

Boric Acid Catalysis of Decomposition of the N-Nitrosohydroxylamine-N-Sulfonate Anion

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The decomposition of $\text{SN}_2\text{O}_5^{2-}$ to N_2O and sulfate is catalyzed both by protons alone and jointly by protons and H_3BO_3 according to the rate law:

$$d \ln [\text{SN}_2\text{O}_5^{2-}]/dt = k_1[\text{H}^+] + k_2[\text{H}^+][\text{H}_3\text{BO}_3].$$

The activation enthalpy and entropy for k_2 are, respectively, 7.8 kcal/mol and -43 cal/degree K. Consideration of these values as well as the influence of $[\text{H}^+]$, $[\text{H}_3\text{BO}_3]$, and ionic strength suggest that the k_1 reaction involves reactants of opposite charge whereas for the k_2 reaction one of the species entering the rate-determining step is of zero electric charge. A mechanism of the latter reaction is postulated in which $\text{B}(\text{OH})_3$ acts as an acceptor of electrons from the nitrosyl nitrogen and one of the OH groups of $\text{B}(\text{OH})_3$ interacts with the SO_3 moiety of the $\text{SN}_2\text{O}_5^{2-}$ anion resulting in a sulfur penta-coordinated species.

INTRODUCTION

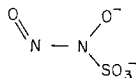
Scrubbing flue gases with basic sulfite solutions is a rapidly developing technology for removing oxides of sulfur by absorption into aqueous solutions. The use of aqueous scrubbing solutions for NO_x abatement has not appeared to hold as much promise as for SO_2 , however, in part because of the low solubility and reactivity of NO in water. This is not the case for NO_2 which is much more soluble, but the pre-oxidation of NO to NO_2 constitutes a complicating process step of additional expense. The oxidation of NO to NO_2 by the oxygen in air, although thermodynamically favored, is too slow for practical utilization in a flue-gas treatment process. The approach of several such

processes under development in Japan is to oxidize the NO in the gas phase by introducing the reagents O_3 or ClO_2 , after which the resulting NO_2 , because of its solubility, is absorbed into water and caused to react with sulfite. Several other such processes incorporate in the scrubbing solution agents such as Fe^{2+} and EDTA which appear to form complexes with the NO thereby increasing its solubility and enhancing its reaction with dissolved sulfite. Except for such work, however, it appears that the reaction of NO with aqueous sulfite has been largely ignored in the technological development of aqueous wet scrubbing in spite of the fact that as early as 1802 Sir Humphrey Davy (1) reported that NO reacted with K_2SO_3 to form a product identified a mere 33 years later in 1835 by Pelouze (2) as $\text{K}_2\text{SO}_3(\text{NO})_2$; Pelouze also showed that this compound decomposed to N_2O and K_2SO_4 upon heating to above

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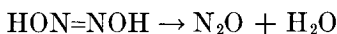
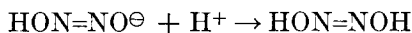
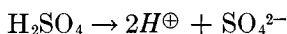
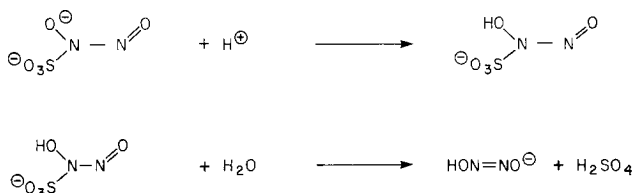
100°C. About another 120 years passed before Degener and Seel (3) confirmed that this potassium compound was a salt of *N*-nitrosohydroxylamine-*N*-sulfonic acid:



The fact that this ion, which is a principal product of the reaction of NO with the sulfite ion in basic solution, can be made to decompose to N₂O and SO₄²⁻ heightens interest in promoting and controlling this reaction. We report below an investigation into the catalytic acceleration of the decomposition of the *N*-nitrosohydroxylamine-*N*-sulfonate anion, a reaction which could become a means of regenerating NO-saturated sulfite scrubbing solutions for flue gas.

Seel and Winkler (4) investigated the acid-catalyzed decomposition of this anion,

and they reported that boric acid also catalyzes the decomposition. The present report focuses on this H₃BO₃-catalyzed decomposition. At the outset it is useful to summarize some of the related findings of Seel and Winkler (4) and Ackermann and Powell (5). These investigators showed the decomposition of *N*-nitrosohydroxylamine-*N*-sulfonate to be acid-catalyzed and proportional to the concentration of the starting material. By means of changing the ionic strength, the activated complex was shown to have a charge of +1. They also reported the activation enthalpy of the acid-catalyzed decomposition as 14.05 kcal/mol and the activation entropy as 22.4 cal/°K. Our recalculation of the results indicates the latter value is incorrect and should have been reported as 17.4 cal/°K. This information led Seel and Winkler to propose the following decomposition scheme:



This mechanism involving a final decomposition of symmetrical hyponitrous acid is in agreement with Clusius and Schumaker (6) who determined that ¹⁵N-labeled O¹⁵N¹⁴NO(SO₃)²⁻ decomposed to give equal amounts of ¹⁵N¹⁴NO and ¹⁴N¹⁵NO.

