Table V. Selected Bond Distances (Å) and Angles (deg) for 7

Te1–Cd1	2.744 (1)	Te1–Si1	2.519 (2)
Te2–Cd1	2.722 (1)	Te2–Si5	2.512 (3)
Cd1–P1	2.691 (2)	Cd1–P2	2.724 (3)
P1–C19	1.778 (11)	P1–C20	1.793 (12)
P1–C21	1.827 (11)	P2–C22	1.828 (10)
P2–C23	1.821 (11)	P2–C24	1.830 (11)
P1–Cd1–P2	78.50 (8)	P1–Cd1–Te1	97.01 (6)
P2–Cd1–Te2	108.98 (6)	P1–Cd1–Te2	115.41 (6)
P2–Cd1–Te2	96.37 (6)	Te1–Cd1–Te2	142.35 (3)
Cd1–Te1–Si1	107.55 (6)	Cd1–Te2–Si5	113.68 (6)
Cd1–P1–C19	118.6 (4)	Cd1–P1–C20	123.8 (5)
Cd1–P1–C21	104.2 (4)	Te1–Si1–Si2	102.27 (10)
Te1–Si1–Si3	114.12 (12)	Te1–Si1–Si4	109.95 (12)

basis of ionic radii (2.01 Å).[40] The Zn–Te bond lengths [2.579 (1) and 2.569 (1) Å] lie between the values determined for terminal and bridging Zn–Te interactions observed in **1**.

In order to remove any ambiguity regarding the structure of the labile cadmium–dmpe adduct **7** (see above), its crystal structure has also been determined. The compound crystallizes in the space group $P2_12_12_1$ with two independent molecules per asymmetric unit. Figure 6 shows an ORTEP view of molecule 1; metrical parameters for the two are identical within experimental error (see Table V). The smallest angle about the pseudotetrahedral cadmium is that due to the bidentate dmpe ligand, which makes a P–Cd1–P angle of 78.50 (8)°. The Te–Cd1–Te angle [142.35 (3)°] is somewhat larger than the corresponding angle in **1**. The Cd1–P bond distances [2.691 (2), 2.724 (3) Å] compare to those in the polymeric selenolate complex $\{Cd_2(\mu\text{-}SePh)_2(SePh)_2](depe)\}_\infty$,[15] where the Cd–P bond length is 2.582 (7) Å. A slight difference in the Cd1–Te bond lengths [2.744 (1) and 2.722 (1) Å] was observed. Only one other cadmium tellurolate has been structurally characterized: the mesityl derivative $[Cd(TeMe_3C_6H_2)_2]_\infty$, which exists as a coordination polymer with bridging mesityl tellurolates. Both the Cd and Te atoms are three-coordinate in this compound, and hence the Cd–Te bond lengths [average 2.837 (9) Å] are significantly longer than those found in **7**.

Conclusions. The sterically demanding sitel anion has been shown to act as a versatile ligand for the formation of novel tellurolate derivatives of zinc, cadmium, and mercury. Compared to related aryltellurolates, the sitel derivatives exhibit a number of appealing characteristics, including their ease of preparation and handling, high crystallinity, and exceptional solubility in hydrocarbon solvents. In addition, their low molecularity and relatively high volatility render them of interest as single-source precursors to II/VI thin-film semiconductors. The results of these studies, and our efforts to extend sitel chemistry to a wider variety of metal compounds, will be described in subsequent publications.

Acknowledgment. We thank Dr. Frederick J. Hollander and Virginia A. Carlson for their assistance with X-ray crystallography and Dr. Graham E. Ball for his invaluable and enthusiastic help with NMR experiments. Financial support from the National Science Foundation (Grant CHE-90-19675), the Department of Education, and UC Berkeley is gratefully acknowledged.

Supplementary Material Available: Details of the structure determinations of **1**, **4**, and **7**, including tables of temperature factor expressions, positional parameters, and intramolecular distances and angles (38 pages); listings of observed and calculated structure factors (136 pages). Ordering information is given on any current masthead page.

---

(40) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925. Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

Contribution from the Department of Chemistry, State University
of New York at Stony Brook, Stony Brook, New York 11794-3400

Kinetic, Isotopic, and ^{15}N NMR Study of *N*-Hydroxybenzenesulfonamide Decomposition: An HNO Source Reaction

Francis T. Bonner* and Younghee Ko

Received December 26, 1991

Decomposition of *N*-hydroxybenzenesulfonamide ($C_6H_5SO_2NHOH$) in alkaline solution to yield N_2O and sulfinate ($C_6H_5SO_2^-$) is first order in $C_6H_5SO_2NHO^-$, with rate constant = 2.44 (±0.23) × 10^{-4} s^{-1} at 25 °C, $\Delta H^{\ddagger}$ = 94.1 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = 6.64 J K^{-1} mol^{-1}. The reaction occurs via reversible release of HNO (and/or its conjugate NO^-), followed by rapid dimerization of the intermediate to form N_2O. It is shown by ^{15}N tracer methods that this species and the NO^- intermediate formed in trioxodinitrate decomposition are capable of codimerization, showing them to be in the same (singlet) electronic state. Protonation of $C_6H_5SO_2NHO^-$ brings about a ^{15}N NMR shift of −28.6 ppm. The free acid and its basic anion exhibit identical, large NOEF values (−4.16), showing that the dissociable hydrogen in $C_6H_5SO_2NHOH$ is bound to oxygen rather than to nitrogen, despite contrary literature reports.

