Registry No. Cr, 7440-47-3; HSCN, 463-56-9.

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Kinetics of the Boric Acid Catalyzed Decomposition of the *N*-Nitrosohydroxylamine-*N*-sulfonate Ion

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The decomposition of the *N*-nitrosohydroxylamine-*N*-sulfonate ion, $ON(SO_3^-)NO^-$, to nitrous oxide and sulfate ion follows the rate law, $-d[ON(SO_3^-)NO^-]/dt = k_1K_1[ON(SO_3^-)NO^-][H^+]$, in the pH range 6–10. K_1 is the equilibrium constant for protonation of $ON(SO_3^-)NO^-$ and k_1 is the rate constant for decomposition of the $ON(SO_3^-)NOH$ ion. Values of k_1K_1 are $4.9 \pm 1.0 \times 10^3$, $9.0 \pm 1.6 \times 10^3$, and $18.9 \pm 4.3 \times 10^3$ M^{-1} sec^{-1} at 15, 25, and 35°, respectively. Activation parameters are $\Delta H^{\ddagger} = 11.4 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2 \pm 3$ eu. *cis*-Hyponitrite is proposed as an intermediate in the decomposition. At pH >13 and temperatures above 35° the decomposition rate increases markedly with increasing hydroxide ion concentration but no simple rate expression was found. The decomposition of $ON(SO_3^-)NO^-$ is specifically catalyzed by boric acid. In the pH range 6–10 the boric acid pathway follows the rate law, $-d[ON(SO_3^-)NO^-]/dt = k_3K_1[H^+]^2[ON(SO_3^-)NO^-][B(OH)_3]/(K_B + [H^+])$, where K_B is the ionization constant of boric acid and k_3 is the rate constant for the reaction of $B(OH)_3$ with $ON(SO_3^-)NOH$. Values of k_3K_1 are $4.2 \pm 0.2 \times 10^7$, $6.2 \pm 0.4 \times 10^7$, and $8.0 \pm 0.2 \times 10^7$ M^{-2} sec^{-1} at 15, 25, and 35°, respectively. $K_B = 6.8 \pm 1.2 \times 10^{-10}$ M at 25°. Activation parameters are $\Delta H^{\ddagger} = 5 \pm 1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6 \pm 2$ eu. A mechanism is proposed in which $B(OH)_3$ coordinates to one of the SO_3 group oxygen atoms of $ON(SO_3^-)NOH$ to promote N–S bond cleavage. $B(OH)_4^-$, lacking additional coordinating ability, does not enhance the rate of $ON(SO_3^-)NO^-$ decomposition.

Introduction

The decomposition of *N*-nitrosohydroxylamine-*N*-sulfonate ion, $ON(SO_3^-)NO^-$, has been studied by Seel and Winkler in the pH range 7–8 at very low ionic strength.[1] Their work in phosphate buffers demonstrated that the decomposition to nitrous oxide and sulfate was specifically catalyzed by hydrogen ion. These authors also reported a specific catalytic effect by borate buffers on $ON(SO_3^-)NO^-$ decomposition but did not investigate this effect. This specific borate buffer catalysis was also noted in the characterization of $ON(SO_3^-)NO^-$ as the product arising from air oxidation of hydroxylamine-*N*-sulfonate ion, $HONHSO_3^-$, in alkaline solution.[2] We now report the results of a study of the kinetics of the decomposition of $ON(SO_3^-)NO^-$ over a broad pH range in the presence of added boric acid. In the course of this study we have had occasion to examine the decomposition of $ON(SO_3^-)NO^-$ in the absence of boric acid over a more extended pH range than was previously studied and report this work as well.

Experimental Section

Materials. Dipotassium *N*-nitrosohydroxylamine-*N*-sulfonate, $K_2N_2O_2SO_3$, was prepared and stored as described.[3] It assayed spectrophotometrically at 99% purity.[2] All other chemicals were reagent grade and used without further purification.

