

Table IV. Correlation of XONO₂ Fundamentals^a

Description	HONO ₂	FONO ₂	CIONO ₂	CF ₃ - OONO ₂
XO stretch	3550	928	780	880
NO antisym stretch	1708	1759	1735	1760
XON bend	1331	303	270	264
NO sym stretch	1325	1301	1292	1305
NO' stretch	879	804	809	783
NO ₂ out-of-plane	762	708	711	702
NO ₂ deformation	647	633	560	600
ONO' bend	579	454	434	436
XO torsion	456	152	121	

^a Values are given to the nearest wave number. Description used is that of ref 20.

failure to observe CF₃OONF₂ and CF₃ONO₂ seems especially puzzling because of the ease with which CF₃ONF₂ and CF₃OONO₂ are obtained. A lower stability of CF₃ONO₂ compared to CF₃OONO₂ might be expected based on the proper-

ties of CF₃OPOF₂ and CF₃OOPF₂.⁴ However, this analogy cannot apply in the case of CF₃OONF₂, and the failure to observe this compound is probably related to the detailed reaction mechanism and not to the intrinsic instability of CF₃OONF₂.

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Registry No. CF₃OOH, 16156-36-8; CF₃OOH, 34511-13-2; CF₃OOOCF₃, 1718-18-9; N₂O₃, 10102-03-1; N₂O₄, 10544-72-6; N₂O₅, 10544-73-7; N₂O, 10024-97-2; NO, 10102-43-9; N₂F₄, 10036-47-2; NH₃, 7664-41-7; CF₃OONO₂, 50311-48-3.

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Nucleophilic Substitution on Nitrogen. Reactions of Hydroxylamine-O-sulfonate with Thiosulfate and Thiourea

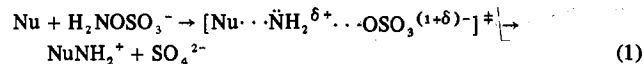
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Hydroxylamine-O-sulfonate, H₂NOSO₃⁻, reacts rapidly with thiosulfate, forming H₂NSSO₃⁻ as an intermediate and tetra-thionate as the final product. Thiourea reacts with H₂NOSO₃⁻ to form the novel cation (H₂N)₂CSNH₂⁺ isolated as the sulfate salt. Each reaction involves the rate law $-d[H_2NOSO_3^-]/dt = k_2[H_2NOSO_3^-][Nu]$, with $k_2 = 0.55 M^{-1} sec^{-1}$ for S₂O₃²⁻ and $1.64 M^{-1} sec^{-1}$ for (H₂N)₂CS at 20.4°. The reactions are interpreted in terms of nucleophilic substitution on the nitrogen center in H₂NOSO₃⁻ with the rate constants taken as a measure of the relative nucleophilicity toward trivalent nitrogen. As found in an earlier study with several other nucleophiles H₂NOSO₃⁻, with its nonbonded electron pair, is more reactive toward thiourea than is molecular H₂NOSO₃. Deuterium isotope effects observed for the reaction of H₂NOSO₃⁻, compared with D₂NOSO₃⁻ in D₂O, are $k_H/k_D = 1.12$ for S₂O₃²⁻ and 1.07 for (H₂N)₂CS. The reaction of S₂O₃²⁻ with H₂NSSO₃⁻ was examined briefly and found to proceed with a first-order hydrogen ion dependence.

Introduction

Studies of nucleophilic substitution processes at several inorganic atom centers, notably platinum(II), peroxide oxygen, and sulfur, have been described in detail.¹ In an attempt to extend such studies to substitution at a nitrogen center, we have reported the kinetics of reactions of hydroxylamine-O-sulfonate ion with various nucleophiles including triphenylphosphine, iodide, and triethylamine.² The reactions are first order in each reactant and involve attack on nitrogen as shown in eq 1. Based on observed second-order



rate constants, the order of nucleophilicity toward this trivalent nitrogen center is (C₆H₅)₃P > I⁻ > (C₂H₅)₃N >> Br⁻, Cl⁻.

We report here results for reaction of H₂NOSO₃⁻ with thiosulfate and with thiourea. The product species anticipated

- (1) (a) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962); (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967; (c) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1964, Chapter 4; (d) L. Cattalini, *Progr. Inorg. Chem.*, **13**, 263 (1970); (e) J. L. Kice, *ibid.*, **17**, 147 (1972).
(2) J. H. Krueger, P. F. Blanchet, A. P. Lee, and B. A. Sudbury, *Inorg. Chem.*, **12**, 2714 (1973).

as a direct consequence of attack on nitrogen are respectively H₂NSSO₃⁻ and (H₂N)₂CSNH₂⁺.

Thiohydroxylamine-S-sulfonate, H₂NSSO₃⁻, has been prepared as the potassium salt by Gosl and Meuwsen.³ Since a route to H₂NSSO₃⁻ was available, we examined its role as an intermediate in the hydroxylamine-O-sulfonate-thiosulfate reaction. Substitution on nitrogen by thiourea would lead to the previously unreported (H₂N)₂CSNH₂⁺ ion. This paper reports the isolation and identification of this species.

