2.00 Å[11]). The longer metal-oxygen distance reflects the decreasing effect of the charge on the metal implied by the ionization potentials. Holah and Fackler[12] have suggested that coordination about the copper atom in $CuCl_2 \cdot 2DMSO$ is octahedral in the solid on the basis of reflectance spectra and X-ray powder data. The unusual ionization potentials might suggest polymerization involving the sulfoxide, but probably reflect the long Cu-O bonds expected for Jahn-Teller distortions in octahedral copper complexes.[13]

We believe the analysis of relative shifts in ionization potential provides a viable method for distinguishing the mode of binding in ambidentate sulfoxides. The great advantage of the ESCA method lies in its theoretical simplicity and absence of ambiguity in peak assignments found with infrared spectra. We anticipate that this method will be widely applicable in the determination of binding mode with other ambidentate ligands.

Experimental Section

All of the compounds were prepared as described in the references indicated in Table I, with the exception of $ZnCl_2 \cdot 2DBSO$ and $SnCl_2 \cdot 2DBSO$, which were prepared in the same manner as the DPSO analogs. Peak ratios of Cl 2p to S 2p IP's were measured in most compounds to confirm their stoichiometry. A Perkin-Elmer 421 infrared spectrophotometer was used to record and check the ir spectra for the compounds to ensure their identity and purity.

The ionization potentials (IP's) were recorded using a Hewlett-Packard 5950A ESCA spectrometer equipped with a monochromatized aluminum X-ray source, a variable-temperature probe, and an electron flood gun. Methylene chloride solutions of the compound were sprayed onto a gold-plated sample holder evaporated to leave a thin layer. The IP values were generally recorded at room temperature and calibrated relative to the Au $4f_{7/2}$ of the sample holder assumed to be at 83.0 eV.[14] The spectrometer is capable of a precision and reproducibility of ±0.01 eV. The use of relative shifts avoids the problems with uncertainties in absolute accuracy (±0.1 eV). Full widths at half-height were between 1.1 and 1.4 eV for S $2p_{3/2}$ and between 1.3 and 1.6 eV for O 1s. All IP's were determined with at least two separate samples. Those showing unusual features were checked with at least four samples. Certain volatile compounds as indicated in Table I were maintained at temperatures below $-100°$ during the recording of the spectra. The flood gun, which compensates for the charging of the sample by neutralizing the charge with a stream of electrons, was operated between 0.1 and 0.3 mA. In most cases the IP's shifted less than 0.2 eV to smaller values when applying the flood gun. The relative shifts from atoms in the same molecule did not change.

Although the approximate separation was evident in the spectrum of $Pd(DMSO)_4(BF_4)_2$, accurate IP's were obtained by deconvolution of the two S $2p_{3/2}$ and two S $2p_{1/2}$ peaks using the program CATACALE and a PDP-12 computer.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We also wish to acknowledge the National Science Foundation for providing a portion of the funds for the purchase of the ESCA spectrometer and the PDP-12.

Registry No. $NiCl_2 \cdot 3DMSO$, 15274-31-4; $CoCl_2 \cdot 3DMSO$, 15274-30-3; $MnCl_2 \cdot 3DMSO$, 51212-01-2; $ZnCl_2 \cdot 2DMSO$, 51194-77-5; $CuCl_2 \cdot 2DMSO$, 14215-41-9; $CdCl_2 \cdot DMSO$, 51194-78-6; $HgCl_2 \cdot DMSO$, 28131-34-2; $SnCl_2 \cdot 2DMSO$, 16674-55-8; $PtCl_2 \cdot 2DMSO$, 15274-33-6; $Pd(DMSO)_4(BF_4)_2$, 51261-62-2; $PdCl_2 \cdot 2DMSO$, 15274-32-5; $AlCl_3 \cdot 6DMSO$, 27385-70-2; $FeCl_3 \cdot 2DMSO$, 51194-49-1; $RhCl_3 \cdot 3DMSO$, 51194-50-4; $SnCl_4 \cdot 2DMSO$, 19979-07-8; $Sn(CH_3)_2Cl_2 \cdot 2DMSO$, 51261-63-3; DMSO, 67-68-5; $Sn(CH_3)_2Cl_2 \cdot DBSO$, 22638-29-5; $ZnCl_2 \cdot 2DBSO$, 51194-51-5; $SnCl_2 \cdot 2DBSO$, 51194-52-6; $PtCl_2 \cdot 2DBSO$, 51261-64-4; $Pd_2Cl_4(DBSO)_2$, 23723-97-9; DBSO, 621-08-9; $SnCl_2 \cdot 2DPSO$, 16674-56-9; $ZnCl_2 \cdot 2DPSO$, 16569-81-6; $CdCl_2 \cdot DPSO$; 51194-53-7; $HgCl_2 \cdot DPSO$, 51194-54-8; $PdCl_2 \cdot 2DPSO$, 16569-80-5; DPSO, 945-51-7.