EXPERIMENTAL

Potassium *N*-nitrosohydroxylamine-*N*-sulfonate was prepared according to literature methods (7). The concentration of this ion was monitored by measuring its uv

band at 2580 Å on either a Cary 14 or Bausch and Lomb Spectronic 700 spectrophotometer. Solutions were prepared of 1.0 × 10⁻² *F* H₃BO₃, 0.1 *F* KH₂PO₄, 0.1 *F* K₂HPO₄, and a stock SN₂O₅²⁻ solution containing 30 mg of K₂SN₂O₅, stabilized by 21 mg of KOH, and 52 mg of Na₂H₂-EDTA·2H₂O. The solutions were maintained in a constant temperature bath, 25°C, until ready for use, at which time samples of each buffer and SN₂O₅²⁻ solutions were added to the cell, and the absorbance at 2580 Å was recorded on a strip chart recorder. The pH was determined with a Fischer Accumet Model 230 pH/ion meter using standard reference buffer solutions.

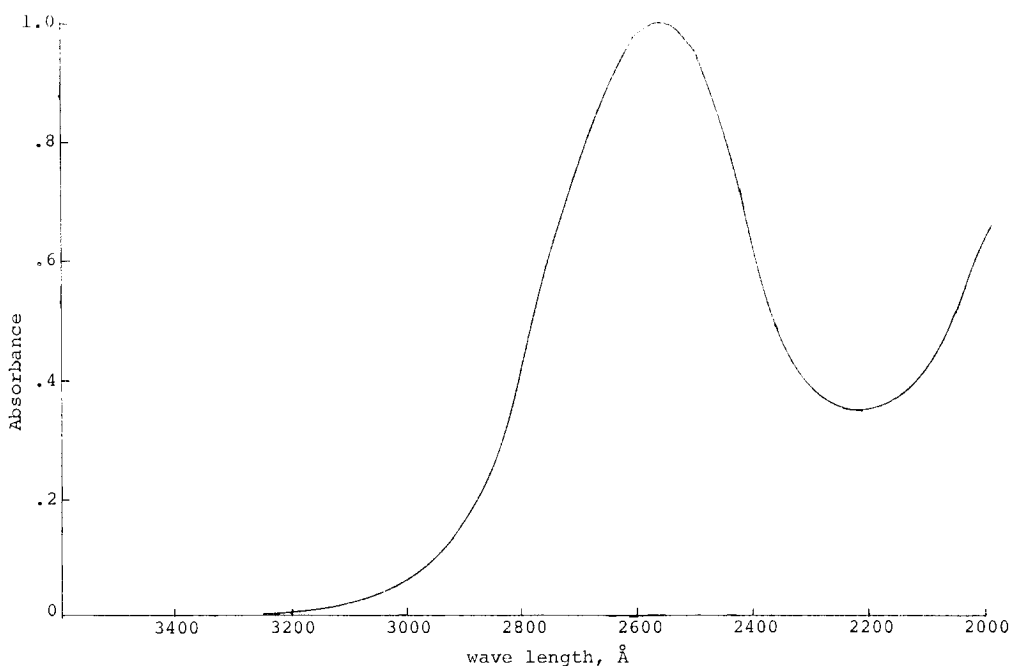


FIG. 1. Absorbance of $1.43 \times 10^{-4} M K_2SN_2O_5$.

Influence of $SN_2O_5^{2-}$. The absorbance of *N*-nitrosohydroxylamine-*N*-sulfonate was observed to decrease exponentially with time thereby suggesting a first-order rate law for the decomposition. Figure 1 depicts the uv spectrum of the $SN_2O_5^{2-}$ anion, and its absorbance at λ_{max} is plotted versus time in Fig. 2 for a typical decomposition experiment (Dtn 13).

Influence of $[H^+]$. The notation which follows is based on the following postulated kinetic rate law which (as will be explained) is supported by the experimental data:

$$-\frac{d \ln [SN_2O_5^{2-}]}{dt} \equiv k_{obs} = k_1[H^+] + k_2[H^+][H_3BO_3],$$

with

$$k_{H_3BO_3} \equiv k_2[H^+][H_3BO_3].$$

Data are recorded in Table 1 for different concentrations of buffer, boric acid, $SN_2O_5^{2-}$ ion, and various values of pH, temperature, and ionic strength. The recorded values of $k_1[H^+]$ have all been corrected to 25°C

and infinite dilution using the activation energy and ionic strength dependence previously published by Seel and Winkler.