Experimental Section

Reagents. Most runs were carried out in doubly distilled water. B & A reagent grade methanol was used to prepare 50.0 wt% methanol-water solvents. Stohler 99.8% D₂O was employed in the deuterated solvent runs. Hydroxylamine-O-sulfonic acid and *N*-methylhydroxylamine-O-sulfonic acid were prepared as described earlier.² Reagent grade salts, K₂S₂O₈ (B & A), KClO₄, and NaClO₄ (used to maintain ionic strength), and the various salts for preparation of buffer solutions were used as received after drying at 110°. MCB reagent grade thiourea was recrystallized from water and dried.

Kinetics. Reactions were followed using a Cary Model 16K spectrophotometer. The decrease in absorbance at 235 nm was monitored in the case of thiourea and the increase in absorbance at 270 nm was followed in the thiosulfate reactions.

Potassium Thiohydroxylamine-S-Sulfonate. H₂NSSO₃K was prepared as described by Gosl and Meuwsen,³ except that it was recryst-

- (3) R. Gosl and A. Meuwsen, *Z. Anorg. Allg. Chem.*, **314**, 334 (1962).

tallized from methanol at 60° followed by addition of ether. $\text{H}_2\text{-NSSO}_3\text{K}$ reacted rapidly with iodide in the presence of acetic acid to produce iodine (0.5 mol/mol of $\text{H}_2\text{-NSSO}_3\text{K}$).³ Iodometric analyses gave purities in the range 92–96%. *Anal.* Calcd for $\text{H}_2\text{NO}_3\text{-S}_2\text{K}$: S, 38.34; N, 8.37. Found: S, 38.17; N, 8.25. (Analyses performed by Galbraith Laboratories, Inc., Knoxville, Tenn.)

Formamidine Disulfide Dichloride. $[(\text{H}_2\text{N})_2\text{CS}]_2\text{Cl}_2$ was prepared by the method of Leitch, *et al.*⁴ *Anal.* Calcd for $\text{C}_2\text{H}_8\text{Cl}_2\text{-N}_2\text{S}_2$: C, 10.76; H, 3.61; N, 25.10; Cl, 31.77. Found: C, 10.87; H, 3.58; N, 24.93; Cl, 31.65.

S-Aminoisothiuronium Sulfate. $[(\text{H}_2\text{N})_2\text{CSNH}_2]_2\text{SO}_4$ was prepared by the reaction of thiourea with hydroxylamine-O-sulfonate ion. H_3NOSO_3 (0.010 mol) was dissolved in 35 ml of absolute ethanol and the resulting solution neutralized by dropwise addition of triethylamine (0.010 mol). Immediately, a previously prepared solution of thiourea (0.010 mol) in 30 ml of ethanol was added dropwise, with cooling and stirring, over a 4-min period. After 5 min of additional stirring, the white solid formed was separated by force filtration and thoroughly washed with several portions of absolute ethanol, care being taken to minimize contact with moisture. The solid was dried under vacuum over P_2O_5 .

Over a 24-hr period the product slowly turned light yellow due to formation of sulfur, despite exclusion of moisture, and in 3 days the purity fell to ~80% of its original value. The compound was readily soluble in water, but in a short time sulfur separated from solution.

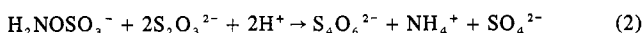
Purity was estimated by iodometric analysis following reaction of the product with iodide in 1 M CH_3COOH (2 mol of I_2 /mol of $[(\text{H}_2\text{N})_2\text{CSNH}_2]_2\text{SO}_4$). Because of a subsequent equilibrium reaction of I_2 with the $(\text{H}_2\text{N})_2\text{CS}$ produced to form $[(\text{H}_2\text{N})_2\text{CS}]_2^{2+}$ and I^- ,⁵ excess KI and slow addition of thiosulfate solution near the end point were necessary. The purity of a freshly prepared sample was typically about 95%. *Anal.* Calcd for $\text{C}_2\text{H}_8\text{N}_2\text{O}_4\text{S}_3$: C, 8.57; H, 4.31; N, 29.98; S, 34.31. Found: C, 8.61; H, 4.26; N, 29.82; S, 34.51.

Infrared Spectra. The ir spectrum (KBr pellet, Perkin-Elmer Model 180 spectrometer) of $\text{H}_2\text{-NSSO}_3\text{K}$ exhibited principal absorptions (cm^{-1}) at 3350 (s), 3270 (s), 1595 (m), 1200 (vs), 1020 (s), 910 (m), 765 (w), 640 (vs), 545 (m), 530 (w), 460 (m), and 410 (m) cm^{-1} . The sharp doublet centered on 3310 cm^{-1} and the 1610- cm^{-1} peak arise from stretching and bending modes, respectively, of NH_2 . Several of the features below 1250 cm^{-1} arise from motions within the S_2O_3 group and are similar to those of free thiosulfate.⁶ The 765- cm^{-1} peak may correspond to an S-N stretch.⁷

The ir spectrum (KBr pellet) of $[(\text{H}_2\text{N})_2\text{CSNH}_2]_2\text{SO}_4$ showed absorptions at 3400–2900 (vs), 1650 (s), 1440 (m), 1390 (sh), 890 (w), 650 (s), 475 (m), and 425 (m) cm^{-1} , plus sulfate absorptions at 1100 (vs) and 610 (s) cm^{-1} . The very broad absorption in the N-H stretching region suggests an overlap of frequencies for the nonequivalent NH_2 groups in the cation. The $(\text{H}_2\text{N})_2\text{CSNH}_2^+$ cation is stabilized by extensive charge delocalization with consequent partial double-bond character in C-N and C-S, and probably in S-N as well, leading to a rather broad range of possible frequencies associated with these bonds. The 890- cm^{-1} absorbance may arise from the S-N stretch,⁸ since there is no comparable absorbance in the thiourea spectrum.⁹