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[11] M. J. Bennett, F. A. Cotton, and D. L. Weaver, *Acta Crystallogr.*, 23, 581 (1967).

[12] D. G. Holah and J. P. Fackler, Jr., *Inorg. Chem.*, 4, 1721 (1965).

[13] We are currently pursuing the possibility that "long" bonds may be conveniently characterized by analysis of ESCA spectra.

[14] A value of 82.8 eV has been used by some workers based upon the studies of J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.*, 125 (1967).

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Nucleophilic Substitution on Nitrogen. Kinetics of Reactions of Hydroxylamine-*O*-sulfonic Acid in Dimethyl Sulfoxide-Water Solvents

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The kinetics of reactions of iodide and triphenylphosphine with hydroxylamine-*O*-sulfonic acid have been examined in dimethyl sulfoxide-water solvents. The reactions involve nucleophilic substitution on nitrogen with sulfate as the leaving group. For triphenylphosphine, rate = $k_2[H_2NOSO_3^-][(C_6H_5)_3P]$ and for iodide, rate = $k_{OS}[H_2NOSO_3^-][I^-] + k_{HOS} \cdot [H_3NOSO_3][I^-]$, with the observed second-order rate constants decreasing markedly on going from 0 to 1.00 mole fraction of dimethyl sulfoxide in the solvent. This solvent effect on rate suggests that, for reaction of H_3NOSO_3, protonation occurs on nitrogen, with SO_4^{2-} rather than HSO_4^- as the leaving group. In 0.96 mole fraction of dimethyl sulfoxide, the reaction of H_3NOSO_3 with iodide is accelerated by added perchloric acid. The iodide dependence of the hydrogen ion dependent pathway is interpreted in terms of a dissociative process, involving either NH_3^{2+} or an NH_3^{2+},OSO_3H^- ion pair as an intermediate, which occurs in competition with direct attack on $H_3NOSO_3H^+$.

Introduction

As part of a study of nucleophilic substitution at trivalent nitrogen, we have reported the kinetics of reactions of a variety of soft-base nucleophiles with hydroxylamine-*O*-sulfonate ion, $H_2NOSO_3^-$, in water.[2,3] These reactions are thought to proceed by direct attack on the nitrogen center

$$Nu + H_2NOSO_3^- \rightarrow [Nu\cdots\ddot{N}H_2^{\delta+}\cdots OSO_3^{(1+\delta)-}]^{\ddagger} \rightarrow NuNH_2^+ + SO_4^{2-} \qquad (1)$$

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[1] NDEA Fellow 1971-1973.

[2] J. H. Krueger, P. F. Blanchet, A. P. Lee, and B. A. Sudbury, *Inorg. Chem.*, 12, 2714 (1973).

[3] P. F. Blanchet and J. H. Krueger, *Inorg. Chem.*, 13, 719 (1974).

with sulfate as the leaving group. In water, protonation of $H_2NOSO_3^-$ results in a moderate decrease in reactivity.[2,3] Although it is generally assumed that protonation occurs primarily on nitrogen,[4] there is no direct evidence to support the existence of $H_3N^+OSO_3^-$ in solution as opposed to H_2NOSO_3H.[5] In the latter case HSO_4^-, rather than the SO_4^{2-}, would be the leaving group in (1).

In this paper we report the kinetics of reactions of triphenylphosphine and iodide ion with hydroxylamine-*O*-sulfonic acid in dimethyl sulfoxide (DMSO) and DMSO-water solvents. Because of the profound difference in the abilities of DMSO and water to solvate a hard-base anion like SO_4^{2-},[6-8] it appeared likely that the influence of solvent on the rates of these reactions would provide a useful means of establishing whether SO_4^{2-} or HSO_4^- was the leaving group involved.

Experimental Section

Solvents and Reagents. Solvent mixtures were prepared from redistilled water and dimethyl sulfoxide as described earlier.[9] The DMSO (VWR Scientific), which was doubly distilled at 10 Torr under N_2, had a water content of *ca.* 0.08 wt % by Karl Fischer titration.

Reagent grade perchloric acid (Mallinckrodt, 70%) was diluted with water to 1-6 *M* before use. *Caution*! Because explosions have been reported on addition of concentrated $HClO_4$ to neat DMSO,[10] partially diluted $HClO_4$ was added slowly to DMSO, with cooling. The water contained in the $HClO_4$ was taken into account in calculating solvent composition.

After drying at 110°, reagent grade potassium salts were used as received. $KClO_4$ was used to maintain ionic strength. When required, neutralization of H_3NOSO_3 in DMSO was effected by addition of one of the bases: potassium acetate, triethylamine, sodium carbonate, or sodium methoxide. Triphenylphosphine was recrystallized twice from cyclohexane (mp 81°).