Preparation of *N*-hydroxybenzenesulfonamide ($C_6H_5SO_2NHOH$, "Piloty's acid") was first reported in 1896.[1] In alkaline aqueous solution this compound undergoes self-decomposition to yield nitrous oxide and benzenesulfinate (eq 1).

$$C_6H_5SO_2NHOH(aq) + OH^-(aq) \rightarrow \tfrac{1}{2}N_2O(g) + C_6H_5SO_2^-(aq) + 1\tfrac{1}{2}H_2O \quad (1)$$

It was first postulated by Angeli[2] that this reaction occurs via elimination of HNO ("nitroxyl") from the conjugate anion (eqs 2 and 3), analogous to the self-decomposition of trioxodinitrate

$$C_6H_5SO_2NHO^- \rightarrow HNO + C_6H_5SO_2^- \quad (2)$$

$$HNO + HNO \rightarrow N_2O + H_2O \quad (3)$$

($Na_2N_2O_3$, "Angeli's salt").[3] This is one of several examples in the literature of organic chemistry for which HNO elimination is strongly indicated. Others include the nitrosative degradation of tertiary amines,[4] conversion of aliphatic secondary nitro compounds to aldehydes or ketones via acid-catalyzed solvolysis,[5] a retro Diels–Alder reaction;[6] and HNO elimination from certain *N*-nitroso organophosphorus compounds.[7] Alkaline *N*-hydroxybenzenesulfonamide is a key reagent in the well-known Angeli–Rimini test for aldehydes,[8] but it has been shown by Smith

---

(1) Piloty, O. *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 1559.

(2) Angeli, A. *Chem. Zentralbl.* **1902**, *73* (II), 691.

(3) (a) Angeli, A. *Chem. Zentralbl.* **1896**, *67* (I), 799. (b) Angeli, A. *Gazz. Chim. Ital.* **1903**, *33* (II), 245.

(4) Smith, P. A. S.; Pars, H. G. *J. Org. Chem.* **1959**, *24*, 1325.

(5) (a) Hawthorne, M. F. *J. Am. Chem. Soc.* **1957**, *79*, 2510. (b) Hawthorne, M. F.; Strahn, R. D. *J. Am. Chem. Soc.* **1957**, *79*, 2515. (c) Ibid. **1957**, *79*, 3471.

(6) Corrie, J. E. T.; Kirby, G. W.; Laird, A. E.; MacKinnon, L. W.; Tyler, J. K. *J. Chem. Soc.* **1978**, 275.

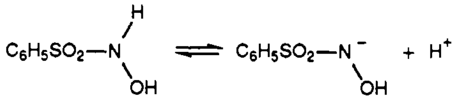
(7) Jorgenson, K. A.; Shabana, R.; Scheibye, S.; Lowenson, S. O. *Bull. Soc. Chim. Belg.* **1980**, *89*, 247.

0020-1669/92/1331-2514$03.00/0

and Hein[9] that the intermediate HNO does not play a part in this reaction.

Our attention has been drawn to *N*-hydroxybenzenesulfonamide decomposition as a source of the intermediate molecule HNO, in continuation of earlier studies of this reactive species.[10] Seel and Blieffert demonstrated mass spectrometrically that HNO is evolved during pyrolysis of the sodium salt $C_6H_5SO_2NHONa$.[11] These authors also performed a kinetic study of the reaction (eq 1) in aqueous solution[12] and proposed a two-step mechanism consisting of reversible HNO release (eq 2) followed by unimolecular N_2O formation (eq 3). The implausibility of the latter hypothesis and other questionable aspects of this treatment (see Discussion) led us to carry out an extended kinetic study of our own to assure adequate understanding of the title reaction.

We have previously reported dissimilarities between the HNO (and NO^-) formed in self-decomposition of monobasic trioxodinitrate anion ($HN_2O_3^-$) and that formed in the reaction between nitric oxide and hydroxylamine and have ascribed the difference to appearance of the anion NO^- in different electronic states.[13-16] It has been shown by ^{15}N NMR spectroscopy that the anion $HN_2O_3^-$ is predominantly N-protonated.[17] Thus the expected decomposition pathway is release of singlet HNO, yielding singlet NO^- upon deprotonation ($pK_a = 4.7$).[18] Exner et al. have interpreted the infrared and ultraviolet spectra of benzohydroxamic acid ($C_6H_5CONHOH$) and its alkyl derivatives under acidic, neutral, and alkaline conditions as showing their dissociable hydrogen atoms to be nitrogen bound.[19] Infrared spectra of these and other compounds and their lithium salts in the crystalline state and in dioxan and chloroform solutions have apparently affirmed this conclusion and extended it to include $C_6H_5SO_2NHOH$.[20] Further evidence for N-deprotonation has been found by solid-state X-ray photoelectron spectroscopy.[21] The dissociation equilibrium thus inferred (eq 4) raises the possibility that the intermediate



$$C_6H_5SO_2-N(H)(OH) \rightleftharpoons C_6H_5SO_2-N^-(OH) + H^+ \qquad (4)$$

species released in the decomposition reaction (eq 2) could be the triplet molecule NOH rather than the singlet HNO. This molecule would yield triplet NO^- upon deprotonation, constituting a second example of the triplet intermediate observed in the $NO-NH_2OH$ reaction. In this paper we report kinetic, isotopic, and NMR studies designed to address this and related questions.

Experimental Section

Reagents. *N*-Hydroxybenzenesulfonamide (grade "puriss", Fluka Chemical Co.), was used without further purification. Its titrimetric purity rating (>99%) was verified, and its UV spectrum (Figure 1) and extinction coefficients were found to be in close correspondence with literature values.[12,22] Although solutions of Piloty's acid display substantial stability at low pH, we found them subject to rapid air oxidation under neutral and alkaline conditions. All measurements were therefore carried out anaerobically, by a combination of vacuum line and argon-purging techniques. Sodium sulfinate (97%, Aldrich Chemical Co.) was employed in the reversibility studies.

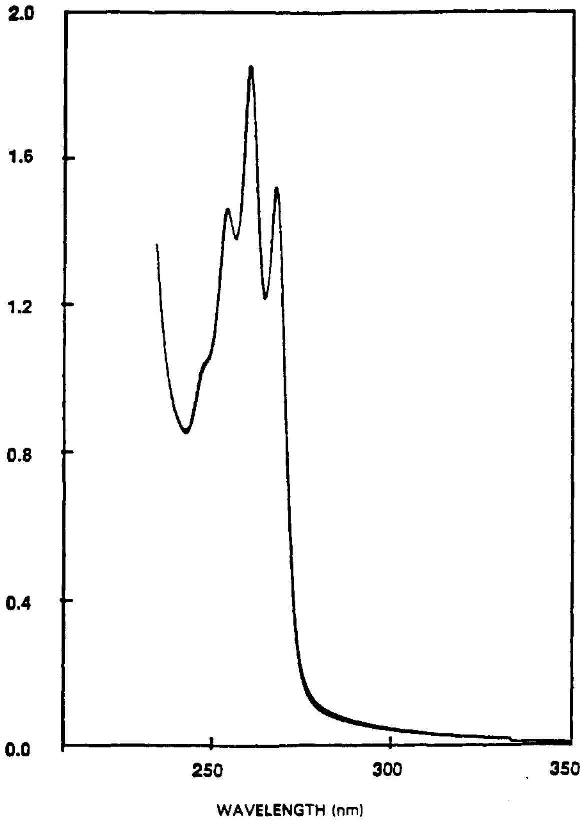


Figure 1. Partial UV spectrum for 1.75 mM $C_6H_5SO_2NHOH$ in water, retraced for six cycles at 10-min intervals at 30.0 °C.