Results

Thiosulfate-Hydroxylamine-O-sulfonate Reaction. The reaction proceeds according to eq 2 throughout the pH range



2.7–7.0. At pH >7, the stoichiometry changes as described below. In the kinetic runs infinite-time absorbances at 270 nm were generally in agreement with calculated values based on $\epsilon_{270}(\text{S}_4\text{O}_6^{2-})$ 316 $M^{-1} \text{cm}^{-1}$ and $\epsilon_{270}(\text{S}_2\text{O}_3^{2-})$ 16 $M^{-1} \text{cm}^{-1}$.¹⁰ Also, in a reaction with 0.083 M $\text{K}_2\text{S}_2\text{O}_3$ and 0.042

(4) L. C. Leitch, B. E. Baker, and L. Brickman, *Can. J. Res., Sect. B*, 23, 139 (1945).

(5) O. Foss, J. Johnsen, and O. Tvedten, *Acta Chem. Scand.*, 12, 1782 (1958).

(6) A. J. Bannister, L. F. Moore, and J. S. Padley in "Inorganic Sulphur Chemistry," Elsevier, New York, N. Y., 1968, p 167.

(7) S-N single-bond frequencies occur in the range 770–840 cm^{-1} . See ref 6, p 155.

(8) See ref 6, p 155.

(9) J. E. Stewart, *J. Chem. Phys.*, 26, 248 (1957).

(10) A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, 73, 1842 (1951).

M H_3NOSO_3 in 25 wt% methanol-water, the principal product isolated was $\text{K}_2\text{S}_4\text{O}_6$ (purity 99 ± 3% by iodate oxidation and by combustion).¹¹

Reactant concentrations were calculated from the observed increase in absorbance at 270 nm. Plots of $\ln([S_2O_3^{2-}]/[H_2NOSO_3^-])$ vs. time were linear for the extent of reaction examined (*ca.*, 2 half-lives) leading to rate law 3. Values of

$$-d[H_2NOSO_3^-]/dt = k_2[H_2NOSO_3^-][S_2O_3^{2-}] \quad (3)$$

k_2 were determined from a least-squares fit of the data to $k_2 = (1/t)([S_2O_3^{2-}]_0 - [H_2NOSO_3^-]_0)^{-1} \ln([S_2O_3^{2-}][H_2NOSO_3^-]_0/[H_2NOSO_3^-][S_2O_3^{2-}]_0)$. Over an 18-fold range in the ratio $[S_2O_3^{2-}]_0/[H_2NOSO_3^-]_0$, the average value of k_2 at 20.4° was $0.550 \pm 0.015 M^{-1} \text{sec}^{-1}$ (Table I). At 10.4°, $k_2 = 0.272 M^{-1} \text{sec}^{-1}$, and at 29.7°, $k_2 = 0.99 M^{-1} \text{sec}^{-1}$ at pH 4.75. Values of $\Delta H^\ddagger = 10.8 \pm 0.1 \text{ kcal/mol}$ and $\Delta S^\ddagger = -23 \pm 1 \text{ eu}$ were calculated from transition-state theory. The k_2 values were independent of pH over the range 2.7–7.0 as expected, since $\text{H}_2\text{NOSO}_3^-$ is the only reactant form present in this range ($K_a = 0.055$ for H_3NOSO_3).² In addition there was no evidence that either buffer anion, acetate or HPO_4^{2-} , reacted with $\text{H}_2\text{NOSO}_3^-$ during the course of the reaction. Acid-catalyzed decomposition of thiosulfate precluded an analysis of the kinetics at lower pH where $\text{H}_3\text{-NOSO}_3$ is present.

Rate constants were also obtained in 99.8% D_2O . From data in Table I at pH 4.75, $k_H/k_D = 1.12 \pm 0.05$. Because amine hydrogens exchange rapidly with the solvent in moderately acidic to basic solutions,^{2,12} k_2 measured in D_2O (k_D) corresponds to reaction of $\text{D}_2\text{NOSO}_3^-$.

Since $\text{S}_2\text{O}_3^{2-}$ undergoes partial ion pairing with K^+ ,¹³ the observed increase in k_2 with an increase in ionic strength arises from the greater reactivity of the ion-pair species KS_2O_3^- , in addition to the normal ionic strength effect. Values of k_2 were obtained for various $[\text{K}^+]$ at $\mu = 0.10 M$, maintained using $(\text{C}_2\text{H}_5)_4\text{NCl}$.¹⁴ For K^+ concentrations of 0.0060, 0.026, 0.056, and 0.096 M, values of k_2 ($M^{-1} \text{sec}^{-1}$, 20.4°) were respectively 0.445, 0.452, 0.502, and 0.550. Assuming a modified form of eq 3, $-d \ln [H_2NOSO_3^-]/dt = k_0[S_2O_3^{2-}] + k_{ip}[KS_2O_3^-]$, and using $K_{ip} = [\text{K}^+][S_2O_3^{2-}]/[KS_2O_3^-] = 0.12^{13}$ led to eq 4. The data above were ana-