Hydroxylamine-*O*-sulfonic acid was prepared and analyzed as described previously.[2] The purity of samples used in the kinetic runs was ⩾96%. $(C_6H_5)_3PNH_2^+ClO_4^-$ was prepared by reaction of triphenylphosphine with hydroxylamine-*O*-sulfonate ion in methanol-water,[2,11] followed by precipitation with aqueous $NaClO_4$. The product was recrystallized from methanol-water, washed with ether, and dried *in vacuo* over phosphorus pentoxide; mp 177-179°.[12]

Measurements. The kinetics were measured using a Cary Model 16K spectrophotometer as described previously.[2] Conductivity studies were carried out using an Industrial Instruments Model RC-16B2 conductivity bridge.

Results

Triphenylphosphine-Hydroxylamine-*O*-sulfonate Reaction. The reaction proceeds according to

$$(C_6H_5)_3P + H_2NOSO_3^- \rightarrow (C_6H_5)_3PNH_2^+ + SO_4^{2-} \qquad (2)$$

as evidenced by the isolation and identification of the aminotriphenylphosphonium ion as the perchlorate. In the kinetic runs followed to completion, the spectrum of the solution below 300 nm was identical with that of a known solution containing $(C_6H_5)_3PNH_2^+$ and the calculated value of ϵ_{267} agreed (±2%) with ϵ_{267} for $(C_6H_5)_3PNH_2^+$.

The reaction was followed by the decrease in absorbance at either 263 or 290 nm, using the method of initial rates. Potassium acetate or sodium methoxide was added to convert H_3NOSO_3 to $H_2NOSO_3^-$. The presence of up to a twofold excess of base had no effect on the rate. In the absence of added base there was no significant reaction between $(C_6H_5)_3P$ and H_3NOSO_3, probably due to protonation of the triphenylphosphine. The results in Table I lead to the rate law $-d[(C_6H_5)_3P]/dt = k_2[(C_6H_5)_3P][H_2NOSO_3^-]$, identical with the form observed in methanol-water solvents.[2] The second-order rate constant decreased markedly with increasing mole fraction of DMSO (Figure 1).

In 0.67 mole fraction of DMSO at 10.2°, $k_2 = (3.40 \pm 0.05) \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$, at 20.3°, $k_2 = (6.6 \pm 0.1) \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$, and at 29.7°, $k_2 = (12.8 \pm 0.3) \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$. Values of $\Delta H^{\ddagger} = 11.1 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -31 \pm 1$ eu were calculated from $k_2 = (kT/h) \exp(-\Delta H^{\ddagger}/RT) \exp(\Delta S^{\ddagger}/R)$. In the highly protic solvent 50 wt % methanol-water, $\Delta H^{\ddagger} = 7.4$ kcal/mol and $\Delta S^{\ddagger} = -32$ eu for reaction 2.[2] Thus, the decrease in rate on going to 0.7 mole fraction DMSO-water solvent arises entirely from an increase in activation enthalpy.

Reaction of I^- with $H_2NOSO_3^-$. The stoichiometry and kinetics of reaction 3 have been reported in water.[2] In the

$$H_2NOSO_3^- + 2H^+ + 3I^- \rightarrow I_3^- + HSO_4^- + NH_3 \qquad (3)$$

present study an initial-rate method (0.5-2% of reaction), utilizing the increase in absorbance at 365 nm, was employed.[13] H_3NOSO_3 was 97% neutralized with added base, the remaining low concentration of H_3NOSO_3 serving as a source of protons in (3) and preventing loss of I_3^- through reaction with base species. The second-order rate constants (k_{OS}) shown in Table II were calculated using the rate law observed for reaction 3 in water $d[I_3^-]/dt = k_{OS}[H_2NOSO_3^-] \cdot [I^-]$. As shown in Figure 1, k_{OS} decreases with decreasing water content of the solvent.

Reaction of I^- with H_3NOSO_3. Reaction 4 was followed

$$H_3NOSO_3 + 2H^+ + 3I^- \rightarrow I_3^- + HSO_4^- + NH_4^+ \qquad (4)$$

as described above. In the presence of added acid, DMSO itself also oxidizes iodide ion (eq 5). Corrections for tri-

$$(CH_3)_2SO + 2H^+ + 3I^- \rightarrow I_3^- + (CH_3)_2S + H_2O \qquad (5)$$

iodide production by DMSO were made either from blank runs (no H_3NOSO_3) or from rate constants reported for reaction 5.[9] Such corrections were less than 10%, except 10-45% for runs involving high hydrogen ion concentrations (Tables III, IV). In DMSO-water molecular H_3NOSO_3, which dissociates to a much smaller extent than in water, reacts more slowly than does $H_2NOSO_3^-$. Thus, in 0.50 and 0.70 mole fraction of DMSO, the rate law for reaction 4 was evaluated by addition of $HClO_4$ sufficient to convert the system completely to the H_3NOSO_3 form, as judged by attainment of a minimum rate (*i.e.*, no contribution from the more rapid $H_2NOSO_3^-$ reaction). The results in Table III were ob-