Stoichiometry. Under all conditions studied the reaction stoichiometry for $ON(SO_3^-)NO^-$ decomposition corresponds to the equation

$$N_2O_2SO_3^{2-} \rightarrow N_2O + SO_4^{2-}$$

The gaseous product was analyzed by infrared spectrometry and gas chromatography. For the chromatographic analysis a 2-m column of 40-50 mesh 5A Molecular Sieve (Varian Aerograph) was used with hydrogen carrier gas. Sulfate was determined gravimetrically as barium sulfate.

Kinetic Procedure. Buffer solutions were prepared from sodium hydroxide, sodium hydrogen carbonate, sodium carbonate, sodium dihydrogen phosphate, sodium hydrogen phosphate, and sodium phosphate. The desired ionic strength was achieved by adjusting the concentrations of the reagents used to prepare the buffer. The pH was measured with a glass electrode on a Beckman Expandomatic pH meter or was calculated from the sodium hydroxide concentration and the ion product of water at the temperature of the kinetic run. The initial concentration of $ON(SO_3^-)NO^-$ was $2\text{-}3.5 \times 10^{-4}$ M. Since heavy-metal ions are known to catalyze the decomposition of $ON(SO_3^-)NO^-$,[1] ethylenediaminetetraacetic acid was added to all runs. Concentrations of 10^{-3}–10^{-5} M were employed and gave reproducible kinetics in this range.

The decomposition of $ON(SO_3^-)NO^-$ was followed spectrophotometrically at 2580 Å (ϵ 7140)[2] on a Gilford-modified Beckman DU spectrophotometer which was thermostated at the desired reaction temperature. For reactions at pH less than 9.5, kinetics were followed continuously in the thermostated spectrophotometer. Reactions at higher pH were carried out in thermostated flasks under a nitrogen atmosphere to prevent oxidation of $ON(SO_3^-)NO^-$ by atmospheric oxygen.[2] Aliquots were withdrawn periodically for spectrophotometric measurements. Runs were extended to at least 2 half-lives except for the slowest ones at high pH and low temperatures. All runs gave good first-order fits for $ON(SO_3^-)NO^-$ decomposition kinetics as determined by graphical analysis.

Results and Discussion

Studies in the Absence of Boric Acid. All kinetic runs for the decomposition of $ON(SO_3^-)NO^-$ fit the simple first-order relationship

$$\text{rate} = k_{\text{obsd}}[ON(SO_3^-)NO^-]$$

Values obtained for k_{obsd} are plotted in Figure 1 as a function of pH. These plots suggest that $ON(SO_3^-)NO^-$ decomposes by at least two different pathways.

In solutions more acidic than pH 9, k_{obsd} is directly proportional to the hydrogen ion concentration and the rate law has the form

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(1) F. Seel and R. Winkler, *Z. Naturforsch., A*, 18, 155 (1963).

(2) M. N. Ackermann and R. E. Powell, *Inorg. Chem.*, 6, 1718 (1967).

(3) S. Nyholm and L. Rannitt, *Inorg. Syn.*, 5, 115 (1957).

$$\text{rate} = k_H[H^+][ON(SO_3^-)NO^-]$$

This agrees with the rate law previously found in the narrower pH range 7-8.[1] Since our data were obtained using both $H_2PO_4^-$-HPO_4^{2-} and HCO_3^--CO_3^{2-} buffers and with varied concentrations of buffer components, there appears to be no evidence for general acid catalysis. Values for k_H at an ionic strength of 0.50 M derived from Figure 1 are $4.9 \pm 1.0 \times 10^3$, $9.0 \pm 1.6 \times 10^3$, and $18.9 \pm 4.3 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ at 15, 25, and 35°, respectively.[4] These values of k_H are smaller than those reported at zero ionic strength as is expected from the observed effect of ionic strength on rate.[1] The enthalpy and entropy of activation are 11.4 ± 1.0 kcal mol^{-1} and -2 ± 3 eu compared with the previously determined values of 14.3 $\pm$ 0.4 kcal mol^{-1} and 9 ± 1 eu at zero ionic strength.[5] The difference in the two sets of activation parameters seems greater than can be attributed to ionic strength effects. We believe our values to be more reliable since the literature values, while derived from a temperature range of 20-40°, are based on only one experiment at 30, 35, and 40°.[1]