$$\frac{-d \ln [H_2NOSO_3^-]/dt}{\Sigma[S_2O_3^{2-}]} = k_2 = \frac{k_0 K_{ip}}{\left(\frac{K_{ip}}{[\text{K}^+]} + 1\right) [\text{K}^+]} + \frac{k_{ip}}{\frac{K_{ip}}{[\text{K}^+]} + 1} \quad (4)$$

lyzed using eq 5, resulting in values of $k_0 = 0.43 \pm 0.02 M^{-1}$

$$k_2 \left(\frac{K_{ip}}{[\text{K}^+]} + 1\right) = \frac{k_0 K_{ip}}{[\text{K}^+]} + k_{ip} \quad (5)$$

sec^{-1} and $k_{ip} = 0.65 \pm 0.03 M^{-1} \text{sec}^{-1}$.

Thiosulfate-Thiohydroxylamine-S-sulfonate Reaction.

(11) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, London, 1959, p 369.

(12) E. F. Caldin, "Fast Reactions in Solution," Wiley, New York, N. Y., 1964, p 244.

(13) F. G. R. Gimblett and C. B. Monk, *Trans. Faraday Soc.*, 51, 793 (1955).

(14) In analyzing the data, ion pairing of $(\text{C}_2\text{H}_5)_4\text{N}^+$ with $\text{S}_2\text{O}_3^{2-}$ was assumed to be negligible, based on spectral properties of $\text{S}_2\text{O}_3^{2-}$ in the presence of K^+ and $(\text{C}_2\text{H}_5)_4\text{N}^+$.

Table I. Kinetic Data for the Thiosulfate-Hydroxylamine-O-sulfonate Reaction at 20.4° and 0.10 M Ionic Strength

$10^3[\text{H}_2\text{NO-SO}_3^-]_0, M$	$10^3[\text{S}_2\text{O}_3^{2-}]_0, M$	pH	$k_2, M^{-1} \text{ sec}^{-1}$
3.00	1.01	2.7 ^b	0.555 (2) ^a
1.00	3.01	4.75 ^c	0.546 (4)
1.00	3.01		0.491 (2) ^d
1.00	6.00 ^f		0.549
1.99	2.00		0.560 (2)
3.05	2.03		0.553
4.00	2.00		0.552
6.00	2.03		0.526
1.00	3.00	5.04 ^c	0.541 (2)
1.00	3.00	5.26 ^c	0.552 (3)
1.00	6.00 ^f		0.552
2.00	2.00		0.565
1.00	3.00	5.33 ^c	0.547 (2)
1.00	3.03	6.19 ^e	0.565
1.00	3.03	7.03 ^e	0.549

^a Number of runs. ^b HClO₄ added. ^c 0.025 M acetate buffer. ^d 99.8% D₂O. ^e Phosphate buffer. ^f Constant infinite-time absorbances were obtained although, at the highest thiosulfate concentration, after 15 min the A_∞ values increased noticeably due to formation of small concentrations of S₂O₆²⁻.

Thiohydroxylamine-S-sulfonate, H₂NSSO₃⁻, is the anticipated intermediate in the thiosulfate-hydroxylamine-O-sulfonate reaction and it has been suggested³ that, in the presence of thiosulfate, it reacts to form tetrathionate. Accordingly, a study of reaction 6 was carried out in which K₂S₄O₆ was

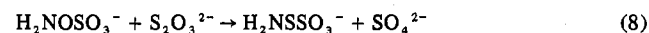


confirmed as the principal product, both by isolation and analysis¹¹ and by observing that, in the kinetic runs, infinite-time absorbances agreed with those calculated from eq 6, using $\epsilon_{270}(\text{H}_2\text{NSSO}_3^-) 55 M^{-1} \text{ cm}^{-1}$.¹⁵

Plots of $\ln([\text{S}_2\text{O}_3^{2-}]/[\text{H}_2\text{NSSO}_3^-])$ vs. time, based on absorbance changes at 270 nm, were linear, indicating a first-order dependence on S₂O₃²⁻ and H₂NSSO₃⁻. Values of $k_2(\text{obsd})$, calculated from data obtained in the pH range 7.8–6.9, increased rapidly with an increase in hydrogen ion concentration (Table II). To account for the variation of $k_2(\text{obsd})$ with pH, rate law 7 was assumed, from which $k_2 - d[\text{S}_2\text{O}_3^{2-}]/dt = (k_a[\text{H}^+] + k_b)[\text{S}_2\text{O}_3^{2-}][\text{H}_2\text{NSSO}_3^-]$ (7)

(obsd) = $k_a[\text{H}^+] + k_b$. A plot of $k_2(\text{obsd})$ vs. $[\text{H}^+]$ was linear over the $[\text{H}^+]$ range $(0.14-1.4) \times 10^{-7} M$ with an apparent (0,0) intercept. A least-squares fit of the data gave $k_a = 7.3 (\pm 0.2) \times 10^7 M^{-2} \text{ sec}^{-1}$ and $k_b = -0.1 (\pm 0.1) M^{-1} \text{ sec}^{-1}$. Thus, within experimental error, S₂O₃²⁻ does not react with the unprotonated form, H₂NSSO₃⁻.