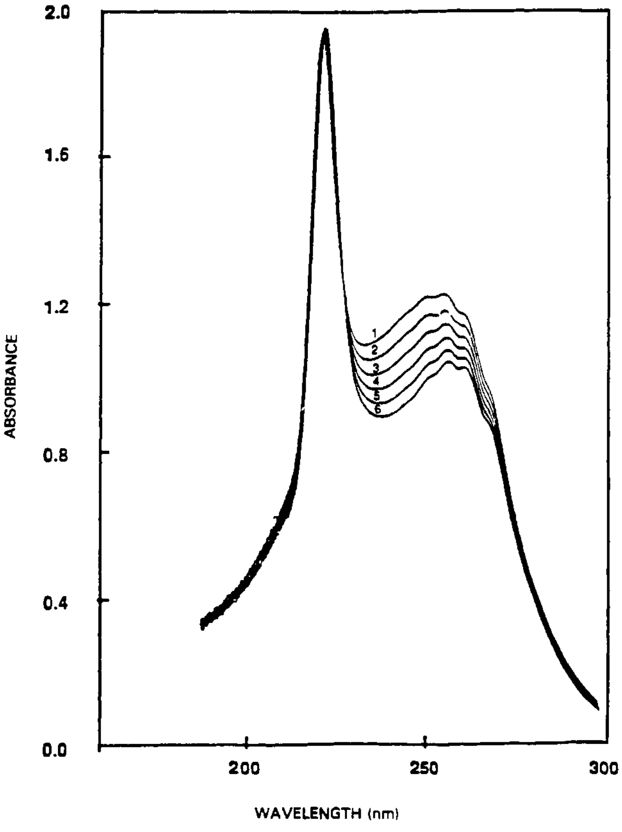


Figure 2. UV spectra for $C_6H_5SO_2NHOH$ ($C_0 = 1.15$ mM) in 0.01 M NaOH: six cycles at 3-min intervals, 30.0 °C.

Kinetics. Kinetic data for the reaction (eq 1) were obtained by measurement of the change in UV absorbance at 250 nm (see Figure 2), employing a Perkin-Elmer Lambda 5 UV/vis spectrophotometer. The

---

(8) In which an aldehyde in the presence of alkaline Piloty's salt gives rise to a characteristic red/blue color when treated with Fe(II); see e.g.: Cheronis, N. D.; Entrikin, J. B.; Hodnett, E. M. *Semimicro Qualitative Organic Analysis*, 3rd ed.; Interscience: New York, 1965; p 394.

(9) Smith, P. A. S.; Hein, G. E. *J. Am. Chem. Soc.* **1960**, *82*, 5731.

(10) Bonner, F. T.; Hughes, M. N. *Comments Inorg. Chem.* **1988**, *7*, 215 and references therein.

(11) Seel, F.; Blieffert, C. *Z. Anorg. Allg. Chem.* **1974**, *406*, 277.

(12) Seel, F.; Blieffert, C. *Z. Anorg. Allg. Chem.* **1972**, *394*, 187.

(13) Bonner, F. T.; Dzelzkalns, L. S.; Bonucci, J. A. *Inorg. Chem.* **1978**, *17*, 2487.

(14) Bonner, F. T.; Akhtar, M. J. *Inorg. Chem.* **1981**, *20*, 3155.

(15) Donald, C. E.; Hughes, M. N.; Thomson, J. M.; Bonner, F. T. *Inorg. Chem.* **1986**, *25*, 2676.

(16) Bonner, F. T.; Wang, N.-Y. *Inorg. Chem.* **1986**, *25*, 1858.

(17) Bonner, F. T.; Degani, H.; Akhtar, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 3739.

(18) Grätzel, M.; Taniguchi, S.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 1003.

(19) Exner, O.; Kakác, B. *Collect. Czech. Chem. Commun.* **1963**, *28*, 1656.

(20) Exner, O. *Collect. Czech. Chem. Commun.* **1964**, *29*, 1337.

(21) Exner, O.; Juska, T. *Collect. Czech. Chem. Commun.* **1984**, *49*, 51.

(22) Sadtler Research Laboratories, Inc. Spectrum 21909 UV.

difference in absorbance between the reactant ($C_6H_5SO_2NHO^-$) and product ($C_6H_5SO_2^-$) anions is small (Figure 2), and infinite time values are subject to substantial error. Rate measurements were therefore carried out by the method of Guggenheim[23] and checked by that of Swinbourne,[24] with concordant results. Kinetic measurements based on the rate of formation of N_2O gas product were carried out in a reaction vessel mounted to a mechanical vibrator for rapid phase mixing, with CF_4 added as a reference gas. Intermittent sampling of the gas phase was followed by gas chromatographic analysis for CF_4 and N_2O, all as described elsewhere.[16,25,26] Temperature control for both methods was maintained by circulation of thermostated water (±0.05 °C).

