

- (12) Although $\text{PW}_{12}\text{O}_{40}^{3-}$ is stable in dilute acidic solutions, similar solutions of yellow $\text{PMo}_{12}\text{O}_{40}^{3-}$ are unstable and are rapidly decolorized upon dilution.
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Kinetics of the Alkaline Hydrolysis of Hydroxylamine-*O*-sulfonic Acid and Its Reactions with Hydrazine and Hydroxylamine

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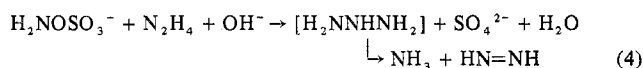
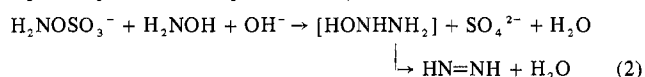
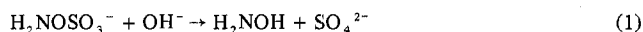
Received July 8, 1974

AIC404463

The kinetics of the hydrolysis of hydroxylamine-*O*-sulfonic acid, H_3NOSO_3 , in alkaline aqueous solution have been studied in the range $[\text{OH}^-] = 0.1\text{--}1.5\text{ M}$ at 26.6° and an ionic strength of 1.5. The observed rate law is $-\text{d}[\text{H}_2\text{NOSO}_3^-]/\text{dt} = (k_A + k_B[\text{OH}^-])[\text{H}_2\text{NOSO}_3^-]$ where $k_A = (0.43 \pm 0.09) \times 10^{-4}\text{ sec}^{-1}$ and $k_B = (1.84 \pm 0.10) \times 10^{-4}\text{ sec}^{-1}\text{ M}^{-1}$. The k_A term is shown to be due to reaction with EDTA^{4-} added to complex trace metal ions. The same rate law is found when the hydrolysis occurs in the presence of a large excess of the diazene scavenger fumarate ion with $k_B = (1.72 \pm 0.07) \times 10^{-4}\text{ sec}^{-1}\text{ M}^{-1}$. The kinetics of the reaction of H_3NOSO_3 with N_2H_4 and H_2NOH in alkaline solution were also studied and found to obey a second-order rate law, rate = $k_{\text{obsd}}[\text{H}_2\text{NOSO}_3^-][\text{M}]$. For $\text{M} = \text{N}_2\text{H}_4$, $k_{\text{obsd}} = 0.010 \pm 0.002\text{ sec}^{-1}\text{ M}^{-1}$ and is hydroxide independent. For $\text{M} = \text{H}_2\text{NOH}$, k_{obsd} is dependent on $[\text{OH}^-]$. The reaction is interpreted as involving the conjugate base of H_2NOH . Taking $\text{p}K_A = 13.7$ for H_2NOH a value of $0.16 \pm 0.06\text{ M}^{-1}\text{ sec}^{-1}$ is found for the reaction of H_2NO^- with $\text{H}_2\text{NOSO}_3^-$. The above data are incorporated into a mechanism for $\text{H}_2\text{NOSO}_3^-$ hydrolysis and shown to fit satisfactorily the overall rate of $\text{H}_2\text{NOSO}_3^-$ by computer simulation. It is concluded that nucleophilic attack at the $\text{H}_2\text{NOSO}_3^-$ sp^3 nitrogen proceeds in the order $\text{H}_2\text{NO}^- > \text{N}_2\text{H}_4 \gg \text{OH}^-$. This observation supports earlier work which proposed that polarizability and ease of oxidation of the nucleophile are more important than proton basicity for attack at this nitrogen center.

Introduction

Since it was first reported in 1914,¹ hydroxylamine-*O*-sulfonic acid, $\text{H}_3\text{N}^+\text{OSO}_3^-$, has proved to be an interesting and useful chemical.² Among the more intriguing of its reactions is the ability to hydrogenate multiple bonds stereospecifically during decomposition in alkaline solution through the formation of the diazene molecule, $\text{HN}=\text{NH}$.²⁻⁵ The postulated intermediacy of diazene stimulated our interest in the mode of decomposition of $\text{H}_2\text{NOSO}_3^-$ in alkaline solution and ultimately led to a synthetic route to monosubstituted alkyldiazenes, $\text{RN}=\text{NH}$, from the reaction of $\text{H}_2\text{NOSO}_3^-$ with *N*-alkylhydroxylamines, RNHOH .⁶ On the basis of reaction chemistry and the use of isotopically labeled nitrogen compounds Schmitz, *et al.*,⁷ have proposed that the alkaline decomposition of $\text{H}_2\text{NOSO}_3^-$ occurs according to eq



1-4. Except for a demonstration by Schmitz that the rate of alkaline hydrolysis of $\text{H}_2\text{NOSO}_3^-$ is accelerated by addition of hydroxylamine and an earlier general study of the stability of $\text{H}_2\text{NOSO}_3^-$ solutions,⁸ the kinetics of the alkaline decomposition have not been studied.