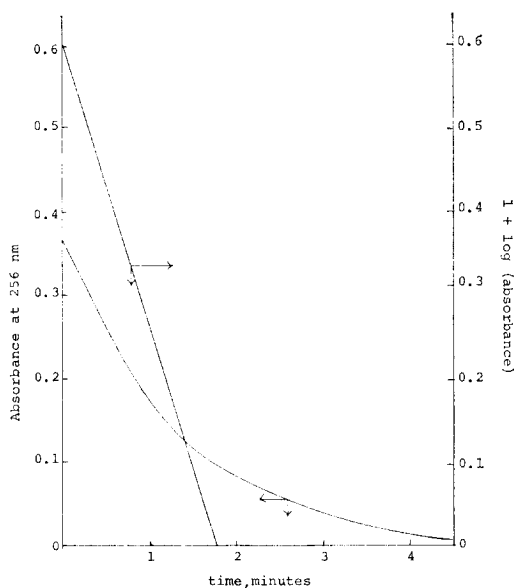


FIG. 2. Absorption and subsequent log plot vs time showing first-order decomposition of $SN_2O_5^{2-}$. Data from determination 13, Table 1.

TABLE 1
Decomposition of *N*-Nitrosohydroxylamine-*N*-sulfonate

Dtn ^a	Concentrations (<i>M</i>)		pH	<i>T</i> ^b (°C)	<i>I</i> (×10 ³)	<i>k</i> _{obs} (min ⁻¹)	<i>k</i> ₁ [H ⁺] ^c (min ⁻¹)	<i>k</i> _{H₃BO₃} (min ⁻¹)	log <i>k</i> ₂ ^d
	SN ₂ O ₃ ²⁻ (×10 ⁵)	Acid (×10 ³)							
1	10.0	0.6	4.0	25.5	5.4	8.8 × 10 ⁻⁴	1.4 × 10 ⁻⁴	7.4 × 10 ⁻⁴	10.03
2	10.0	4.5	4.5	25.5	5.4	0.034	0.001	0.033	9.88
3	10.0	4.5	9.1	25.5	9.9	0.019	0.001	0.019	9.91
4	10.0	0.91	9.1	25.5	4.9	0.0021	0.0003	0.0018	9.88
5	10.0	2.3	4.5	25.5	5.4	0.0104	0.0006	0.0098	9.92
6	10.0	13.5	13.5	25.5	55	Nil	—	—	—
7	6.3	48	48	23	196	0.084	0.084	—	—
8	6.0	46	46	23	187	0.46	0.084	0.38	9.86
9	6.1	46	46	23	191	0.240	0.084	0.156	9.76
10	5.7	44	44	23	179	0.73	0.084	0.65	9.80
11	6.1	47	47	23	191	0.193	0.084	0.109	9.60
12	6.0	46	46	23	187	0.43	0.084	0.35	9.83
13	5.7	44	44	23	179	0.78	0.084	0.70	9.83
14-16	10.6	45.5	45.5	19.5	193	0.0631 ± 0.0003	—	—	—
17	10.6	45.5	45.5	16.2	193	0.0195	0.0195	—	—
18	10.1	44	44	16.5	185	0.110	0.020	0.090	9.25
19	9.7	42	42	16.5	177	0.197	0.020	0.177	9.26
20	9.3	40	40	16.5	170	0.278	0.020	0.258	9.26
21	10.1	44	44	16.6	185	0.117	0.020	0.097	9.28
22	9.7	42	42	16.6	177	0.200	0.021	0.179	9.26
23	9.3	40	40	16.7	170	0.28	0.021	0.26	9.24
24	9.0	39	39	16.8	163	0.35	0.022	0.32	9.26
25	9.0	39	39	16.8	163	0.36	0.022	0.33	9.27
26	10.6	46	46	17.0	193	0.0222	0.0222	—	—
27	10.6	46	46	25.5	183	0.104	0.104	—	—

TABLE 1—(Continued)

