc., Palo Alto, Calif., 1963, p 271.

[18] J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).