Isotopic Tracer Experiments. Sodium trioxodinitrate with ^{15}N label at the nitroso position ($Na_2O^{15}NNO_2$, ca. 96 atom %) was synthesized as described elsewhere.[17] Labeled Piloty's acid ($C_6H_5SO_2{}^{15}NHOH$) was synthesized by a modification of the method of Aurich et al.,[27] in which the reaction between benzenesulfonyl chloride and hydroxylamine hydrochloride ($^{15}NH_2OH{\cdot}HCl$, Stohler, 95.5 atom % ^{15}N) is followed by ether extraction of the product acid. Better than 95% chemical purity was indicated by UV absorbance. Isotopic analyses were carried out with a Kratos MS 890/DS 90 mass spectrometer.[28]

Nitrogen-15 NMR Spectroscopy. Chemical shift measurements were carried out with a Bruker MSL 400 NMR spectrometer operating at 40.55 MHz for ^{15}N. A single-frequency solenoid coil was employed. The temperature was maintained at 2 °C to slow down the decomposition reaction ($t_{1/2} > 10$ h at 2 °C and pH 13). Typical parameters were 10-μs pulse (corresponding to 45°), 5-s relaxation delay and sweep width 8000 Hz. FIDs were recorded as 8K complex points giving a digital resolution of 2 Hz/point.

NOE difference measurements were performed on a Bruker AC-25 instrument operating at 25.345 MHz. A 10-mm broad-banded probe was used with a 90° pulse length of 40 μs. Relaxation delays were 220 s at low pH and 300 s at high pH, on the basis of rough T_1 measurements. The FIDs were collected as 32K complex points covering a spectral width of 20000 resulting in a digital resolution of 1.2 Hz/point. The temperature was maintained between 0 and 2 °C. The data with and without proton irradiation were collected with interleaving, eight scans per loop. Typically 512 FIDs were collected per experiment in this manner.

Results

Stoichiometry. Piloty[1] and subsequently Raschig[29] have reported the formation of *trans*-hyponitrite in $C_6H_5SO_2NHOH$ decomposition under strongly alkaline conditions. Piloty's experiments were repeated by Seel et al.,[12] who reported finding appreciable $N_2O_2^{2-}$ for decompositions carried out at $[OH^-] > 10$ M, but none for solutions at pH ≤13. We examined solutions in which complete decomposition of Piloty's acid had been carried out at OH^- concentrations of 0.1, 1.0, 2.0, and 4.0 M for evidence of hyponitrite formation. While we did not specifically detect hyponitrite at any of these concentrations the kinetic data suggest the possibility of its formation to a minor extent at high $[OH^-]$ (see below). Reaction gas products were examined in a search for evidence of another possible side reaction, i.e. reduction of the intermediate HNO by its parent anion $C_6H_5SO_2NHO^-$, analogous to the well-established reduction of HNO by NH_2O^-.[13] No N_2 product, hence no evidence for this reaction, was found. Mass balance experiments based on gas chromatographic determination of total N_2O recovery following complete decomposition of $C_6H_5SO_2NHOH$ dissolved in 10.0 mL of 0.100 M NaOH gave the following results:

I. initial amount of $C_6H_5SO_2NHOH = 6.58 \times 10^{-4}$ mol

amount of N_2O recovered $= 3.20 \times 10^{-4}$ mol

nitrogen recovery = 97.3%

II. initial amount of $C_6H_5SO_2NHOH = 2.63 \times 10^{-3}$ mol

amount of N_2O recovered $= 1.31 \times 10^{-3}$ mol

nitrogen recovery = 99.6%

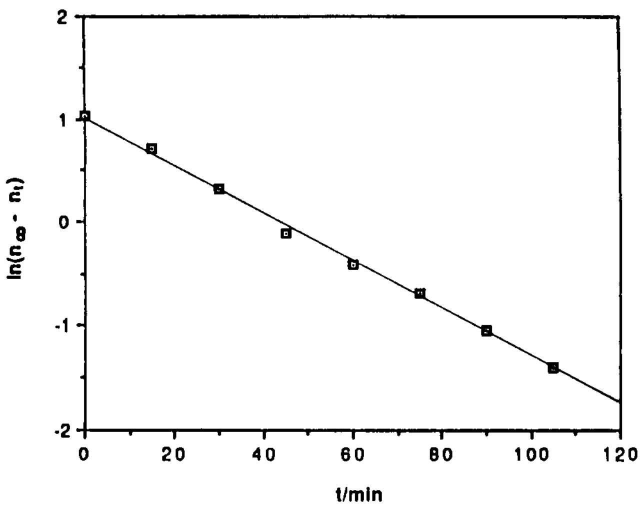


Figure 3. First-order kinetic plot based on total moles of N_2O (experiment 11, Table I).

Table I. Measured Rate Constants for $C_6H_5SO_2NHOH$ Decomposition at 25.0 °C

expt no.	pH	buffer[a]	10^3C_o/M[b]	I/M	10^4k_{obs}/s^{-1}	method[c]
1	9.0	b	2.2	0.071	1.29	s
2	9.5	b	2.3	0.085	2.62	s
3	9.8	b	33.0	0.13	3.18	g
4	10.0	b	2.2	0.094	3.47	s
5	11.0	p	4.5	0.88	4.00	s
6	12.0	k	4.3	0.062	4.15	s
7	13.0	n	2.7	0.10	3.95	s
8	13.0	n	33.0	0.13	4.52	g
9	13.0	n	33.0	0.13	4.46	g
10	13.0	n	33.0	0.13	4.05	g
11	13.0	n	33.0	0.47	4.09	g
12	13.0	n	16.5	0.12	4.09	g
13	13.0	n	66.0	0.17	4.37[d]	g
14	14.0	n	4.0	1.0	2.53	s
15	14.3	n	4.2	2.0	1.90	s
16	14.6	n	3.1	4.0	1.64	s

[a] b = borate; p = phosphate; k = KCl/KOH; n = NaOH. [b] Initial concentration $[C_6H_5SO_2NHOH]_o$. [c] s = spectroscopic; g = gas chromatographic. [d] Mean value for experiments 7–13: $k = (4.22 \pm 0.23) \times 10^{-4}$ s^{-1}.

In agreement with Seel et al.[12] we conclude that under the conditions principally employed in this study (pH ≤13) the reaction stoichiometry corresponds entirely to that expressed in eq 1.

UV Spectroscopy. The characteristic UV spectrum of the free acid $C_6H_5SO_2NHOH$ dissolved in water is shown in Figure 1. Since this spectrum was generated by six successive scans taken at 10-min intervals, the figure also illustrates the stability of the compound in weakly acidic solution ($pK_a = 9.29$).[12] Spectroscopic changes that occur during decomposition at pH 13 are illustrated in Figure 2.