Dtn ^a	Concentrations (M)			pH	T ^b (°C)	I (× 10 ³)	k _{obs} (min ⁻¹)	k ₁ [H ⁺] ^c (min ⁻¹)	k _{H₃BO₃} (min ⁻¹)	log k ₃ ^d
	SN ₂ O ₅ ²⁻ (× 10 ⁵)	Acid (× 10 ³)	Base (× 10 ³)							
28	10.6	27	27	6.82	25.5	110	0.110	0.110	—	—
29	10.6	13.6	13.6	6.80	25.5	56	0.126	0.126	—	—
30	10.6	4.5	4.5	6.82	25.5	20	0.114	0.114	—	—
31	10.6	4.5	4.5	6.82	26.5	20	0.107	0.107	—	—
32	10.6	4.5	4.5	6.82	26.2	20	0.114	0.114	—	—
33	10.6	4.5	4.5	6.82	26.4	20	0.115	0.115	—	—
34	10.6	9.1	9.1	6.82	26.4	38	0.115	0.115	—	—
35	10.6	9.1	9.1	6.82	26.4	38	0.119	0.119	—	—
36	10.6	9.1	9.1	6.82	26.4	38	0.130	0.130	—	—
37	10.6	9.1	9.1	6.82	24.6	38	0.099	0.099	—	—
38	10.6	9.1	9.1	6.82	25.0	38	0.100	0.100	—	—
39	10.6	9.1	9.1	6.82	25.2	38	0.095	0.095	—	—
40	10.6	9.1	9.1	6.82	25.7	38	0.115	0.115	—	—
41	10.6	13.6	13.6	6.80	25.8	56	0.110	0.110	—	—
42	10.6	13.6	13.6	6.80	25.9	56	0.118	0.118	—	—
43	10.6	13.6	13.6	6.80	26.0	56	0.111	0.111	—	—
44	10.6	18.2	18.2	6.83	26.0	75	0.120	0.120	—	—
45	10.6	18.2	18.2	6.83	26.0	75	0.108	0.108	—	—
46	10.6	18.2	18.2	6.83	25.0	75	0.107	0.107	—	—
47	10.6	18.2	18.2	6.83	25.2	75	0.1003	0.1003	—	—
48	10.6	18.2	18.2	6.83	25.3	75	0.1049	0.1049	—	—
49	10.6	18.2	18.2	6.83	25.0	74	0.83	0.83	0.729	9.73
50	10.6	13.6	13.6	6.88	25.0	56	0.83	0.83	0.757	9.80
51	10.6	9.1	9.1	6.92	25.0	38	0.79	0.79	0.700	9.81
52	10.6	4.5	4.5	6.98	25.0	20	0.70	0.70	0.62	9.81
53	10.6	9.1	18.2	7.15	25.0	56	0.42	0.42	0.38	9.77
54	10.6	9.1	27.3	7.31	25.0	103	0.28	0.025	0.25	9.75

TABLE 1—(Continued)

Dtn ^a	Concentrations (M)			pH	T ^b (°C)	I (×10 ³)	k _{obs} (min ⁻¹)	k ₁ [H ⁺] ^c (min ⁻¹)	k _{H₃BO₃} (min ⁻¹)	log k ₂ ^d
	SN ₂ O ₃ ²⁻ (×10 ⁵)	Acid (×10 ³)	Base (×10 ³)							
55	10.6	9.1	36.4	9.1	7.45	130	0.20	0.017	0.18	9.75
56	10.6	9.1	45.5	9.1	7.55	158	0.160	0.012	0.148	9.76
57	10.6	27.3	27.3	9.1	6.83	110	0.82	0.080	0.79	9.77
58	10.6	18.2	9.1	9.1	6.54	47.3	1.56	0.183	1.38	9.72
59	10.6	27.3	9.1	9.1	6.42	56.4	2.59	0.24	2.35	9.83
60	10.6	41	41	9.1	6.83	169	0.94	0.63	0.88	9.81
61	10.6	45	50	9.1	7.83	156	0.083	0.0064	0.077	9.75
62	10.6	—	—	9.1	7.98	1.0	0.041	0.0125	0.028	9.47
63	10.6	16.1	16.1	9.7	6.80	66	1.07	0.127	0.95	9.79
64	10.6	16.1	16.1	9.7	6.80	66	1.08	0.127	0.96	9.79
65	10.6	16.1	16.1	9.7	6.80	66	1.14	0.127	1.01	9.82
66	10.6	16.1	16.1	9.7	6.80	66	1.12	0.127	0.99	9.81
67	10.6	6.5	25.8	9.7	7.72	89	0.123	0.0139	0.109	9.89
68	10.6	6.5	25.8	9.7	7.72	89	0.138	0.0139	0.124	9.95
69	10.6	6.5	25.8	9.7	7.72	89	0.121	0.0139	0.107	9.89
70	10.6	6.5	25.8	9.7	7.72	89	0.142	0.0139	0.127	9.96
71	10.6	0.5	22.1	9.7	7.41	58	0.0533	0.0533	—	—
72	10.6	16.1	16.1	9.7	6.80	70	1.29	0.21	1.08	9.88
73	10.6	16.1	16.1	9.7	6.80	70	1.41	0.21	1.20	9.89
74	10.6	16.1	16.1	9.7	6.80	70	1.37	0.21	1.17	9.88

^a Acid = H₃BO₃ for Dtn 1-5, NaH₂BO₃ for Dtn 6, KH₂PO₄ for Dtn 7-74; base = NaH₂BO₃ for Dtn 1-5, Na₂HBO₃ for Dtn 6, K₂HPO₄ for Dtn 7-74. Temperatures of cell were assumed equal to ambient room temperature for Dtn 7-26; for other determinations temperature of liquid in cell was measured directly at end of experiment.