We propose the following mechanism for the acid-dependent reaction.

$$ON(SO_3^-)NO^- + H^+ \overset{K_1}{=} ON(SO_3^-)NOH \qquad (1)$$

$$ON(SO_3^-)NOH + H_2O \xrightarrow{k_1} cis\text{-}HONNO^- + SO_4^{2-} + 2H^+ \qquad (2)$$

$$cis\text{-}HONNO^- \xrightarrow{\text{fast}} N_2O + OH^- \qquad (3)$$

In the rate law $k_H = k_1K_1$. The ion $ON(SO_3^-)NOH$ decomposes too rapidly to permit a separate determination of K_1 and thereby k_1. The separate formation of *cis*-hyponitrous acid rather than direct formation of nitrous oxide from $ON(SO_3^-)NOH$ follows from the work of Clusius and Schumacher.[6] These authors prepared $ON(SO_3^-)NO^-$ selectively labeled with N-15 at the nitrogen atom to which the SO_3 group is *not* bonded. Since they found that equal quantities of $N^{15}NO$ and ^{15}NNO were produced in the acid decomposition, an intermediate is required which permits the two nitrogen atoms to become equivalent before N_2O formation. In *cis*-HONNO$^-$ this equivalence can be accomplished by proton exchange with the solvent at the two oxygen atoms. Since proton-transfer reactions are extremely rapid, *cis*-HONNO$^-$ may easily be long-lived relative to proton exchange but still decompose too rapidly to be observable in our studies.

Previous workers were unable to decide whether the cis or the trans form of hyponitrous acid was an intermediate in the acid decomposition of $ON(SO_3^-)NO^-$.[1] We have selected the cis form as the intermediate based upon our failure to detect the ultraviolet absorption spectrum of *trans*-HONNO$^-$ in runs at pH 6.[7] Under these conditions the rate of decomposition of $ON(SO_3^-)NO^-$ is at least a factor of 10 greater than that of *trans*-HONNO$^-$ which, if formed, should accumulate to a detectable level. No kinetic measurements on *cis*-hyponitrous acid have been reported, but its salts decompose rapidly when dissolved in aqueous solutions.[8] The steady-state concentration of *cis*-HONNO$^-$ is probably too low to be detectable in our reaction system. The intermediacy of *cis*-HONNO$^-$ reflects the configuration of the hyponitrite group in $ON(SO_3^-)NO^-$.[9] The nitrogen-nitrogen bond has partial double bond character and is not expected to undergo rotation to the trans configuration readily.

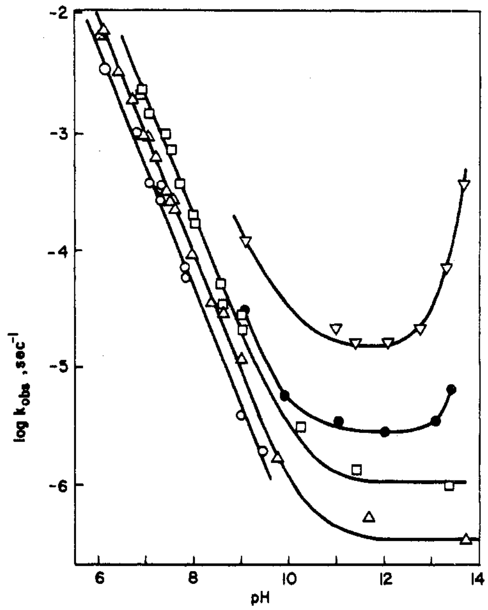

Figure 1. Dependence of the logarithm of the pseudo-first-order rate constant for the decomposition of $ON(SO_3^-)NO^-$ on pH: circles, 15.0°; triangles, 25.0°; squares, 35.0°; full-shaded circles, 45.0°; inverted triangles, 60.0°. $\mu = 0.50\ M$ with the following exceptions: at 45.0°, $\mu = 1.0\ M$ at pH 13.40; at 60.0°, $\mu = 1.0\ M$ at pH 13.02, $\mu = 2.1\ M$ at pH 13.34, and $\mu = 4.5\ M$ at pH 13.68. The set of three parallel lines at the left of the figure are drawn with a slope of −1.