At sufficiently high pH, the rate of reaction 6 is small compared with that measured for reaction 2 at pH < 7. If H₂NSSO₃⁻ is the intermediate in reaction 2, then the stoichiometry of (2) should change with pH and approach that in eq 8 at pH > 9. Rate measurements at pH 9.3 (borate buffer)



with $[\text{S}_2\text{O}_3^{2-}]_0 = 3.00 \times 10^{-3} M$ and $[\text{H}_2\text{NOSO}_3^-]_0$ in the range $(5.0-10.0) \times 10^{-3} M$ supported this conclusion. Infinite-time absorbances were in agreement with those expected for H₂NSSO₃⁻ as the product, if allowance was made for small concentrations of the much more highly absorbing

(15) The uv-visible spectrum of thiohydroxylamine-S-sulfonate ion has not been reported previously. In the region of interest, the absorbance of a solution of H₂NSSO₃⁻ K in water increases continuously below 300 nm, with ϵ values of 27, 55, 106, and 174 M⁻¹ cm⁻¹ at 280, 270, 260, and 250 nm, respectively.

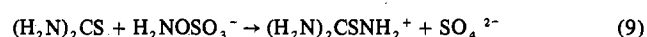
Table II. Kinetic Data for the Thiosulfate-Thiohydroxylamine-S-sulfonate Reaction at 20.4° and 0.10 M Ionic Strength

$10^3[\text{S}_2\text{O}_3^{2-}]_0, M$	$10^3[\text{H}_2\text{NS-SO}_3^-]_0, M$	pH ^a	$k_2, M^{-1} \text{ sec}^{-1}$
2.00	0.849	6.87	10.0
2.00	0.849	6.87	9.4
3.00	1.00	7.40	2.56
2.00	0.849	7.42	2.49
3.02	1.00	7.43	2.39
3.01	1.00	7.43	2.47
3.00	1.00	7.84	0.93
3.02	1.00	7.87	1.00
3.01	1.00	7.87	0.98

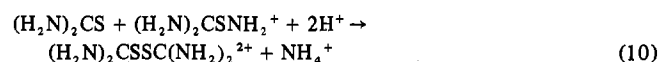
^a Phosphate buffer.

tetrathionate ion. An average value of $k_2 = 0.54 M^{-1} \text{ sec}^{-1}$ was obtained, essentially the same as that observed for reaction 2 at pH < 7. Thus, at pH < 7 where the reaction of S₂O₃²⁻ with H₂NSSO₃⁻ is very rapid, reaction 8 is rate determining.

Thiourea-Hydroxylamine-O-sulfonate Reaction. Formation of (H₂N)₂CSNH₂⁺. The reaction is accompanied by a large decrease in absorbance at 235 nm. Throughout the pH range 1.0–11.7, with $[\text{H}_2\text{NOSO}_3^-]_0 \gg [(\text{H}_2\text{N})_2\text{CS}]_0$, the infinite-time absorbances corresponded to a product with $\epsilon_{235} \approx 1500 M^{-1} \text{ cm}^{-1}$ (assuming 1 mol of (H₂N)₂CS per absorbing species). The reaction of 2 mol of (H₂N)₂CS/mol of H₂NOSO₃⁻ to form (H₂N)₂CSSC(NH₂)₂²⁺ clearly is ruled out when thiourea is the limiting reagent since ϵ_{235} is 1.7×10^4 for (H₂N)₂CSSC(NH₂)₂²⁺. Rather, the experimental results support eq 9 as the correct stoichiometry. The (H₂-



(H₂N)₂CSNH₂⁺ species, prepared independently as the sulfate, was found to have an ϵ_{235} of approximately $1400 M^{-1} \text{ cm}^{-1}$ at pH 4.75,¹⁶ in agreement with absorbance data for the product solutions. Further reaction with thiourea at the 10⁻⁵ M level occurs only slowly, but at the 10⁻³ M level, reaction with added thiourea takes place to give a solution with spectral characteristics corresponding to those of (H₂-N)₂CSSC(NH₂)₂²⁺, probably *via* (10). When $1.2 \times 10^{-4} M$



H₂NOSO₃⁻ and $0.4 \times 10^{-4} M$ (H₂N)₂CS were allowed to react and the product solution was treated with excess KI and acetic acid, the number of moles of I₂ produced was equal to the original number of moles of H₂NOSO₃⁻, eliminating the possibility that the presumed (H₂N)₂CSNH₂⁺ solutions contain only hydrolyzed, nonoxidizing species.

Kinetics of the Thiourea-Hydroxylamine-O-sulfonate Reaction. The rate was measured with H₂NOSO₃⁻ in large excess. Plots of $\ln(A - A_\infty)$ vs. time were linear for the extent of reaction examined, 3–4 half-lives. Pseudo-first-order rate constants were measured for a variety of initial hydroxylamine-O-sulfonate concentrations leading to the rate law $-d[(\text{H}_2\text{N})_2\text{CS}]/dt = k_2[(\text{H}_2\text{N})_2\text{CS}][\text{H}_2\text{NOSO}_3^-]$. The second-order rate constants were independent of pH over the range 4.1–11.7 with an average value at 20.4° of $1.64 \pm 0.04 M^{-1} \text{ sec}^{-1}$ (Table III). At 10.4°, $k_2 = 1.02 \pm 0.04 M^{-1} \text{ sec}^{-1}$, and at 29.7°, $k_2 = 2.44 \pm 0.05 M^{-1} \text{ sec}^{-1}$, giving $\Delta H^\ddagger = 7.4 \pm 0.2 \text{ kcal/mol}$ and $\Delta S^\ddagger = -32 \pm 2 \text{ eu}$. In

(16) The absorbance of a (H₂N)₂CSNH₂⁺ solution increases continuously at wavelengths less than 265 nm. Spectral analysis immediately following preparation of the solution gave $\epsilon_{235} 1300 M^{-1} \text{ cm}^{-1}$. However, the absorbance increased slowly thereafter due to hydrolysis and subsequent formation of sulfur.