^b k_1 [H⁺] values in this table were calculated directly from our experimental results in cases where no H₃BO₃ was present. When H₃BO₃ was present the value of k_1 [H⁺] recorded is that obtained from the best value of k_1 , the known value of [H⁺], an Arrhenius temperature correction, and an ionic-strength correction computed from the form of the Bronsted equation reported by Seel and Winkler.

^d Units of k_2 are liters²/mol²-min.

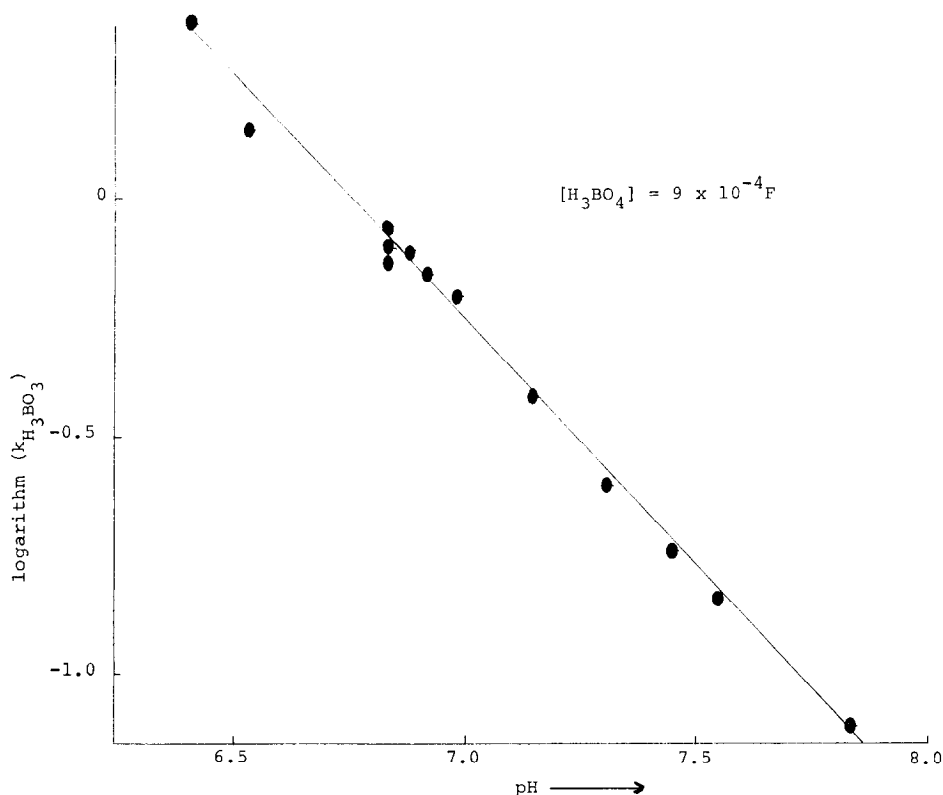


FIG. 3. pH dependence of the boric acid-catalyzed decomposition of *N*-nitrosohydroxylamine-*N*-sulfonate. The slope of 1.04 shows a direct dependence on the activity of H^+ . Units of $k_{H_3BO_3}$ are minute^{-1} . See Dtn 49-62 of Table 1.

The graph of $\log(k_{H_3BO_3})$ vs pH plotted in Fig. 3 has a slope of -1 in accord with the foregoing kinetic rate law which postulates that the H_3BO_3 -catalyzed decomposition is also specific acid-catalyzed and first order in $[H^+]$, i.e., $k_{H_3BO_3} \sim [H^+]$. At the H_3BO_3 composition $[9 \times 10^{-4} F]$ corresponding to Fig. 3 the rate of $SN_2O_5^{2-}$ decomposition is increased eightfold over the case of no H_3BO_3 but identical temperature, pH, and ionic strength.

Influence of ionic strength. Using the following relationships,

$$\log(k_1) = \log(k_1[H^+]) + \text{pH},$$

$$\log(k_2[H_3BO_3]) = \log k_{H_3BO_3} + \text{pH},$$

the values of $\log(k_1)$ and $\log(k_2[H_3BO_3])$ are plotted versus $\log(\gamma_{\pm}) = 0.509(I)^{1/2}/[1 + (I)^{1/2}]$ in Figs. 4a and 4b, respectively;

here I is the ionic strength. The slope of the Fig. 4a graph for the (non-boric acid) acid catalysis is -2.7 and close to the value of -3.02 observed by Seel and Winkler (4) thereby indicating reactive species of opposite charge. The slight offset of the Seel and Winkler data from our own measurements might possibly be ascribed to different concentrations of EDTA used in the different investigations. The data plotted in Fig. 4b for constant, non-zero H_3BO_3 concentration suggest a line of zero slope, thereby indicating that in the H_3BO_3 -catalyzed reaction one of the reactant species entering the rate-determining step is of zero electric charge.