Kinetics. Rate constants measured by monitoring UV absorbance at 250 nm were determined from the resulting, rigorously linear plots of $\ln [A(t) - A(t + \delta t)]$ versus time t (Guggenheim method), where $\delta t = 30$ min at pH 13, 45 min at pH 10, 60 min at pH 9.5, and 90 min at pH 9. Rate constants measured by gas chromatographic analysis for N_2O reaction product were determined from plots of the quantity $\ln [n(\infty) - n(t)]$ versus time t, where n = total moles of N_2O released. Linearity in the Guggenheim absorbance plots is not of itself a proof of first-order kinetic behavior, but the linearity of the latter function over as many as 4 half-lives (Figure 3) leaves no doubt about this point.

pH Dependence of the Rate Constant. Measured rate constants at 25.0 °C over the pH range 9.0–13.0 are summarized in Table I and displayed in Figure 4. The table shows satisfactory concordance between the two experimental methods employed and illustrates the pH dependence of rate constant. The seven mea-

---

(23) Guggenheim, E. A. *Philos. Mag.* **1926**, *2*, 538.
(24) Swinbourne, E. S. *Aust. J. Chem.* **1958**, *11*, 314.
(25) (a) Bonner, F. T.; Pearsall, K. A. *Inorg. Chem.* **1982**, *21*, 1973. (b) Pearsall, K. A.; Bonner, F. T. *Inorg. Chem.* **1982**, *21*, 1978.
(26) Pearsall, K. A.; Bonner, F. T. *J. Chromatogr.* **1980**, *200*, 224.
(27) Aurich, H. G.; Schmidt, M.; Schwerzel, T. *Chem. Ber.* **1985**, *118*, 1103.
(28) Stony Brook Mass Spectrometry Facility, courtesy Dr. C. Iden.
(29) Raschig, F. *Schwefel- und Stickstoffstudien*; Verlag Chemie: Leipzig-Berlin, 1924; pp 83–89.

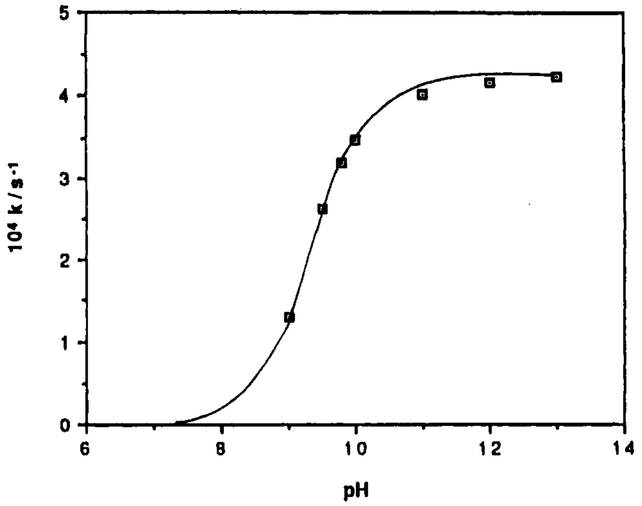


Figure 4. First-order rate constant as a function of pH: (□) measured values (Table I); (solid curve) calculated, using pK_a = 9.29 and k = 4.22 × 10^{-4} s^{-1}.

Table II. Effect of Added Sulfinate on the Rate Constant for $C_6H_5SO_2NHOH$ Decomposition[a]

expt no.	$[C_6H_5SO_2Na]$/M	I/M	$10^4k/s^{-1}$
1	0	0.13	4.22[b]
2	0.11	0.24	3.04
3	0.22	0.35	2.51
4	0.33	0.46	2.00
5	0.56	0.69	1.73
6	0.76	0.89	1.35
7	0.99	1.12	1.37

[a] Conditions: pH = 13.0; t = 25.0 °C; $[C_6H_5SO_2NHOH]_0$ = 0.033 M; measurements by the gas chromatographic method. [b] Mean value from Table I.

surements carried out at pH 13.0 yield the mean value k = (4.22 ± 0.23) × 10^{-4} s^{-1}, which we take to be the rate constant for decomposition of the fully deprotonated species $C_6H_5SO_2NHO^-$. Figure 4 displays the experimental values of the rate constant k up to pH 13, superimposed on a titration curve based on the rate law

$$-d[C_6H_5SO_2NHOH]/dt = k[C_6H_5SO_2NHO^-] \quad (5)$$

and constructed using the values k = 4.22 × 10^{-4} s^{-1} and pK_a = 9.29.[12] Close agreement between experimental values and the titration curve confirms the rate law eq 5.

Table I also includes rate constant measurements carried out under the high-basicity conditions $[OH^-]$ = 1.0, 2.0, and 4.0 M. The apparent decline of the rate constant exhibited by these values may reflect some diversion of HNO/NO^- to *trans*-hyponitrite (see Discussion).

Nondependence of the Rate Constant on Ionic Strength. Most of the values of k shown in Table I were measured at ionic strengths in the vicinity of 0.1 M, but one measurement was carried out at the substantially higher ionic strength 0.47 M by addition of NaCl (experiment 11). This result and the appropriate fit to the titration curve (Figure 4) of the pH 11 measurement, for which I = 0.88 M, suggest that for pH ≤13 the rate constant is no more than weakly dependent on ionic strength.

Reversibility of the Decomposition Reaction. Rate constants measured in the presence of deliberately added sodium sulfinate ($C_6H_5SO_2Na$) are summarized in Table II and displayed in Figure 5. These results confirm the presence of reversibility in the HNO-releasing process (eq 2), as suggested by Seel et al.[12] The fact that the rate constant levels off at high sulfinate concentration implies the existence of an alternate decomposition pathway. It is notable also that although the initial part of the curve in Figure 5 is extremely steep, sulfinate produced in the normal course of the decomposition reaction has not been observed to affect the linearity of individual kinetic plots (see Figure 3).