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(4) (a) K. W. C. Burton and G. Nickless in "Inorganic Sulfur Chemistry," Elsevier, New York, N. Y., 1968, p 644; (b) U. Wannagat and R. Pfeiffenschneider, *Z. Anorg. Allg. Chem.*, **297**, 151 (1958); (c) N. C. Baenziger, R. F. Belt, and C. V. Goebel, *Inorg. Chem.*, **6**, 511 (1967); (d) J. P. Candlin and R. G. Wilkins, *J. Amer. Chem. Soc.*, **87**, 1490 (1965).

(5) The zwitterionic form has been confirmed in the solid and inferred from the single line observed in the ^1H nmr spectrum in dimethylformamide: R. E. Richards and R. W. Yorke, *J. Chem. Soc.*, 2821 (1959).

(6) Anions with a large negative charge density and low polarizability are only poorly solvated by dipolar aprotic solvents in contrast to the extensive solvation they experience in solvents capable of hydrogen bonding. Because of strong intermolecular interactions, DMSO-H_2O mixtures in the range of 0.50-1.00 mole fraction of DMSO also solvate SO_4^{2-} less effectively than does water; *i.e.*, selective solvation of ions by H_2O molecules is not important in DMSO-H_2O mixtures.[7,8]

(7) T. R. Stengle, Y. E. Pan, and C. H. Langford, *J. Amer. Chem. Soc.*, **94**, 9037 (1972).

(8) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(9) J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966).

(10) I. M. Kolthoff and T. B. Reddy, *J. Electrochem. Soc.*, **108**, 980 (1961).

(11) R. Appel, W. Buchner, and E. Guth, *Justus Liebigs Ann. Chem.*, **618**, 53 (1958).

(12) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Amer. Chem. Soc.*, **81**, 2982 (1959).

(13) In 0.5-1.0 mole fraction of DMSO, ϵ is 25,800 $M^{-1}\ \text{cm}^{-1}$ for I_3^- at λ_{max} 365 nm.

Table I. Kinetics of the Triphenylphosphine–Hydroxylamine-*O*-sulfonate Reaction in DMSO–Water Solvents at 20.3° and 0.100 *M* Ionic Strength[a]

Mole fraction of DMSO[b]	$10^3[H_2NOSO_3^-]_0$, *M*	$10^4[(C_6H_5)_3P]_0$, *M*	10^3k_2, M^{-1} sec^{-1}	10^3k_2(av), M^{-1} sec^{-1}
1.00	10.2	2.44	2.28	
1.00	10.3	2.70	1.69	
1.00	13.7	1.83	2.08	2.0 ± 0.3
0.90	10.0	2.62	2.51	
0.90	10.0	2.62	2.36	
0.90	10.0	2.46	2.36	2.4 ± 0.1
0.70	1.99	2.53	5.90	
0.70	9.70	1.26	5.42[c]	
0.70	9.70	1.26	6.10[c,d]	
0.70	9.70	2.53	5.80	5.8 ± 0.3
0.69	9.35	1.23	5.84[c]	
0.69	9.35	2.47	6.03	5.9 ± 0.1
0.50	1.02	2.42	27.8	
0.50	9.75	2.90	27.4	27.6 ± 0.2
0.30	0.20	2.42	206	
0.30	0.40	2.37	238	
0.30	2.01	2.37	238[d]	230 ± 15

[a] Method of initial rates at 263 nm, except as noted. [b] Solvent composition reproducible to within ±0.5%. [c] At 290 nm. [d] Reaction followed to 100% completion.

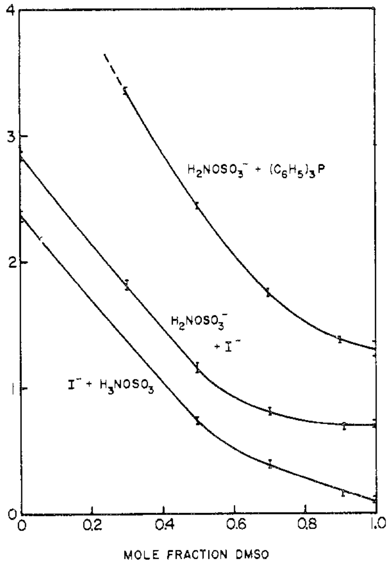

Figure 1. log of second-order rate constants plotted as a function of mole fraction of DMSO for DMSO–H$_2$O solvents. Data in water are from ref 2.

tained using the rate law $d[I_3^-]/dt = k_{HOS}[H_3NOSO_3][I^-]$.[2,14]

In 0.90 and 1.00 mole fraction of DMSO, hydrogen ion added to protonate $H_2NOSO_3^-$ led to an *increase* in rate (*vide infra*). Thus, k_{HOS} was evaluated in these solvents without added HClO$_4$, using the composite rate law (6) in

$$(d[I_3^-]/dt)/(\Sigma[H_3NOSO_3])[I^-] = \alpha k_{OS} + (1 - \alpha)k_{HOS} \quad (6)$$

which α is the fraction dissociation of H_3NOSO_3. Taking values of k_{OS} from Table II and values of α, calculated as described below, the values of k_{HOS} shown in Table III were obtained.