Effect of H_3BO_3 . The data of Dtn 17-26, at essentially constant pH (6.93) and temperature ($\approx 17^\circ\text{C}$), are plotted in Fig. 5

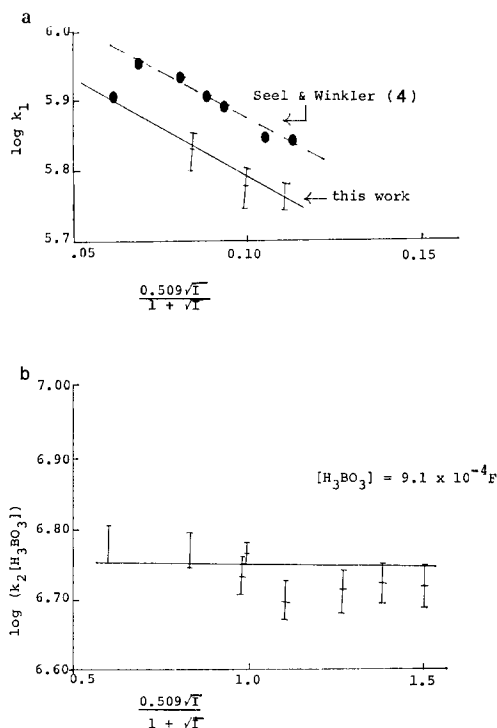


FIG. 4. Effect of ionic strength on rate of (a) acid-catalyzed decomposition and (b) H_3BO_3 -catalyzed decomposition. (a) Acid-catalyzed decomposition: Variation with ionic strength shows slope of 2.7 for current measurements (solid line) and 3.02 for data of Seel and Winkler (dotted line) indicating a +1 charge on the activated complex. Units of k_1 are minutes $^{-1}$. See Dtn 27-48. (b) Boric acid-catalyzed decomposition: Variation with ionic strength shows zero slope thereby suggesting that the activated complex does not involve the combination of two charged species. Units of $k_2[\text{H}_3\text{BO}_3]$ are liter-mole $^{-1}$ -minute $^{-1}$. See Dtn 49-55.

versus $[\text{H}_3\text{BO}_3]$ to demonstrate the linear dependence of k_{obs} on boric acid concentration in accord with the postulated rate law. To show further that only H_3BO_3 (and not borate ion species) is involved in the reaction, Dtn 1-7 were conducted at constant temperature but at differing values of pH and I by using various proportions of 0.1 F H_3BO_3 and 0.1 F NaOH in the reaction mixture. The results are plotted in Fig. 6 as $\log(k_2[\text{H}_3\text{BO}_3])$ vs $\log([\text{H}_3\text{BO}_3])$ thereby producing a straight line with a slope very close to unity as expected for first-order catalysis involving only H_3BO_3

and not H_2BO_3^- or HBO_3^{2-} . Thus $k_{\text{H}_3\text{BO}_3} = k_2[\text{H}^+][\text{H}_3\text{BO}_3]$ in accord with the postulated rate law.

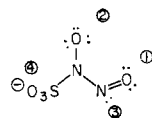
Effect of temperature. Corresponding values of k_2 and temperature are tabulated in Table 2 and plotted as $\log(k_2/T)$ vs $1/T$ in Fig. 7. The slope and intercept of this graph provide estimates of $\Delta H^* = 7.8$ kcal/mol and $\Delta S^* = -43$ cal/ $^\circ\text{K}$ in the expression

$$k_2 = \frac{RT}{Nh} \exp\left(\frac{+\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right),$$

where R , T , N , and h have the usual symbolism. A similar treatment of our data for k_1 gives $\Delta H^* = 13.8 \pm 0.2$ and $\Delta S^* = 15.8 \pm 1.4$ for the acid-catalyzed reaction as compared to the corresponding values of 14.05 kcal/mol and 17.4 cal/ $^\circ\text{K}$ found previously (4).

DISCUSSION

Because ionic strength does not influence k_2 , the activated complex of this reaction may well be formed by the attack of H_3BO_3 , a neutral species, on HSN_2O_5^- . The latter ion is the activated complex previously postulated (4) for the acid-catalyzed decomposition in the absence of boric acid. Because the activation enthalpy ($\Delta H^* = 7.8$ kcal/mol) for the reaction involving H_3BO_3 is less than the corresponding value for the formation of HSN_2O_5^- (reported as 14.05 kcal/mol by Seel and Winkler), the site of protonation may be different in each case. Assuming that any lone pair of electrons can be protonated, then the complex:



may have the following sites for proton attack: A. oxygen atoms {1} or {2} attached to nitrogen; B. the nitrogen atom {3} not attached to sulfur; C. a sulfite