Table III. Kinetics of the Thiourea-Hydroxylamine-*O*-sulfonate Reaction at 20.4° and 0.10 *M* Ionic Strength

$10^3 [\text{H}_2\text{NO}-\text{SO}_3^-]_0, M$	$10^5 [(\text{H}_2\text{N})_2\text{CS}]_0, M$	pH	$k_2, M^{-1} \text{sec}^{-1}$
1.01	4.01	4.05 ^b	1.62 (2) ^a
2.03	4.01		1.63 (2)
0.99	2.01	4.75 ^b	1.67
1.00	4.00		1.63 (4)
1.05	6.00		1.67
2.04	3.98		1.67 (2)
3.03	2.00		1.62
6.06	2.00		1.63
1.99	4.01	5.35 ^b	1.60
1.03	4.15	6.41 ^c	1.64 (2)
1.03	4.15	7.21 ^c	1.64 (2)
1.03	4.15	7.76 ^c	1.63 (2)
1.02	4.15	8.46 ^d	1.64 (3)
2.02	3.98		1.69
1.03	4.15	9.06 ^d	1.60 (2)
0.98	4.09	11.0 ^e	1.66
0.98	4.09	11.7 ^e	1.62

^a Number of runs. ^b Acetate buffer. ^c Phosphate buffer. ^d (HO-CH₂)₃CNH₂ buffer. ^e Added NaOH.

50.0 wt % methanol-water (pH 5.75), $k_2 = 0.75 \pm 0.03 M^{-1} \text{sec}^{-1}$. For runs carried out in 99.8% D₂O, $k_2 = 1.53 \pm 0.04 M^{-1} \text{sec}^{-1}$, leading to $k_{\text{H}}/k_{\text{D}} = 1.07 \pm 0.05$.

Several runs were carried out under second-order conditions with $[(\text{H}_2\text{N})_2\text{CS}]_0 = 5.9 \times 10^{-5} M$ and $[\text{H}_2\text{NOSO}_3^-]_0$ in the range $(12.5-36.8) \times 10^{-5} M$. The k_2 values obtained at pH 4.7 and 8.5, based on the stoichiometry in eq 9, agreed closely with the results in Table III.¹⁷

In a series of runs at low pH, values of k_2 increased as $[\text{H}^+]$ increased from 10^{-3} to $10^{-2} M$, reaching a maximum of $2.2 M^{-1} \text{sec}^{-1}$ at pH 2.0, and then decreased below pH 2.0. At pH 1.15, $k_2 = 1.21 M^{-1} \text{sec}^{-1}$. The eventual falloff in rate at low pH is reminiscent of results in our earlier study² of reaction of $\text{H}_2\text{NOSO}_3^-$ with iodide and triphenylphosphine in which decreasing reactivity was associated with protonation of nitrogen in $\text{H}_2\text{NOSO}_3^-$. Presumably, protonation of the nitrogen lone pair of electrons is responsible for the decrease in rate of the thiourea reaction as well, although we are unable to account for the intervening increase in k_2 . Protonation of thiourea apparently is not involved, since $pK_a \cong -1.0$ for its conjugate acid.

The reaction of thiourea with the *N*-methyl-substituted species $\text{CH}_3\text{NHOSO}_3^-$ was examined briefly at pH 4.75 by the method of initial rates. The reaction was assumed to be first order in thiourea and over a range of $(3.0-12.0) \times 10^{-3} M$ in $[\text{CH}_3\text{NHOSO}_3^-]_0$, slopes were proportional to $[\text{CH}_3\text{NHOSO}_3^-]_0$, indicating a first-order dependence on *N*-methylhydroxylamine-*O*-sulfonate as well. The resulting average value of the second-order constant at 20.4° was $(1.6 \pm 0.1) \times 10^{-3} M^{-1} \text{sec}^{-1}$. Thus, replacement of H on nitrogen with CH₃ reduces reactivity by 10^3 . Comparable behavior was observed for (C₆H₅)₃P and I⁻ as nucleophiles,² demonstrating the pronounced susceptibility of sp³ nitrogen to steric effects in the transition state.

Discussion

For each reaction bimolecular substitution involving attack on nitrogen is supported by the second-order rate law, a large, negative activation entropy, and identification of a product or intermediate containing a nitrogen-sulfur bond. The mechanism of the $\text{H}_2\text{NOSO}_3^- \text{S}_2\text{O}_3^{2-}$ reaction involves eq

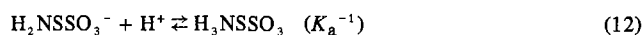
(17) With thiourea in excess, useful results could not be obtained due to concomitant production of small concentrations of $(\text{H}_2\text{N})_2\text{C}-\text{SSC}(\text{NH}_2)_2^{2+}$ according to eq 10.