The present kinetic study has shown the Schmitz mechanism, with minor modification, can satisfactorily explain the rate data. Among the reactions we have investigated are the alkaline decomposition of $\text{H}_2\text{NOSO}_3^-$ in both the presence and absence of fumarate ion (a diazene scavenger) and the reaction of $\text{H}_2\text{NOSO}_3^-$ with hydroxylamine and hydrazine.

Our results are also of interest in relationship to the recent use of $\text{H}_2\text{NOSO}_3^-$ as a model to study nucleophilic attack at an sp^3 nitrogen center.^{9,10}

Experimental Section

Materials. Hydroxylamine-*O*-sulfonic acid, H_3NOSO_3 , was prepared by treating hydroxylammonium sulfate with freshly distilled chlorosulfonic acid¹¹ and stored *in vacuo* over phosphorus pentoxide. It assayed at 98+% purity by iodometry,¹² the low assay being due to the presence of some unconverted hydroxylammonium sulfate. Slight hydrolysis (<4%) of the H_3NOSO_3 to hydroxylamine from exposure to moisture during handling was monitored by periodic reanalysis. The sodium salt of fumaric acid was prepared by neu-

trahzation of the reagent grade acid with sodium hydroxide and purified by recrystallization. Carbonate-free sodium hydroxide solutions were prepared by diluting aliquots of a saturated sodium hydroxide solution with boiled and deaerated water. All other chemicals were reagent grade and used without further purification.

Analyses. Hydrazine was determined spectrophotometrically as the azine formed by reaction with *N,N*-dimethylaminobenzaldehyde.¹³ Samples for ammonia analysis were first acidified and boiled to hydrolyze any $\text{H}_3\text{NOSO}_3^-$ to hydroxylamine. Hydroxylamine and/or hydrazine present were then oxidized by addition of bromine; excess bromine was next reduced with sulfite. Finally the ammonia was determined by the Kjeldahl method. Use of known mixtures demonstrated that the analyses for $\text{H}_3\text{NOSO}_3^-$, hydrazine, and ammonia were reliable in the presence of one another and/or hydroxylamine at concentrations of the potentially interfering substances greater than those encountered in the experiments of interest, except for apparently high ammonia values in the presence of fumarate. We were unable to determine hydroxylamine satisfactorily in the presence of the other substances at the levels present in our study.

Gaseous products were analyzed by gas chromatography using a 2-m column packed with Linde 5A molecular sieve and a thermal conductivity detector. Nitrogen and nitrous oxide were determined using hydrogen as carrier gas, while hydrogen was determined with argon carrier gas. Both analyses were done at room temperature. Each determination was preceded by calibration with known gas mixtures.

Stoichiometry Studies. An aqueous solution containing all reagents except $\text{H}_3\text{NOSO}_3^-$ was placed in a side-arm flask on a vacuum line and degassed by three or four freeze-thaw cycles. This solution, warmed to the reaction temperature, was then added to solid $\text{H}_3\text{NOSO}_3^-$ followed by rapid mixing. The reaction was allowed to sit for ~ 1 day. The total volume of gases generated was measured and then analyzed by gas chromatography. Aliquots of the solution were analyzed for residual $\text{H}_3\text{NOSO}_3^-$, hydrazine, and ammonia as described above.

Kinetic Procedures. For studies in which the concentration of $\text{H}_3\text{NOSO}_3^-$ was monitored a procedure and reaction vessel previously described were used.¹⁴ All reagents except $\text{H}_3\text{NOSO}_3^-$ were in the solution. This was added to the reaction vessel as a solid under a nitrogen purge at the last minute to prevent possible hydrolysis due to contact with water vapor during the degassing procedure. Ten-ml samples were withdrawn into a calibrated vessel and quenched under nitrogen in 160 ml of 0.55 *N* sulfuric acid. The $\text{H}_3\text{NOSO}_3^-$ content was determined iodometrically.¹² The liberated iodine was titrated to a starch end point with freshly diluted 0.01 *M* thiosulfate solution. Each run was continued for 2–3 half-lives. In all cases graphical analysis showed good first-order behavior for disappearance of $\text{H}_3\text{NOSO}_3^-$.