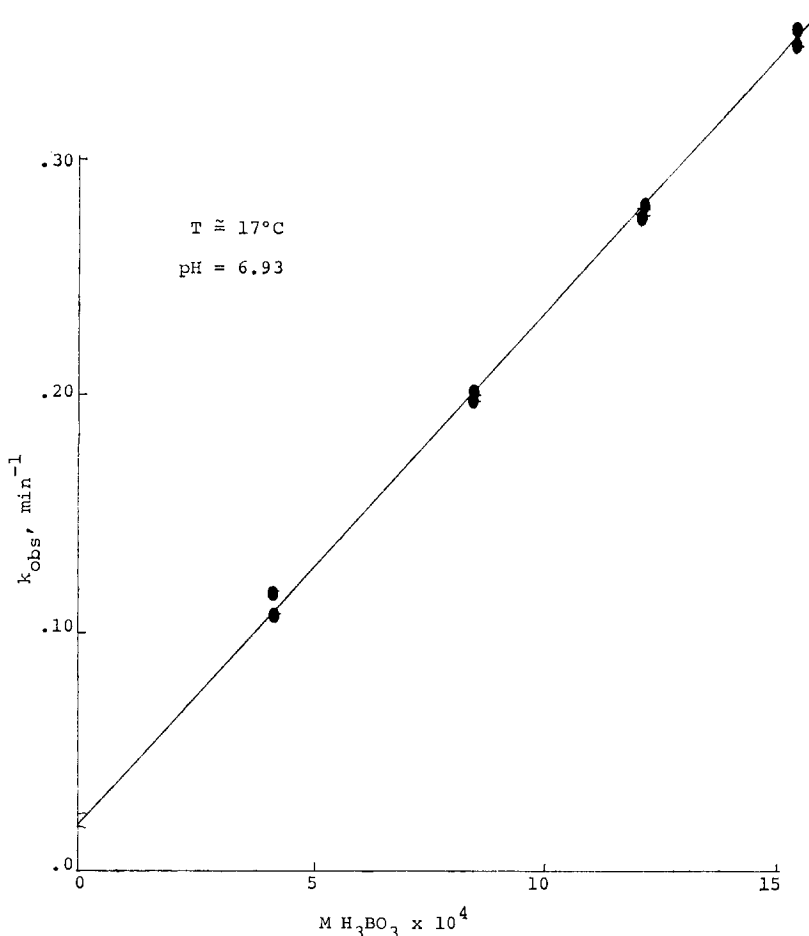
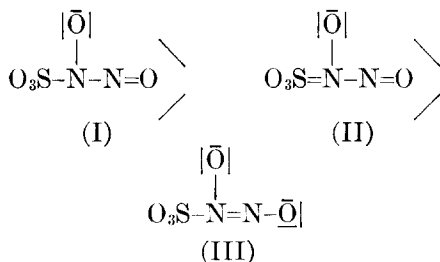


FIG. 5. Effect of boric acid concentration on the decomposition of *N*-nitrosohydroxylamine-*N*-sulfonate at pH 6.93 and 16–17°C. See Dtn 17–26 of Table 1.

oxygen {4}. If the activation energy is of the same order as the pK for each site, then the reaction site probability sequence would be $2 < 4 < 3 < 1$. Drago (8) indicates from ir evidence that there is considerable single-bond character in the N–N bond and he postulates that resonance structures I, II, and III are most significant:



Cox *et al.* (9) and Evans and Gergely (10) assign double-bond character to the N=N bond.

If we consider the decomposition to proceed by the formation of N=N and weakening of the S–N bond, protonation of oxygen {1} would be the choice for acid-catalyzed decomposition. This would not take place as readily as protonation at oxygen {2} which would be the most probable site for protonation of the active intermediate in the H_3BO_3 -catalyzed decomposition. A specific interaction involving H_3BO_3 with HSN_2O_5^- must occur to form a complex which easily dissociates to N_2O . An interaction in which $\text{B}(\text{OH})_3$ acts

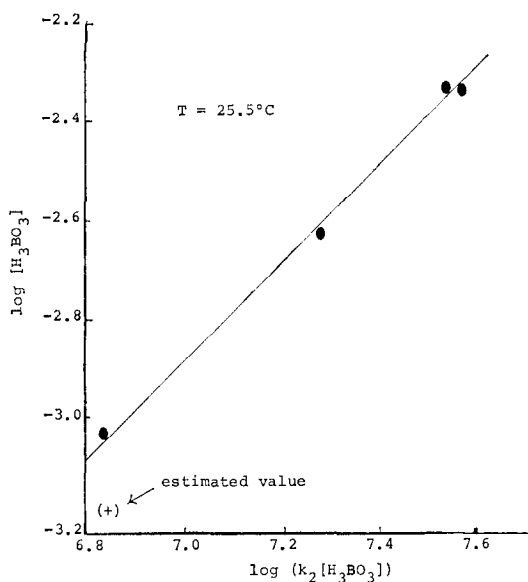


Fig. 6. Specific catalysis of H_3BO_3 in decomposition of $\text{SN}_2\text{O}_5^{2-}$ in boric acid buffer. Slope of 1.02 is consistent with first-order dependence on the H_3BO_3 activity. Units are: $[\text{H}_3\text{BO}_3]$, moles per liter; and $k_2[\text{H}_3\text{BO}_3]$, liter-mole $^{-1}$ -minute $^{-1}$. See Dtn 1-7 of Table 1.