Values of α were obtained from conductance studies (Figure 2) of the neutralization reaction

$$H_3NOSO_3 + (C_2H_5)_3N \rightarrow (C_2H_5)_3NH^+ + H_2NOSO_3^- \quad (7)$$

The equivalent conductances of 1.30 × 10^{-3} *M* $(C_2H_5)_3NH^+$-$H_2NOSO_3^-$ were 34.6 and 32.8 ohm^{-1} cm^2 mol^{-1} in 1.00 and

Table II. Kinetics of the Reaction of $H_2NOSO_3^-$ with I^- in DMSO–H$_2$O Solvents at 20.3° and 0.100 *M* Ionic Strength.

Mole fraction of DMSO	$10^3[I^-]_0$, *M*	$10^3 \times [H_2NOSO_3^-]_0$, *M*		10^4k_{OS}, M^{-1} sec^{-1}
1.00	2.58	10.2		4.6[a]
	6.80	1.43		5.4[a]
	10.2	1.93		5.3[a]
	10.2	1.93		5.4[b]
			Av	5.2 ± 0.3
0.90	0.57	6.80		4.4[a]
	2.45	3.57		5.5[d]
	2.45	7.14		5.7[d]
	2.65	5.35		4.6[d]
	2.65	5.35		4.5[d]
	2.85	6.80		5.2[a]
	4.28	1.02		4.3[a]
			Av	4.9 ± 0.5
0.70	10.0	0.97		6.3[c]
	10.0	1.33		6.4[c]
	10.0	1.39		6.4[c]
			Av	6.4 ± 0.1
0.50	2.20	9.75		12.9[a]
	3.00	2.79		15.2[c]
			Av	14.1 ± 1.2
0.30	2.00	0.93		63[c]
	2.02	0.40		66[c]
	2.02	2.01		71[c]
			Av	66 ± 4

[a] Added base triethylamine. [b] Added base potassium *tert*-butoxide. [c] Added base sodium hydroxide. [d] Added base potassium acetate.

0.90 mole fraction of DMSO, respectively, in good agreement with results for similar univalent electrolytes in DMSO.[15] The nonzero intercept in Figure 2 apparently arises from ionic impurities in the H_3NOSO_3. The extent to which the conductance of the H_3NOSO_3 solution (no triethylamine added) lies above the intercept provides a measure of the fraction of dissociation of H_3NOSO_3. Since the equivalent conductance of $H^+H_2NOSO_3^-$ is essentially equal to that of $(C_2H_5)_3NH^+H_2NOSO_3^-$,[16] α can be estimated from the ratio of specific conductances (55 − 28)/(479 − 28) = 0.060 in 1.00

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(14) The rate constants k_{OS}, k_{HOS}, and k_{HOSH} are defined by the rate terms $k_{OS}[H_2NOSO_3^-][I^-]$, $k_{HOS}[H_3NOSO_3][I^-]$, and $k_{HOSH}[H^+][H_3NOSO_3][I^-]$.

(15) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

(16) In 1.00 and 0.90 mole fraction of DMSO, titration of a solution of the strong electrolyte HClO$_4$ with $(C_2H_5)_3N$ resulted in a less than 5% change in conductance upon full neutralization. Thus, H$^+$ and $(C_2H_5)_3NH^+$ have similar ionic mobilities in these solvents.

Table III. Kinetics of the Reaction of I^- with H_3NOSO_3 in DMSO-H_2O Solvents at 20.3° and 0.100 *M* Ionic Strength

Mole fraction of DMSO	$10^3[I^-]_0$, *M*	$10^3[H_3NOSO_3]_0$, *M*	$10^3[HClO_4]_0$, *M*	10^4k_{HOS}, M^{-1} sec^{-1}
1.00	0.66	3.50		1.16
	0.66	35.0		1.24
	1.29	3.50		1.25
	1.29	3.50		1.28
	2.62	5.40		1.30
				Av 1.25 ± 0.05
0.90	2.85	6.80		1.45
	4.28	10.2		1.45
	10.0	1.97	4.26	1.52
				Av 1.47 ± 0.04
0.70	10.0	0.99	16.7	2.52
	10.0	0.99	33.3	2.51
	10.0	0.99	50.0	2.53
	10.0	4.85	7.3	2.56
	44.8	0.92	11.0	2.44
				Av 2.52 ± 0.05
0.50	1.33	1.86	55.5	4.7
	2.00	2.79	33.3	5.7
	2.20	0.98	100	5.5
				Av 5.4 ± 0.4