8 as the rate-determining step, followed by eq 6, which is rapid relative to 8 when pH < 7. For substitution at sp³ carbon there exists a series of reactions analogous to eq 8



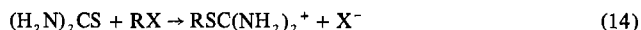
leading to the formation of alkyl thiosulfates (Bunte salts).

The results of the $\text{H}_2\text{NSSO}_3^- \text{S}_2\text{O}_3^{2-}$ study in the pH range 6.9-7.8 are of importance in that they provide strong evidence for $\text{H}_2\text{NSSO}_3^-$ as the intermediate in reaction 2. The fact that conversion of $\text{H}_2\text{NSSO}_3^-$ to $\text{S}_4\text{O}_6^{2-}$ occurs *via* a hydrogen ion dependent pathway only suggests the following mechanism involving NH₃ as the leaving group



Using the third-order rate constant from eq 7, $k_a = 7.3 \times 10^7 M^{-2} \text{sec}^{-1}$ and $K_a \approx 10^{-1}$;¹⁸ k_r is estimated to be $7 \times 10^6 M^{-1} \text{sec}^{-1}$ at 20.4°.

For the thiourea reaction a single rate-determining step, eq 9, is proposed. The fact that k_2 is independent of pH from 4.1 to at least 11.7 suggests that $\text{H}_2\text{NOSO}_3^-$ is the only reactive form in this range and that attack by base buffer species is negligible. Reactions of the type



involving substitution at an alkyl carbon are analogous to 9. $(\text{H}_2\text{N})_2\text{CSNH}_2^+$, which possesses sufficient stability to be regarded as the product formed from substitution by thiourea on $\text{H}_2\text{NOSO}_3^-$, appears to be a new species. We are unaware of any report of its isolation, although a series of related compounds of the type $\text{R}_2\text{NSC}(=\text{NR}')\text{N}(\text{CH}_3)_2$ has been described briefly.¹⁹ The well-characterized series of *S*-alkylisothiuronium salts, $\text{RSC}(\text{NH}_2)_2^+ \text{X}^-$,²⁰ suggests the name *S*-aminoisothiuronium ion for $(\text{H}_2\text{N})_2\text{CSNH}_2^+$.²¹

The deuterium isotope effect for $\text{S}_2\text{O}_3^{2-}$ (1.12)^{22,23} and for $(\text{H}_2\text{N})_2\text{CS}$ (1.07), like the effects noted earlier² for I⁻ (1.3) and (C₆H₅)₃P (1.5), arise from a combination of a secondary effect for substitution on the sp³ nitrogen and a solvent effect. The similarity in the values supports but does not itself require a common mechanism.

It has been suggested that, based on the HSAB principle, trivalent nitrogen should be particularly susceptible to substitution by soft bases.^{1a} The present kinetic results, together with those of our earlier study, support this prediction. Trivalent nitrogen in $\text{H}_2\text{NOSO}_3^-$ resembles both peroxide oxygen and platinum(II) as an electrophilic center. Studies on more basic nucleophiles are in progress to make possible a comparison of trivalent nitrogen with the isoelectronic sp³ carbon center.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by

(18) At 20° and 0.1 *M* ionic strength an approximate value of $K_a = 10^{-1}$ for H_3NSSO_3 was obtained. The possibility that the pH dependence in the 7-8 range arises from deprotonation to form HNSSO_3^{2-} can be excluded since there is no evidence of further loss of a proton throughout the pH range 3-12.

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(21) The corresponding free base is *S*-aminoiminomethylthiohydroxylamine.

(22) For substitution by $\text{S}_2\text{O}_3^{2-}$ at sp³ carbon, $k_{\text{H}}/k_{\text{D}} = 1.03$ and 0.97 for reactions of $\text{CD}_3\text{Br}^{23a}$ and $\text{CD}_3\text{I}^{23b}$ respectively.

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the American Chemical Society, for support of this research.

Registry No. $\text{H}_2\text{NOSO}_3^-$, 41380-12-5; $\text{H}_2\text{NSSO}_3^-$, 49559-18-4;

$\text{CH}_3\text{NHOSO}_3^-$, 41380-13-6; $\text{S}_2\text{O}_3^{2-}$, 14383-50-7; $(\text{H}_2\text{N})_2\text{CS}$, 62-56-6; $\text{H}_2\text{NSSO}_3\text{K}$, 49559-20-8; $[(\text{H}_2\text{N})_2\text{CSNH}_2]_2\text{SO}_4$, 49559-21-9.

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Five-Coordinate and Three-Coordinate Manganese(II). Hydrated and Dehydrated Crystal Structures of Partially Manganese(II)-Exchanged Zeolite A

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The crystal structures of hydrated ($a = 12.268$ (4) Å) and vacuum-dehydrated ($a = 12.175$ (3) Å) Mn(II)-exchanged zeolite A have been determined by single-crystal X-ray diffraction techniques in the cubic space group $Pm\bar{3}m$. Chemical analyses revealed 4.5 Mn(II) ions per unit cell following an exchange period of either 3 weeks or 3 months. The 4.5 Mn(II) ions are distributed over an eightfold equipoint on threefold axes near the centers of the six-oxygen windows in each structure. In the hydrated structure, the probable positions of 29.5 water molecules have been determined and the Mn(II) ions are found to be pentacoordinate in a trigonal-bipyramidal manner: axially by two water molecules of hydration and in the plane by three framework oxygen atoms. These Mn(II)-O closest approaches are 2.03 (6) and 2.06 (7) Å to the two axial (water) ligands and 2.28 (1) Å to the three equivalent oxygen atoms. In the dehydrated material, only the latter three donor atoms remain, and Mn(II) ions coordinate to these at distances of 2.11 (1) Å in a near trigonal-planar manner. In the dehydrated structure, the remaining three Na^+ ions, also three-coordinate, are located in the otherwise unoccupied six-oxygen windows.