Our early kinetic work showed erratic behavior in what should have been identical runs. Addition of ethylenediaminetetraacetate (EDTA) corrected this behavior which suggests that catalysis by metal ions was the likely cause.⁸ Consequently all reactions described in this paper were carried out at 4.8×10^{-3} *M* EDTA⁴⁻ unless otherwise noted.

The rate of the reaction of $\text{H}_3\text{NOSO}_3^-$ with hydrazine and hydroxylamine is too rapid to be monitored by the aliquot procedure. In these studies the same procedure was used as in the stoichiometry studies with the hydrochloride salt of hydrazine or hydroxylamine being dissolved in the aqueous solution. After addition of the degassed, prewarmed solution to the solid $\text{H}_3\text{NOSO}_3^-$, the increase in the nitrogen pressure was monitored with a mercury manometer. The nitrogen evolved is related to $\text{H}_2\text{NOSO}_3^-$ consumed by the stoichiometric eq 6 and 7. Individual runs for both systems gave satisfactory second-order plots corresponding to the rate law

$$\text{rate} = k[\text{H}_2\text{NOSO}_3^-][\text{M}]$$

where M is N_2H_4 or NH_2OH . The concentration of $\text{H}_2\text{NOSO}_3^-$, designated x , reacted at any time was calculated from the pressure of the nitrogen gas in the calibrated volume and the ideal gas equation. The two integrated second-order rate expressions used for plotting the data are as follows: for NH_2OH

$$\frac{2.3}{b-a} \log \frac{a(b-x)}{b(a-x)} = kt$$

for N_2H_4

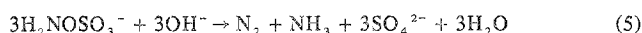
$$\frac{2.3}{b-a/2} \log \frac{a(b-x/2)}{b(a-x)} = kt$$

where a and b are the initial concentrations of $\text{H}_2\text{NOSO}_3^-$ and NH_2OH or N_2H_4 , respectively.

Kinetic Simulation. The kinetics of the full mechanism (*vide infra*) were simulated by a numerical solution of the resulting coupled nonlinear differential rate equations by the method of Runge-Kutta to fourth order.¹⁵ Simulation of a 240-min run to a concentration accuracy of 1% or better requires a step size in time of 0.01 min and takes 6 min on an IBM 360/44 computer.

Results

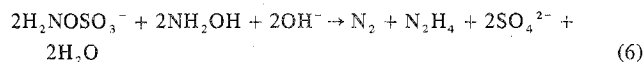
Stoichiometry. Alkaline hydrolysis of $\text{H}_2\text{NOSO}_3^-$ produces three major nitrogen-containing products: nitrogen, ammonia, and hydrazine. Taken together the nitrogen content of these three products accounts for the original $\text{H}_3\text{NOSO}_3^-$ within experimental error (Table I). Although we could not satisfactorily analyze for hydroxylamine, the other data indicate that it is apparently present in only small concentration. Analysis of the gaseous products revealed only traces of nitrous oxide and hydrogen. The limiting stoichiometry (eq 5) noted



in early work¹⁶ on $\text{H}_2\text{NOSO}_3^-$ is approached only in the solutions of low hydroxide concentrations for the low $\text{H}_2\text{NOSO}_3^-$ concentrations employed in our work. Both the stoichiometry studies (Table I) and the final hydrazine concentration measured in the kinetic runs (Table II) show that hydrazine becomes a more significant product as the hydroxide concentration increases.