Table IV. Iodide Dependence of the Hydrogen Ion Dependent Path[a]

$10^3[I^-]_0$, *M*	10^3k_{HOSH}, M^{-2} sec^{-1}	$10^3[I^-]_0$, *M*	10^3k_{HOSH}, M^{-2} sec^{-1}
0.300	11.6	4.00	6.05
0.400	11.4	5.00	5.67
0.500	10.5	10.0	4.28
1.00	9.56	20.0	3.35
2.00	7.75	30.0	3.17
3.00	6.70	40.0	3.07

[a] 0.96 mole fraction of DMSO at 20.3° and 0.100 *M* ionic strength; $[H_3NOSO_3]_0 = 0.0125$ *M* and $[H^+]_0 = 0.0463$ *M*.

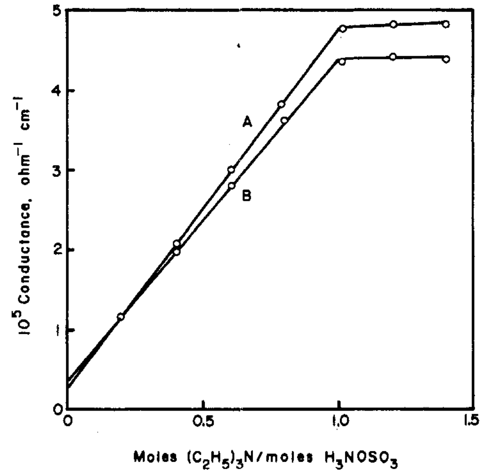

Figure 2. Specific conductance plot for the neutralization of hydroxylamine-*O*-sulfonic acid by triethylamine in (A) 1.00 mole fraction of DMSO and (B) 0.90 mole fraction of DMSO.

mole fraction of DMSO. In 0.90 mole fraction of DMSO α = 0.075. The values of α obtained in this way probably are reliable to ±15%, leading to a maximum error in k_{HOS} of about 3% (eq 6).

Reaction 4 was examined for catalysis by Br^- and Cl^- in 0.70-1.00 mole fraction of DMSO. Neither KBr nor KCl, added in a concentration equal to that of I^- present, increased the rate of (4). Thus, if these anions react at all, an upper limit for their reactivity is approximately 10% of that for I^-. Since Br^- and Cl^- exhibit a high degree of nucleophilicity toward hard-acid centers in DMSO solvents,[8,9,17] the nitrogen center in H_3NOSO_3 probably possesses considerable soft-acid character.

H_3NOSO_3-I^- Reaction in the Presence of Added $HClO_4$. The effect of added hydrogen ion on the rate of reaction 4 was examined in 0.96 mole fraction of DMSO. The dependence of *k*(obsd) on $[H^+]$, as defined by eq 8, is shown in

$$\frac{d[I_3^-]/dt}{[H_3NOSO_3][I^-]} = k(\text{obsd}) = k_{HOS} + k_{HOSH}[H^+] \qquad (8)$$

Figure 3. With $[H_3NOSO_3]_0 = 6.0 \times 10^{-3}$ *M* and $[I^-]_0 = 1.43 \times 10^{-3}$ *M*, $k_{HOSH} = 7.9 \times 10^{-3}$ M^{-2} sec^{-1}. The value of $k_{HOS} = 1.0 \times 10^{-4}$ M^{-1} sec^{-1}, obtained from the intercept in Figure 3, is somewhat lower than values in Table III. The difference probably is not significant in that we experienced a 5-10% variation in reproducibility of runs in the presence of added acid, presumably due to a dependence on the precise water content of these solvent mixtures.

The dependence on H_3NOSO_3 was examined at $[I^-]_0 = 1.50 \times 10^{-3}$ *M* and $[H^+]_0 = 0.0463$ *M*, in which case >70% of reaction occurs *via* the hydrogen ion dependent path. Values of k_{HOSH}, calculated from eq 8, were independent of $[H_3NOSO_3]_0$ over the range (1.25-12.5) × 10^{-3} *M*, confirming the first-order dependence on H_3NOSO_3. Variation of $[I^-]_0$ (Table IV) showed that the hydrogen ion dependent path is not first order in iodide. The detailed dependence of rate on $[I^-]_0$ is described in conjunction with a proposed mechanism (*vide infra*).