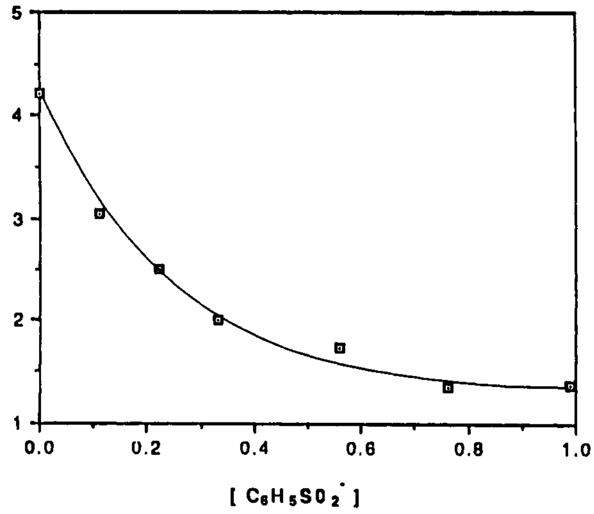


Figure 5. First-order rate constant as a function of added benzenesulfinate ion concentration.

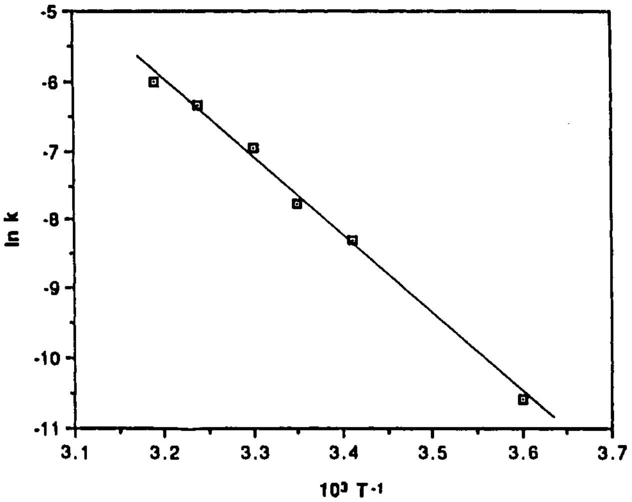


Figure 6. Arrhenius plot for $C_6H_5SO_2NHO^-$ decomposition reaction.

Table III. Temperature Dependence of Rate Constant for $C_6H_5SO_2NHOH$ Decomposition[a]

expt no.	t/°C	$10^3T^{-1}/K^{-1}$	$10^4k/s^{-1}$
1	5.0	3.60	0.257
2	20.0	3.41	2.53
3	25.0	3.35	4.22[b]
4	30.0	3.30	9.50
5	35.0	3.24	17.8
6	40.0	3.19	24.5

[a] Conditions: pH = 13.0; $[C_6H_5SO_2NHOH]_0$ = 0.0022 M; I = 0.10 M; measurements by the spectroscopic method. [b] Mean value from Table I.

Temperature Dependence of the Rate Constant. Measurements of the rate constant at pH 13.0, carried out by UV spectroscopy at five additional temperatures in the range 5–40 °C, are shown in Table III. The Arrhenius plot shown in Figure 6 yields the value 96.4 kJ mol^{-1} for the activation energy E_a. By Eyring plot treatment we obtain activation parameter values $\Delta H^\ddagger$ = 94.1 kJ mol^{-1} and $\Delta S^\ddagger$ = 6.64 J K^{-1} mol^{-1}.

Nitrogen-15 Tracer Experiments. Using the known 25 °C rate constants for self-decomposition of Piloty's acid (Table I) and trioxodinitrate[30] and the values pK_a = 9.29 for $C_6H_5SO_2NHOH$[12] and pK_{II} = 9.70 for $H_2N_2O_3$,[31] we calculate that an equimolar

---

(30) Hughes, M. N.; Wimbledon, P. E. *J. Chem. Soc., Dalton Trans.* **1976**, 703.

(31) Sturrock, P. E.; Ray, J. D.; Hunt, H. R., Jr. *Inorg. Chem.* **1963**, *2*, 649.

Table IV. Mass Spectrometry of N_2O Produced by $HO^{15}NNO_2^-$ Decomposition Alone and in the Presence of Simultaneously Decomposing $C_6H_5SO_2NHO^-$ [a]

mass No.	relative abundance	
	without $C_6H_5SO_2NHO^-$	with $C_6H_5SO_2NHO^-$
46	0.9312	0.1455
45	0.0670	0.3967
44	0.0018	0.4579

[a] Conditions: pH = 9.8; t = 25.0 °C; $[Na_2{}^{15}NNO_3]_0$ = $[C_6H_5SO_2NHOH]_0$ = 8.0 mM; reaction time = 24 h.

Table V. ^{15}N Chemical Shift in $C_6H_5SO_2NHOH$ at 2 °C

pH	$\delta(^{15}N)$[a]	pH	$\delta(^{15}N)$[a]
0	160.0	8.92	172.3
2.08	160.3	9.02	176.3
3.60	160.4	9.50	180.6
7.50	161.1	9.66	180.6
8.34	164.2	9.90	183.7
8.43	166.5	10.2	185.9
8.50	168.1	13.0	188.6
8.75	169.9		

[a] ppm measured relative to external 1.0 M HNO_3 and reported relative to anhydrous NH_3; correction constant = 375.80.[32]

solution of the two compounds at 25 °C and pH 9.75 should release HNO from the two source reactions at nearly equal rates. Two experiments were carried out at 25 °C and pH 9.8, with $[Na_2O^{15}NNO_2]_0$ = $[C_6H_5SO_2NHOH]_0$ = 8.0 mM. A third tracer experiment was carried out under similar conditions, using $C_6H_5SO_2{}^{15}NHOH$ and unlabeled $Na_2N_2O_3$. Isotopic analysis of the product gas in all three experiments revealed a substantial content of N_2O of mass 45, as illustrated for one of them in Table IV. The abundance values shown there correspond to the expected, overall 96.5% ^{15}N content in the N_2O produced by labeled trioxodinitrate alone and 34.4% in N_2O produced in the presence of decomposing, unlabeled *N*-hydroxybenzenesulfonamide. The relative abundances observed in the mass spectrum at masses 31 and 30 (not shown) indicate that the N_2O of mass 45 consists of approximately equal proportions of the isotopomers $^{15}N^{14}NO$ and $^{14}N^{15}NO$, consistent with its formation by dimerization of the intermediate species HNO or NO^-. The striking increase at mass 45 clearly indicates that intermediates from the two reaction sources interact freely in a codimerization process.