TABLE 2

Temperature Dependence of the Boric Acid-Catalyzed Decomposition of *N*-Nitrosohydroxylamine-*N*-sulfonate^a

Dtn	<i>T</i> (°C)	<i>k</i> _{obs} ^b	pH	log (<i>k</i> ₂) ^c
75	19.2	0.302	7.78	9.60
76	19.5	0.303	7.78	9.60
77	19.7	0.328	7.78	9.64
78	25.3	0.429	7.77	9.75
79	25.4	0.435	7.76	9.74
80	25.2	0.408	7.79	9.74
81	28.9	0.491	7.80	9.83
82	28.9	0.537	7.76	9.83
83	28.8	0.483	7.77	9.80
84	32.0	0.602	7.76	9.88
85	32.3	0.590	7.77	9.88
86	32.5	0.580	7.78	9.89

^a Composition is $9.1 \times 10^{-4} M \text{KH}_2\text{PO}_4$, $8.18 \times 10^{-3} M \text{K}_2\text{HPO}_4$, $4.5 \times 10^{-3} M \text{H}_3\text{BO}_3$, and $1.5 \times 10^{-4} M \text{K}_2\text{SN}_2\text{O}_5$. The acid-catalyzed reaction was about 1% of the boric acid-catalyzed reactions under the stated conditions.

^b Units of *k*_{obs} are minutes $^{-1}$.

^c Units of *k*₂ are liters 2 - mole $^{-2}$ - minute $^{-1}$.

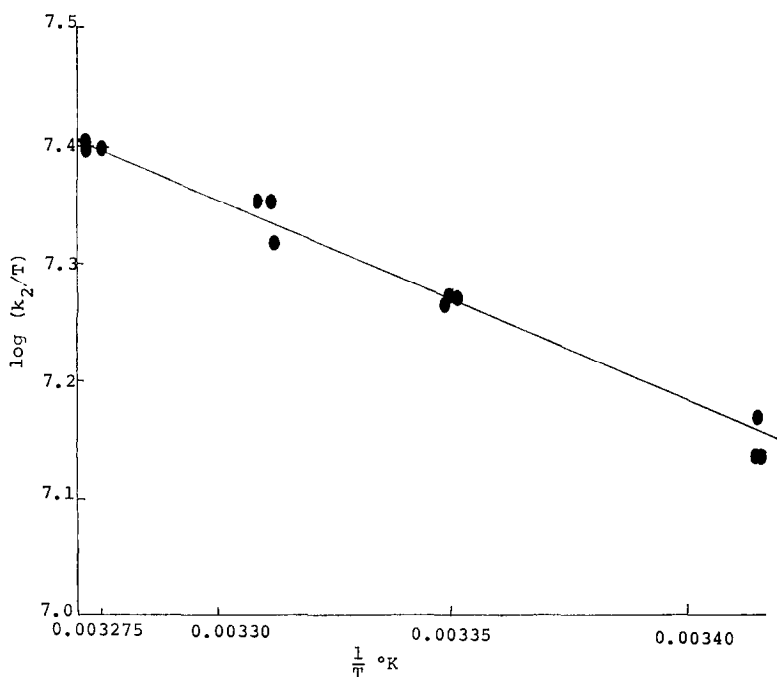
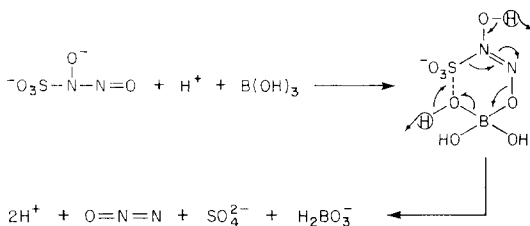


Fig. 7. Temperature variation of H_3BO_3 -catalyzed decomposition of $\text{SN}_2\text{O}_5^{2-}$. The value determined for ΔH is 7.8 kcal/mol and S^* is -43 cal/°K. Data are taken from Dtn 75-86 of Table 2. Units of k_2/T are liters 2 -moles $^{-2}$ -minute $^{-1}$ -°K $^{-1}$.

as an acceptor of electrons from oxygen {1} would permit one of the OH groups to interact with the SO_3^- moiety to form a sulfur penta-coordinated species according to the reaction scheme:



This would also account for the very large negative ΔS^* which is observed for this reaction.

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