Discussion

Solvent Effect on the Leaving Group. The kinetics observed indicate that the mechanisms (eq 1) described in ref 2 may be extended from water to DMSO-H_2O solvent mixtures. The second-order rate constants are rather sensitive to the composition of the solvent (Figure 1). Change in dielectric constant of the medium plays a minor role at best in the decrease in rate constants since (i) plots of log *k* *vs.* ϵ^{-1} are nonlinear, (ii) the decrease in k_{OS} on going from H_2O to 50 wt % MeOH-H_2O (ϵ 56) is only a factor of 2,[2] whereas the decrease in k_{OS} from H_2O to 0.70 mole fraction of DMSO (ϵ 57) is 100-fold, and (iii) the decrease is nearly the same for reactions 2 and 4, which are of different charge type.

A significant feature of Figure 1 is the parallel decrease in rate constants for three different reactions, which we suggest arises because SO_4^{2-}, rather than HSO_4^-, is the leaving group in each case. In DMSO, SO_4^{2-} is solvated to a much smaller

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[17] J. H. Krueger and T. R. Webb, *Inorg. Chem.*, **12**, 1587 (1973).

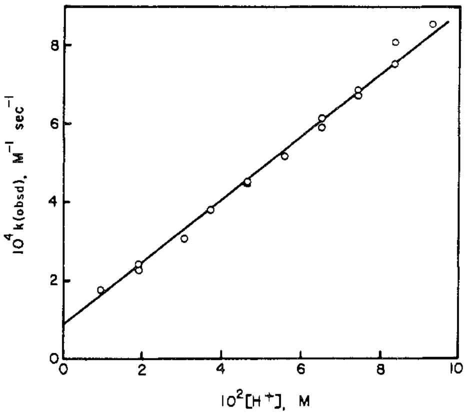


Figure 3. *k*(obsd) from eq 8 plotted as a function of hydrogen ion concentration for the reaction of hydroxylamine-*O*-sulfonic acid with iodide in 0.96 mole fraction of DMSO.

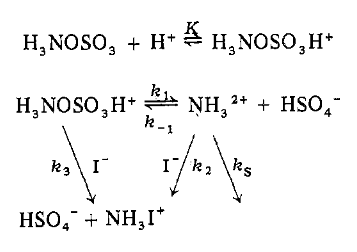
extent than is HSO_4^-; for example, $K_1 > 1$, but $K_2 \approx 10^{-14.5}$ for sulfuric acid in DMSO.[18] Also, despite a greater solvation of Na^+ in DMSO than in water,[8] Na_2SO_4 has a low solubility in DMSO, and Na^+ and SO_4^{2-} are known to undergo extensive association in DMSO.[17] Thus, the rate behavior in Figure 1 can be understood in terms of a rather loose transition-state structure

$$\overset{\delta-}{Nu}\cdots\overset{\delta+}{NH_2}\cdots\overset{(1+\delta)-}{OSO_3}$$

in which the developing SO_4^{2-} ion is increasingly more poorly solvated in solvents of increasing DMSO content, thereby raising activation energies.[19] Upon protonation of $H_2NOSO_3^-$, one might have expected an increase in reactivity arising from the formation of H_2NOSO_2OH, since an HSO_4^- leaving group would lower the transition state energy. The parallel decrease observed in k_{OS} and k_{HOS} argues strongly for essentially exclusive N-protonation in hydroxylamine-*O*-sulfonic acid in all of the DMSO-H_2O mixtures. Evidently, preassembly of $-OSO_3H$, which in the transition state would be the preferred leaving group, is precluded by the low proton basicity of the $-OSO_3^-$ moiety in $H_2NOSO_3^-$.[20]

H_3NOSO_3-I^-. The H^+-Dependent Path. The reactions in Scheme I are capable of accounting for the variable order with respect to I^- in the hydrogen ion dependent path. The k_s

Scheme I



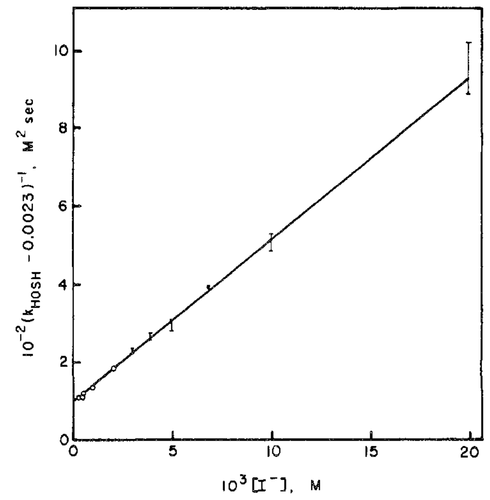


Figure 4. $(k_{HOSH} - k_3K)^{-1}$ plotted as a function of iodide concentration for the hydroxylamine-*O*-sulfonic acid–iodide reaction in 0.96 mole fraction of DMSO.