At pH values above 10 the rate of $ON(SO_3^-)NO^-$ decomposition begins to level off and then at higher temperatures starts to increase markedly with increasing pH. Since these runs were made under an atmosphere of nitrogen and no nitrite was found among the reaction products, the faster than expected rates cannot be due to the oxidation reaction (eq 4) which occurs at high pH.[2] When no precautions were

$$O_2 + ON(SO_3^-)NO^- + 2OH^- \rightarrow 2NO_2^- + SO_4^{2-} + H_2O \qquad (4)$$

taken to exclude atmospheric oxygen, nitrite was formed and the decomposition rate was increased. Catalysis by heavy-metal ions is also ruled out since substantially increasing the ethylenediaminetetraacetate ion concentration in the solution did not decrease the rate.

Both a pH-independent and a hydroxide-dependent reaction may be important above pH 10. However, the data at temperatures below 60° provide no information about the hydroxide dependence of $ON(SO_3^-)NO^-$ decomposition and the data at 60° do not permit a clear determination of the order of the hydroxide dependence. Values at 60° for pH, k_{obsd} (sec^{-1}), and ionic strength are: 9.10, 1.2×10^{-4}, 1.0; 11.0, 2.2×10^{-5}, 1.0; 11.4, 1.7×10^{-5}, 1.0; 12.1, 1.7×10^{-5}, 1.0; 12.7, 1.9×10^{-5}, 1.0; 13.3, 7.4×10^{-5}, 2.1; 13.7, 3.7×10^{-4}, 4.5. Above pH 13 the rate increases more rapidly than the first power of the hydroxide ion concentration. This rate increase is too great to be due to the ionic strength differences. At these high hydroxide concentrations correlation of the rate data with a basicity function[10] would be desirable

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(4) For this and subsequent calculations standard deviations are cited as uncertainties.

(5) These latter values have been recalculated from the data in ref 1 using the standard state of moles per liter rather than that of moles per milliliter.

(6) K. Clusius and H. Schumacher, *Helv. Chim. Acta*, **40**, 1137 (1957).

(7) J. R. Buchholz and R. E. Powell, *J. Amer. Chem. Soc.*, **85**, 509 (1963).

(8) R. W. Asmussen, *Acta Chem. Scand.*, **11**, 1435 (1957).

(9) G. A. Jefferey and H. P. Stadler, *J. Chem. Soc.*, 1783 (1949); 1467 (1951).

(10) C. H. Rochester, "Acidity Functions," Academic Press, New York, N. Y., 1970.

but the data are not extensive enough to permit such an analysis.

Studies with Added Boric Acid. A series of runs were carried out in which the amount of boric acid was varied but the pH held constant. All runs gave good first-order kinetics. A plot of the observed pseudo-first-order rate constant, k, *vs.* the concentration of total boric acid present fits the relationship

$$k = k_A + k_B[B(OH)_3]_T$$

where $[B(OH)_3]_T$ represents the total concentration of boric acid added irrespective of its actual form in the solution. A typical plot to determine k_A and k_B for such a set of runs is shown in Figure 2. The rate constants determined in this manner at a number of pH values and temperatures and a constant ionic strength of 0.50 M are collected in Table I. The k_A term is the same as that found for the hydrogen ion catalyzed pathway discussed above and is numerically equal to $k_H[H^+]$. The k_B values decrease with increasing pH. At low pH the k_B term exhibits a simple first-order dependence on hydrogen ion concentration as shown by the constant value of $k_B/[H^+]$. At high pH $k_B/[H^+]$ decreases with increasing pH.