^{15}N NMR Spectroscopy of Piloty's Acid: Chemical Shift and NOEF. Measured values of the chemical shift $\delta(^{15}N)$ for $C_6H_5SO_2NHOH$ over the pH range 0–13, shown in Table V and Figure 7, display the characteristics of a titration curve. Protonation of the conjugate anion $C_6H_5SO_2NHO^-$ is accompanied by a total upfield shift of $\Delta\delta(^{15}N) = -28.6$ ppm. For comparison, protonation of the trioxodinitrate species $N_2O_3{}^{2-}$ to form the monoanion $HN_2O_3{}^-$ causes a shift of similar magnitude: $\Delta\delta(^{15}N) = -23.9$ ppm.[17] No significant variation in resonance line sharpness was observed for Piloty's acid over the entire pH range examined, in contrast to the substantial line broadening observed to accompany $N_2O_3{}^{2-}$ protonation.[17]

The nuclear Overhauser enhancement factors (NOEF) measured for the free acid $C_6H_5SO_2NHOH$ at pH 4 and its conjugate anion at pH 13 are −4.15 and −4.16, respectively. For comparison, the NOEF previously reported for trioxodinitrate monobasic anion $HN_2O_3{}^-$ is −2.1.[17]

Discussion

The results of our kinetic study show unambiguously that *N*-hydroxybenzenesulfonamide decomposition is rate-controlled by a reversible HNO-releasing step (eq 2), followed by rapid dimerization to form N_2O (eq 3). While our conclusion concerning reversibility is in agreement with that of Seel and Blieffert,[12] theirs was based on observations of pH change occurring in the range 10.5–9.5 during decomposition of unbuffered, 0.02 M $C_6H_5SO_2NHONa$ solutions with and without added sulfinate ($C_6H_5SO_2Na$). This approach, dependent on the pK_a difference between $C_6H_5SO_2NHOH$ (9.29)[12] and $C_6H_5SO_2H$ (2.76),[33] was justified in ref 12 by an (incorrect) observation that the decomposition rate is not appreciably dependent on alkalinity. It was stated from these observations that the reaction can be brought to a virtual standstill by addition of sulfinate in 30-fold excess, but our results (Table II) show that a 30-fold excess causes only an approximately 3-fold reduction in rate constant.

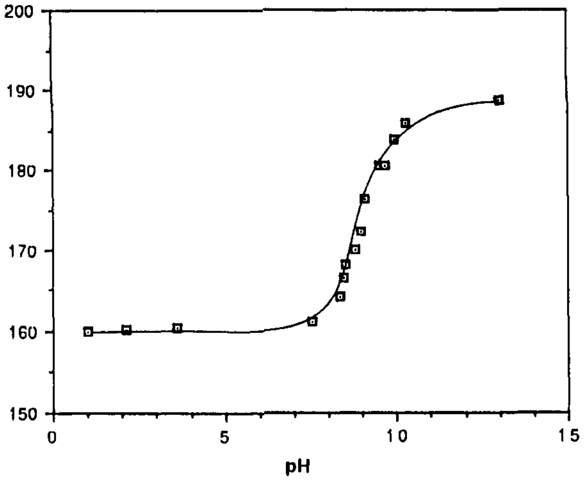


Figure 7. Variation of ^{15}N chemical shift in $C_6H_5SO_2NHOH$ with pH.

The rate measurements reported in ref 12 were carried out by acidimetric titration (again in unbuffered systems). Three representative kinetic plots were shown, all at initial concentration $[C_6H_5SO_2NHO^-]_0$ = 0.01 M, and one without added sulfinate, the others containing 0.0125 and 0.1 M $C_6H_5SO_2Na$. Plots of Piloty's salt concentration vs time (Figure 4, ref 12) exhibit two very nearly equal successive half-lives (i.e. first-order kinetics) for the first two of these cases, while in the case of 0.1 M sulfinate only slightly more than 1 half-life is displayed. The same data redisplayed logarithmically (Figure 5, ref 12) show the first and second runs as departing substantially from linearity. However, when data are taken directly from Figure 4, ref 12, and replotted logarithmically, three of the four are found to be linear, yielding rate constants in rough agreement with our values (Tables I and II). The supposed nonlinearity of Figure 5, ref 12, was taken to indicate kinetic inhibition caused by reaction-produced sulfinate, an effect that our data (Figure 3) show to be absent. Reference 12 includes a steady-state analysis based on forward and reverse rates for the HNO-producing reaction (eq 2) and an assumed first-order rate constant for the formation of N_2O from HNO. Kinetic parameters based on this mechanism were determined graphically, but three of the four plots shown for this purpose (Figure 6, ref 12) contain only two data points each. In sum, the data of ref 12 appear to have been seriously misinterpreted, and the accompanying mechanistic interpretation is without merit. Dehydrative dimerization of HNO/NO^- is clearly a bimolecular process.[34]

The close conformance of our measured rate constants to the titration curve (Figure 4) leave no doubt about the validity of the rate law eq 5 at pH values up to 13. As reported, however, the rate constant appears to fall off again in the high basicity region $[OH^-]$ = 1–4 M. Although we did not specifically identify *trans*-hyponitrite as a product, the extinction coefficient for $N_2O_2{}^{2-}$ (6900 M^{-1} cm^{-1})[35] at 248 nm is 7 times greater than that of $C_6H_5SO_2NHO^-$ at that wavelength (Figure 2), and a minor

---

(32) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley: New York, 1979; p 32.

(33) DeFilippo, D.; Momicchioli, F. *Tetrahedron* **1969**, *25*, 5733.

(34) A rate constant value of 1.8 × 10^9 L mol^{-1} s^{-1} has been estimated for this process: Bazylinski, D. A.; Hollocher, T. C. *Inorg. Chem.* **1985**, *24*, 4285.

(35) Conner, C. N.; Donald, C. E.; Hughes, M. N.; Sami, C. *Polyhedron* **1989**, *8*, 2621.

diversion of HNO/NO^- from N_2O in the gas phase to $N_2O_2^{2-}$ in solution could possibly have given the appearance of a decline in the decomposition rate. However, it must also be pointed out that we made no attempt to assess the ionic strength dependence of the rate constant in this very high pH region.