Introduction

By determining the structures of transition metal ion exchanged zeolite 4A, the unusual coordination geometries of these ions in an unaccommodating medium may be learned. Also the changes in the aluminosilicate framework itself under varying degrees of ion exchange and dehydration can be observed. Furthermore, complexes of the dehydrated materials can be prepared which should elucidate the structural basis for their pronounced catalytic activity in a wide range of chemical processes.

Different limits to the degree of cation exchange have been noted,¹⁻⁴ indicative either of the formation of stable ion and solvent configurations within the zeolitic channels and cavities or perhaps of a natural limit to the unevenness of positive charge distribution stabilizing the anionic framework.

A preliminary account of this work has been reported.⁵

Experimental Section

Two exchange experiments were done, one for 3 weeks and one for 3 months. In each trial approximately 0.5 g of cubic single crystals (0.03–0.07 mm on an edge), previously prepared,^{1,2,6,7} were allowed to exchange at 28° with 50 ml of a 0.1 M solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Both samples were placed in solutions containing a large excess of Mn(II) ions and were periodically agitated to ensure a uniform Mn(II) ion concentration in the vicinity of the crystals. In both cases, the crystals were pinkish tan. Subsequent chemical analyses revealed 4.4 Mn(II) ions per unit cell for the 3-week exchange and 4.5 Mn(II) ions for the 3-month exchange. Apparently the exchange, which is initially rapid, stops or slows appreciably after about 4.5 Mn(II) ions per unit cell have entered the structure. This limits the number of remaining Na^+ ions to 3 and results in the following unit cell stoichiometry, $[\text{Mn}^{2+}_{4.5}\text{Na}^+_3(\text{Si}_{12}\text{Al}_{12}\text{O}_{48})^{12-}] \cdot x\text{H}_2\text{O}$. This structure will be referred to henceforth as Mn[A].

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A cubic single crystal 0.0065 cm on an edge was mounted at the tip of a glass fiber and maintained at 20° and a relative humidity of 30%. Diffraction intensities were collected using graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\text{K}\alpha_1$, λ 0.70926 Å; $\text{K}\alpha_2$, λ 0.71354 Å). The second crystal, 0.0070 cm on an edge, was prepared by a procedure similar to that employed before⁶ in dehydrating zeolite 4A. The capillary containing the single crystal was sealed off under vacuum after a 24-hr dehydration period at 350° and 10^{-5} Torr. Upon dehydration, the color of the crystal became tan, without a pink component. Subsequent diffraction intensities were collected at 19° for $0^\circ < 2\theta < 70^\circ$. The space group $Pm\bar{3}m$ (no systematic absences) was used instead of $Fm\bar{3}c$ for reasons discussed earlier.^{1,2,6-8}

A Syntex four-circle computer-controlled diffractometer with a pulse height analyzer was used throughout for preliminary experiments and for the collection of diffraction intensities. In each case the cubic cell constants, $a = 12.268$ (4) Å for the hydrated crystal and $a = 12.175$ (3) Å for the dehydrated one, were determined by a least-squares treatment of 15 intense reflections for which $20^\circ < 2\theta < 24^\circ$.

The θ - 2θ scan technique was employed with a scan rate (ω) variable, under computer control, between 0.5 and 24°/min in 2θ . More time was spent on the weaker reflections to minimize their standard deviations. All unique reciprocal lattice points (881 and 862 for the hydrated and dehydrated crystals, respectively) for which $2\theta < 70^\circ$ were examined. The high upper limit was chosen for 2θ to maximize the size of the data sets even though few reflections with large 2θ values showed significant intensity. Half of the total scan time for each reflection was spent counting background at each end of the scan range, which varied from 2.0° at $2\theta = 3^\circ$ to 2.5° at $2\theta = 70^\circ$. Two check reflections, monitored after every 100 reflections during the course of data collection, showed no significant trends in intensity.

Standard deviations were assigned according to the formula

$$\sigma(I) = [\omega^2 \{CT + 0.25(t_c/t_b)^2(B_1 + B_2)\} + (pI)^2]^{1/2}$$

where CT is the total integrated count obtained in a scan time of t_c , B_1 and B_2 are the background counts each obtained in time t_b , and $I = \omega[CT - 0.5(t_c/t_b)(B_1 + B_2)]$. A value of 0.02 was assigned to the empirical parameter p to account for instrument instability. The net counts were then corrected for Lorentz and polarization effects. Absorption corrections were unnecessary: $\mu = 12.8$ and 12.5 cm^{-1} for the hydrated and dehydrated crystals, respectively, and transmission coefficients ranged from 0.921 to 0.930 and from 0.916 to 0.926.

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