The predominant boron-containing species present at the low concentrations of total boric acid used in this study are the monomeric species $B(OH)_3$ and $B(OH)_4^-$.[11] The first-order dependence of the k_B term on total boric acid concentration supports catalysis by a monomeric boron-containing species. The decreasing value of the ratio $k_B/[H^+]$ with increasing pH suggests that the active species is $B(OH)_3$ which becomes a smaller fraction of the total boric acid present at higher pH values. We therefore propose the following mechanism for the boric acid catalyzed decomposition of $ON(SO_3^-)NO^-$.

$$ON(SO_3^-)NO^- + H^+ \overset{K_1}{=} ON(SO_3^-)NOH \tag{1}$$

$$B(OH)_3 + H_2O \overset{K_B}{=} B(OH)_4^- + H^+ \tag{5}$$

$$ON(SO_3^-)NOH + B(OH)_3 \xrightarrow{k_3} B(OH)_3 + N_2O + HOSO_3^- \tag{6}$$

For this mechanism the rate law is

$$\text{rate} = k_3K_1[H^+]^2[ON(SO_3^-)NO^-][B(OH)_3]_T/(K_B + [H^+])$$

or

$$\text{rate} = k_B[ON(SO_3^-)NO^-][B(OH)_3]_T \tag{7}$$

where

$$k_B = k_3K_1[H^+]^2/(K_B + [H^+]) \tag{8}$$

and K_B is the ionization constant of boric acid. The expression for k_B may be rearranged to

$$k_B = k_3K_1[H^+] - k_BK_B/[H^+] \tag{9}$$

which when treated by the method of least squares[12] yields $k_3K_1 = 6.2 \pm 0.4 \times 10^7\ M^{-2}\ sec^{-1}$ and $K_B = 6.8 \pm 1.2 \times 10^{-10}\ M$ at 25.0° and ionic strength 0.50 M.[4] These values are obtained using all of the data at 25° in Table I. The value of k_3K_1 may also be calculated from the low pH data only where eq 8 reduces to $k_B = k_3K_1[H^+]$. This approach gives $k_3K_1 = 6.1 \pm 0.4 \times 10^7\ M^{-2}\ sec^{-1}$ for the data at pH 6.10–7.53 inclusive. Assuming this latter value of k_3K_1 to be somewhat better, K_B may be calculated using only the data under conditions where ionization of $B(OH)_3$ to $B(OH)_4^-$ becomes significant. This yields $K_B = 7.7 \pm 1.5 \times 10^{-10}\ M$ for the data at pH 8.39–9.69. Within the uncertainty limits both approaches yield the same numbers. The value of K_B obtained from this kinetic study compares reasonably with that of $1.29 \times 10^{-9}\ M$ determined for the ionization of boric acid in 0.36 M sodium chloride solution at 25.0°.[13] Figure 3 compares experimental values of $k_B/[H^+]$ with those calculated from the theoretical expression $k_3K_1[H^+]/(K_B + [H^+])$ using our value of k_3K_1 and K_B from our work and that of Owen and King.

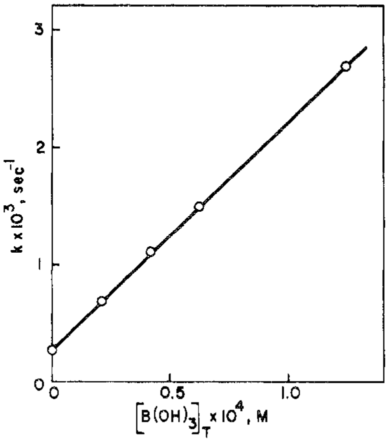

Figure 2. Dependence of k on total boric acid concentration at fixed pH: $T = 25.0°$, pH 7.53, $\mu = 0.50\ M$, $k_A = 2.7 \times 10^{-4}\ sec^{-1}$, $k_B = 1.8\ M^{-1}\ sec^{-1}$.