The results of our isotopic tracer experiments cleanly rule out the possibility of NO^- release in the triplet state in Piloty's acid decomposition reaction. The NO^- released in trioxodinitrate decomposition is singlet, and codimerization of the two intermediates would not be expected to occur unless the other species were also a singlet. Thus if the anion $C_6H_5SO_2NHO^-$ is not N-deprotonated, as in eq 4, it would not decay by sulfur–nitrogen bond breakage to release the triplet molecule NOH. While the N-deprotonated configuration has been established for this species in the solid state[21] and in dioxan solution,[20] the situation in aqueous solution may well be different. We turn to the evidence of ^{15}N NMR spectroscopy for further information.

The large negative NOEF observed for the acid form $C_6H_5SO_2NHOH$ (−4.15, i.e. 84% of the theoretical maximum value −4.93 for ^{15}N)[36] is expected for this species since it is known to contain a nitrogen-bound proton. The fact that at high pH the anionic form $C_6H_5SO_2NHO^-$ displays essentially the same NOEF (−4.16) shows unambiguously that the N-bound proton remains undisturbed by titration. Thus it must be the oxygen-bound proton that is removed, leaving an HNO^- group bound to sulfur, which then yields HNO upon heterolysis of the nitrogen–sulfur bond. This is consistent with the isotopic evidence of codimerization of this intermediate with the singlet species released in $HN_2O_3^-$ decomposition. It also explains the complete absence of line broadening upon protonation of $C_6H_5SO_2NHO^-$, in contrast to the very substantial line broadening that occurs upon protonation of $N_2O_3^{2-}$. Clearly, the N-protonated tautomer precedes HNO release in both decomposition reactions. While it appears to be the only significant form in both acid and anionic forms of Piloty's acid, the smaller observed NOEF −2.1 and line broadening are consistent with occurrence of an equilibrium mixture of tautomers in the case of trioxodinitrate monoanion.

The protonation shift $\Delta\delta(^{15}N)$ observed for $C_6H_5SO_2NHO^-$ (−28.6 ppm) is similar to that found for $N_2O_3^{2-}$ (−23.9 ppm).[17] The fact that the new value corresponds to neighbor O-atom protonation rather than direct N-atom protonation may place in question our earlier interpretation of trioxodinitrate.[17,37] The magnitude of the shift in that case made it unambiguously clear which of the two nonequivalent nitrogen atoms is involved, and both line broadening and a significant NOEF indicate the occurrence of at least partial N-protonation. In the most closely analogous case of hyponitrite ($N_2O_2^{2-}$), in which protonation is known to occur at oxygen, attachment of a single proton causes a shift $\Delta\delta(^{15}N)$ of only −3 ppm, and the total shift for two protons is only −15 ppm.[38]

There are striking similarities in the spectroscopic properties of trioxodinitrate and hyponitrite, and in the kinetic properties of their decomposition reactions as well, despite the mechanistic difference that HNO release does not occur in the course of $HN_2O_2^-$ decomposition.[38] Both $N_2O_3^{2-}$ and $N_2O_2^{2-}$ are destabilized by the *addition* of a proton, while $C_6H_5SO_2NHOH$ self-decomposition occurs upon *removal* of a proton. Otherwise, there are kinetic similarities between the $C_6H_5SO_2NHO^-$ and $HN_2O_3^-$ decomposition reactions. These include rate constants (4.2×10^{-4} and 6.8×10^{-4} s^{-1}) and activation enthalpies $\Delta H^{\ddagger}$ (94.1 and 100 kJ mol^{-1}).[39] Both reactions can be retarded by deliberate addition of a product species, i.e. sulfinate or nitrite, but in both cases the rate behavior at any given set of conditions shows no sign of reversibility due to formation of that same product in the normal course of reaction (e.g. the linearity in Figure 3 over 4 half-lives). This indicates that the actual immediate precursor to HNO release in these reactions remains unidentified. In each case there appears to be a rate-determining step that is itself reversible and exhibits a net rate fixed by overall macroscopic system conditions yet involves no more than a minute fraction of the anionic reaction species present. Similarly, in interpreting the kinetics of reactions between trioxodinitrate and heme proteins, Hollocher et al. found it necessary to postulate an "activated" form of $HN_2O_3^-$.[40]

Finally, although it seemed possible at the outset that Piloty's acid might yield triplet NO^-, it cannot be considered surprising that it does not. Whereas HNO is a known, identified, and thoroughly characterized molecule, no direct observation of NOH has been reported, and it remains characterized primarily by calculations that show HNO to be the clear and strongly thermodynamically favored configuration.[41–44] While its conjugate triplet NO^- has been observed in trioxodinitrate photolysis,[15] its occurrence as an intermediate in the reaction between NO and NH_2O^- remains unique as an example of triplet NO^- release in a chemical reaction at thermal energy.[13–16]

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The Bruker AC-250 NMR spectrometer was obtained with instrumentation grants from the NIH (RR05547A) and NSF (CHE 8911350) and with support from the Center for Biotechnology and from the State University of New York at Stony Brook. We are grateful to Dr. George Crull for invaluable assistance in performance of the nitrogen-15 NMR measurements and thank Prof. Martin N. Hughes for helpful discussions.

Registry No. $PhSO_2NHOH$, 599-71-3.

---

(36) Reference 32, p 6.

(37) See also: Witanowski, M.; Stefaniak, L.; Webb, G. A. *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: New York, 1986; Vol. 18, p 78.

(38) Akhtar, M. J.; Balschi, J. A.; Bonner, F. T. *Inorg. Chem.* **1982**, *21*, 2216.

(39) Hughes, M. N.; Wimbledon, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1650.

(40) Bazylinski, D. A.; Goretski, J.; Hollocher, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 7986.

(41) Gallup, G. A. *Inorg. Chem.* **1975**, *14*, 563.

(42) Wu, A. A.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys. Lett.* **1975**, *35*, 316.

(43) Bruna, P. J.; Marian, C. M. *Chem. Phys. Lett.* **1979**, *67*, 109.

(44) Bruna, P. J. *Chem. Phys.* **1980**, *49*, 39.