In the presence of a high concentration of the unsaturated carboxylate anion fumarate, the percentage of nitrogen formed increases while that of ammonia and hydrazine decreases. A marked decrease in final hydrazine concentration is also noted in the kinetic runs (Table II). These observations are consistent with diversion of most of the diazene formed to use in reduction of fumarate to succinate.^{2b}

Reaction of $\text{H}_2\text{NOSO}_3^-$ with excess hydroxylamine in base has the stoichiometry of eq 6. Thus at $[\text{OH}^-] = 0.41$ *M*,



$[\text{H}_2\text{NOH}] = 0.20$ *M*, and $[\text{H}_2\text{NOSO}_3^-] = 0.027$ *M* the 2.02 mmol of $\text{H}_2\text{NOSO}_3^-$ produced 1.04 mmol of nitrogen and 0.90 mmol of hydrazine. In another run 2.00 mmol of $\text{H}_2\text{NOSO}_3^-$ gave 0.97 and 0.90 mmol of nitrogen and hydrazine, respectively. The slightly low hydrazine yield may arise from

Table I. Stoichiometry of Hydroxylamine-*O*-sulfonate Ion Decomposition in Aqueous Sodium Hydroxide

$[\text{OH}^-]$, <i>M</i>	Added $\text{H}_2\text{NO}-$ SO_3^- , mmol ^a	N_2 , ^b mmol of N	NH_3 , ^b mmol of N	N_2H_4 , ^b mmol of N
0.48	4.22	2.62 (62)	1.43 (34)	0.18 (4)
1.37	4.00	2.00 (50)	1.28 (32)	0.55 (14)
In Presence of 0.40 <i>M</i> Fumarate Ion				
0.42	4.99	3.46 (69)	0.21 (4)	0.18 (4)
0.54	3.87	2.56 (66)	0.69 (18)	0.13 (3)
1.13	4.01	3.26 (81)	0.35 (9)	0.04 (1)

^a Initial concentration 0.05–0.08 *M*. ^b Number in parentheses is the percentage of the nitrogen originally introduced as $\text{H}_3\text{NOSO}_3^-$ which appears in the product indicated. Estimated uncertainty in millimoles $\pm 5\%$.

Table II. Rate Data for the Hydrolysis of Hydroxylamine-*O*-sulfonate Ion in Aqueous Sodium Hydroxide Solution at 26.6°^a

[OH ⁻], <i>M</i>	10 ⁻³ <i>k</i> _{obsd} , sec ⁻¹	10 ³ [N ₂ H ₄] _{final} , <i>M</i>
0.115	0.059 ₂	0.23
0.262	0.087 ₂	0.23
0.472	0.136 ^b	0.33
0.484	0.136 ^c	1.04
0.502	0.141	0.71
0.833	0.197	0.80
1.20	0.257	1.06
1.47	0.317	1.77

Runs with Added Fumarate Ion

[OH ⁻], <i>M</i>	[Fumarate] ₀ , <i>M</i>	10 ⁻³ <i>k</i> _{obsd} , sec ⁻¹	10 ³ [N ₂ H ₄] _{final} , <i>M</i>
0.131	0.167	0.0447	0.13
0.312	0.200	0.0747	0.08
0.487	0.317	0.107	0.06
0.498	0.167	0.105	0.07
0.954	0.167	0.184	0.06
0.986	0.100	0.193	0.37

^a Ionic strength 1.5 *M* adjusted with sodium chloride. Initial concentration of H₂NOSO₃⁻ is typically about 0.012 *M*. All runs 4.8 × 10⁻³ *M* in ethylenediaminetetraacetate ion. ^b 0.10 *M* SO₄²⁻ present initially. ^c Initial H₂NOSO₃⁻ concentration 0.036 *M*.

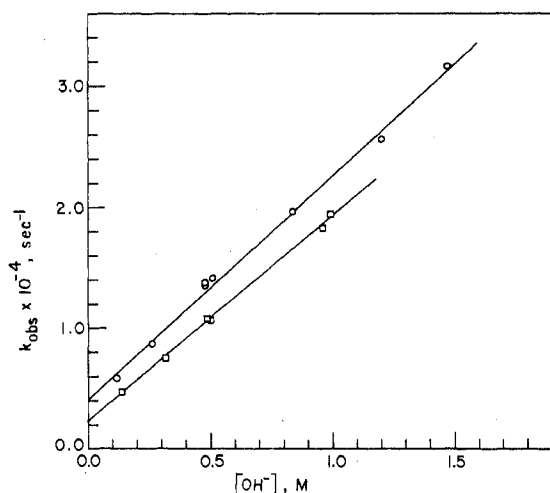
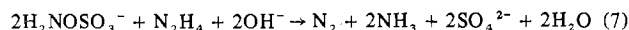


Figure 1. Plot of the observed pseudo-first-order rate constant for the hydrolysis of H₂NOSO₃⁻ as a function of [OH⁻] at 26.6°, μ = 1.5 *M*, and [EDTA⁴⁻] = 4.8 × 10⁻³ *M*: circles, without fumarate ion; squares, with fumarate ion present.

some of it reacting with H₂NOSO₃⁻ in the later stages of the reaction.