Table I. Rate Constants for the Boric Acid Catalyzed Decomposition of *N*-Nitrosohydroxylamine-*N*-sulfonate Ion[a]

pH	Max[b] $[B(OH)_3]_T$, $10^3\ M$	10^4k_A, sec^{-1}	k_B, $sec^{-1}\ M^{-1}$	$10^{-7}k_B/[H^+]$, $sec^{-1}\ M^{-2}$
		$T = 25.0°$		
6.10	1.37	70	48	6.1
6.40	0.15	32	22	5.5
6.68	0.39	19	13	6.2
7.18	6.55	5.9	4.4	6.6
7.51	3.90	2.5	2.0	6.4
7.53	12.4	2.7	1.8	6.1
8.39	17.2	0.34	0.20	4.9
8.96	24.2	0.12	0.037	3.4
9.30–9.57	101		0.0081	2.3[c]
9.51–9.69	40.4		0.0041	1.6[c]
		$T = 15.0°$		
6.12	0.50	33	31	4.1
6.80	1.00	9.7	6.8	4.3
		$T = 35.0°$		
6.86	10.0	21	11	8.0
7.36	25.0	9.6	3.5	8.0
7.68	5.00	3.6	1.7	8.0

[a] All data at ionic strength of 0.50 M. [b] $[B(OH)_3]_T$ represents the total concentration of boric acid added irrespective of its actual form in solution. [c] $[H^+]$ at the midpoint of the pH range quoted in column one was used for this calculation.

Values of k_3K_1 determined at 15.0 and 35.0° at low pH where all added boric acid is present as $B(OH)_3$ are given in Table I and are $4.2 \pm 0.2 \times 10^7$ and $8.0 \pm 0.2 \times 10^7\ M^{-2}\ sec^{-1}$, respectively. The enthalpy and entropy of activation for k_3K_1 are 5 ± 1 kcal mol^{-1} and −6 ± 2 eu. Both param-

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[11] N. P. Nies and G. W. Campbell, "Boron, Metallo-Boron Compounds and Boranes," R. M. Adams, Ed., Wiley, New York, N. Y., 1964, pp 72–76, 87–88.

[12] J. Mande, "The Statistical Analysis of Experimental Data," Wiley, New York, N. Y., 1964, Chapter 7.

[13] B. B. Owen and E. J. King, *J. Amer. Chem. Soc.*, **65**, 1612 (1943).

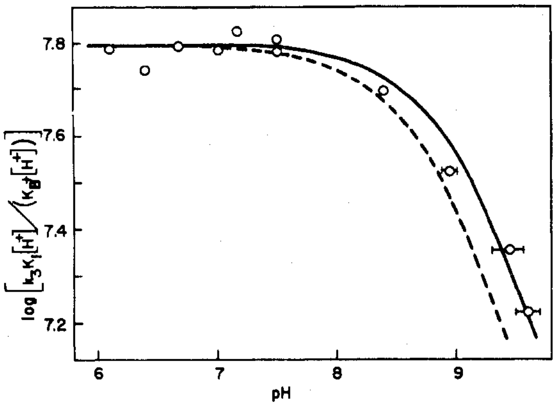

Figure 3. Comparison of experimental values of $k_B/[H^+]$ as a function of pH with the function $k_3K_1[H^+]/(K_B + [H^+])$ predicted by the proposed reaction mechanism: $k_3K_1 = 6.2 \times 10^7\ M^{-2}\ sec^{-1}$, $\mu = 0.50\ M$, $T = 25.0°$; dashed line, $K_B = 1.29 \times 10^{-9}$ from ref 13; continuous line, $K_B = 6.8 \times 10^{-10}$ from this work.

eters are numerically smaller than those found for the hydrogen ion catalyzed pathway.