path represents scavenging of NH_3^{2+} by a solvent species or impurity. Assuming that NH_3^{2+} reaches a steady-state concentration and that $k_{-1}[HSO_4^-]$ is negligible ($k_2[I^-]$ is expected to be much greater than $k_{-1}[HSO_4^-]$), the corresponding rate law is

$$\frac{d[I_3^-]/dt}{[H_3NOSO_3][H^+][I^-]} = \frac{k_1k_2K}{k_2[I^-] + k_s} + k_3K \tag{9}$$

for which, from eq 8

$$k_{HOSH} = \frac{k_1k_2K}{k_2[I^-] + k_s} + k_3K \tag{10}$$

A plot of k_{HOSH} *vs.* $[I^-]^{-1}$, which was distinctly nonlinear,[21] as expected, gave an $[I^-]^{-1} = 0$ intercept of $k_3K = (2.3 \pm 0.2) \times 10^{-3} M^{-2}$ sec^{-1}. The data in Table IV were then analyzed using eq 11, obtained from eq 10. A plot of

$$\frac{1}{k_{HOSH} - k_3K} = \frac{[I^-]}{k_1K} + \frac{k_s}{k_1k_2K} \tag{11}$$

$(k_{HOSH} - k_3K)^{-1}$ *vs.* $[I^-]$, using $k_3K = 2.30 \times 10^{-3} M^{-2}$ sec^{-1}, is linear, with slope = 4.1×10^4 *M* sec and an intercept of 100 M^2 sec. These values and the linearity in Figure 4 are quite sensitive to the choice of k_3K, the $2.30 \times 10^{-3} M^{-2}$ sec^{-1} value giving the best fit. Although correlation of the data by eq 11 supports the mechanism in Scheme I, the suggestion that NH_3^{2+} is present as an intermediate must be regarded as tentative.[22] NH_3^{2+} represents the protonated form of the singlet nitrenium ion, NH_2^+,[24] and is isoelectronic with CH_3^+. Thus, NH_3^{2+} would be expected to react rapidly either with H_2O to form NH_3OH^+ or with DMSO to form $(CH_3)_2S(O)NH_2^+$.[25]

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(18) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, 90, 5961 (1968).

(19) Of the several solvation effects which may occur in these reactions, that involving SO_4^{2-} will predominate. It is unlikely that changes in solvation of the nucleophiles alone would account for the rate decreases. For example, the rate of reaction of I^- with $Pt(py)_2Cl_2$, a soft electrophilic species somewhat resembling $H_2NOSO_3^-$,[2] is only slightly lower in DMSO than in methanol: U. Belluco, M. Martelli, and A. Orio, *Inorg. Chem.*, 5, 582 (1966).

(20) A reviewer has pointed out that the lower reactivity of the $H_3N^+OSO_3^-$ form suggests that for the closely related acid-catalyzed reactions of peroxides with nucleophiles, a model for the transition state of the type Nu···O(R)···ORH is preferable to one involving protonation on the oxygen undergoing attack.

(21) This nonlinearity eliminates, as an alternative to Scheme I, a mechanism involving competitive, second-order attack on $H_3NOSO_3H^+$ by I^- and a solvent species.

(22) Mechanisms of the type described by Sneen,[23] involving competitive attack on the *ion pair* $NH_3^{2+}OSO_3H^-$, would also correlate the data. The results available do not permit a distinction between the mechanisms.

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Dipole Moments of Several Tertiary Phosphine Oxides, Sulfides, and Selenides and of Some Tertiary Arsine Oxides and Sulfides

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Dipole moments of thirteen phosphine and two arsine chalcogenide derivatives were determined in benzene solution at 20°. The results show that (1) the arsine compounds are more polar than the corresponding phosphine compounds, (2) the polarity of tertiary phosphine derivatives increases in the series oxide < sulfide < selenide, and (3) electronegative groups decrease the polarity of the derivative. Group bond moments, which were calculated from the net dipole moments of the molecule and the known structural parameters, give trends that follow electronegativities of the group and permit calculation of chemically reasonable M–X charge separations. Within a derivative series, *e.g.*, the oxides, the magnitude of $\delta\pm$ decreases with increasing electronegativity of the group. For a given group, *e.g.*, C_6H_5, the charge separation produces the trend oxide > sulfide ≈ selenide. The trends in the M–X bond moments and charge separations are discussed in terms of the relative amounts of double-bond character in the different M–X bonds.

Introduction

A great deal of controversy exists in the literature concerning the nature of the M–X bond (where M = P or As, and X = O, S, or Se). It has been argued that the M–X bond is (1) a dative bond,[1] (2) a double bond, or (3) a bond possessing a character intermediate between a single bond and a double bond, depending upon the extent of $p\pi$–$d\pi$ bonding between M and X.[2] Physical measurements such as (1) dissociation energies of the M–X bond,[3] (2) infrared stretching frequencies of the M–X group,[4-15] (3) nmr studies,[6b,15-21] and (4) donor properties of the M–X group toward Lewis acids such as phenol, chloroform, and iodine[22-28] indicate that the M–X bond is more accurately described by type (3) above. However, the determination of the amount of π bonding in the M–X group by these physical methods is

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