N-Nitrosohydroxylamine-*N*-sulfonate and nitrohydroxamate, $^-ONNO_2^-$, may be viewed as *cis*-hyponitrite with an SO_3 group or oxygen atom added to one of the nitrogen atoms. Since decomposition of neither nitrohydroxamate nor *trans*-hyponitrite shows specific catalysis by borate buffers,[2] some specific interaction between the SO_3 group and $B(OH)_3$ would appear to be involved in the transition state for the decomposition of the sulfonate. An attractive possibility is coordination of the boron atom to one of the oxygen atoms of the SO_3 group as is found in $B(HSO_4)_4^-$ in concentrated sulfuric acid.[14] This coordination has the effect of reducing the electron density of the sulfur atom since one of its three oxygen atoms can no longer effectively donate electron density through p_π-d_π bonding. This facilitates breaking the N-S bond since the nitrogen atom already bears a positive formal charge of 1. Initial products from step 6 are then *cis*-$HONNO^-$ and $O_2SOB(OH)_3$. The latter hydrolyzes to sulfuric and boric acids while the *cis*-$HONNO^-$ decomposes as discussed earlier. Since $B(OH)_4^-$ is unable to undergo additional coordination, the catalytic activity of boric acid on the decomposition of $ON(SO_3^-)NO^-$ decreases at high pH.

The proposed mechanism requires that the isotopic experiment of Clusius and Schumacher[6] give equal amounts of ^{15}NNO and $N^{15}NO$ if carried out in the presence of boric acid. Unfortunately, the catalytic activity of boric acid was unknown to these authors and no such experiment was performed.

Solvated heavy-metal ions also catalyze the decomposition of $ON(SO_3^-)NO^-$ to form nitrous oxide and sulfate ion. Although their effect has not yet been the subject of a detailed study, we might anticipate that the activity of such metals arises from their coordination ability which would allow them to play a role similar to that which we have proposed for boric acid. The equal amounts of ^{15}NNO and $N^{15}NO$ found with cupric ions as a catalyst[6] are consistent with coordination at the SO_3 group and indirectly offer support for the boric acid model. However, metal ions have more than one potential coordination site and could also promote decomposition through the formation of a chelate complex utilizing both oxygen atoms of the *cis*-hyponitrite group in $ON(SO_3^-)NO^-$. Cleavage of the N-S bond then permits the two nitrogen atoms to become equivalent. With only one coordination site available boric acid cannot act in this way.

Registry No. $K_2N_2O_2SO_3$, 26241-10-1; $B(OH)_3$, 10043-35-3.

Acknowledgments. This work was supported by the National Science Foundation through a grant to Oberlin College. E. G. S. and G. A. D. were NSF undergraduate research participants.

[14] R. Flowers, R. J. Gillespie, and J. V. Oubridge, *J. Chem. Soc.*, 1925 (1956).

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Spectra and Structure of Phosphorus-Boron Compounds.[1] II. A Vibrational and Nuclear Magnetic Resonance Spectral Investigation of Phosphine-Trichloroborane

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The infrared (45-3000 cm^{-1}) and Raman (50-2700 cm^{-1}) spectra of $H_3P \cdot BCl_3$ and $D_3P \cdot BCl_3$ in the solid state at −196° have been recorded. The spectra have been interpreted on the basis of C_{3v} molecular symmetry and 11 of the 12 fundamental vibrations have been assigned. The molecule was found to be completely dissociated at 0° which is in marked contrast to its previously reported stability. The high frequency of the P-H stretching mode is consistent with a shortening of this bond with coordination. A normal-coordinate calculation was carried out and the force constant of 1.96 mdyn/Å for the P-B stretch is compared to the similar quantity of several other phosphorus-borane molecules. Nuclear magnetic resonance and infrared studies of a solution of $H_3P \cdot BCl_3$ in benzene suggest that the adduct is in equilibrium with the free acid and base.

Introduction

There have been several recent microwave investigations of phosphorus-borane compounds and a wide range of P-B bond distances have been determined. For example, in trifluorophosphine-borane[4] and difluorophosphine-borane[5] the P-B bond distance was found to be 1.836 ± 0.012 and

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[1] Part I: J. R. Durig, Y. S. Li, L. A. Carreira, and J. D. Odom, *J. Amer. Chem. Soc.*, **95**, 2491 (1973).

[2] Taken from the thesis of S. Riethmiller.[3]

[3] To be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.