Reaction of H₂NOSO₃⁻ with excess hydrazine in base showed that for [OH⁻] = 0.50 *M*, [N₂H₄] = 0.50 *M*, and [H₂NOSO₃⁻] = 0.082 *M* the 4.09 mmol of H₂NOSO₃⁻ yielded 1.99 mmol of nitrogen and 3.30 mmol of ammonia. Although the measured ammonia is somewhat low, the stoichiometry may be reasonably written as in eq 7.



Kinetics. The rate of hydrolysis of H₂NOSO₃⁻ in aqueous hydroxide solution follows good pseudo-first-order kinetics. The observed rate constants over a range of hydroxide ion concentration are summarized in Table II and plotted in Figure 1. The pattern is of the form

$$k_{\text{obsd}} = k_A + k_B [\text{OH}^-]$$

where $k_A = (0.43 \pm 0.09) \times 10^{-4} \text{ sec}^{-1}$ and $k_B = (1.84 \pm 0.10) \times 10^{-4} \text{ sec}^{-1} \text{ M}^{-1}$.¹⁷ The k_A term arises from reaction of H₂NOSO₃⁻ with the EDTA⁴⁻ added to inhibit erratic behavior

Table III. Rate Data for Reaction of Hydroxylamine-*O*-sulfonate Ion with Hydrazine at 26.6°^a

[OH ⁻], <i>M</i>	[H ₂ NO-SO ₃ ⁻], <i>M</i>	[N ₂ H ₄], <i>M</i>	<i>k</i> _{obsd} , <i>M</i> ⁻¹ sec ⁻¹
0.494	0.080	0.100	0.0108
0.498	0.080	0.200	0.0093
0.506	0.082	0.301	0.0107
0.245	0.080	0.200	0.0095
pH 10.7 ^b	0.079	0.200	0.0119

^a All runs include added ethylenediaminetetraacetate ion of 5.0 × 10⁻³ *M* concentration and were done at ionic strength 1.5 *M*. ^b Na₂-HPO₄-Na₃PO₄ buffer.

due to trace metal ions (see Experimental Section), while the k_B term reflects the overall rate of disappearance of H₂NOSO₃⁻ represented in eq 1, 2, and 4.

That the k_A term is due to reaction of H₂NOSO₃⁻ with EDTA⁴⁻ is supported by a series of kinetic runs at 26.6° and 1.5 *M* ionic strength at several EDTA⁴⁻ concentrations with [OH⁻] = 0.076 *M*. Runs at 4.8, 9.8, and 14.4 × 10⁻³ *M* EDTA⁴⁻ gave k_{obsd} values of 0.52, 0.86, and 1.21 × 10⁻⁴ *M*⁻¹ sec⁻¹, respectively. A plot of k_{obsd} vs. [EDTA⁴⁻] is linear with a slope of 0.0071 *M*⁻¹ sec⁻¹. The comparable value from Figure 1 is $k_A/[\text{EDTA}^{4-}]$ which gives 0.0087 ± 0.0017 *M*⁻¹ sec⁻¹. The values agree satisfactorily within experimental error with the value from Figure 1 probably the less reliable of the two.

Attempts to study the kinetics of the EDTA⁴⁻-H₂NOSO₃⁻ reaction in phosphate buffer at pH ~10.5 where the hydroxide contribution should be negligible were only marginally successful. Initial rates gave rate constants in agreement with those cited above but reaction times were long and first-order plots showed substantial curvature. That H₂NOSO₃⁻ reacts with EDTA⁴⁻ is not surprising since it reacts with other amines. It seems likely that the reaction is similar to the reaction of H₂NOSO₃⁻ with glycine to give hydrazine and glycolic acid.¹⁸ Preliminary attempts to identify the products were not fruitful, and we have not pursued this reaction further.

The rate of hydrolysis of H₂NOSO₃⁻ in the presence of added fumarate ion showed a pattern similar to that observed in its absence. The results are displayed in Table II and Figure 1. The hydroxide-dependent rate constant is (1.72 ± 0.07) × 10⁻⁴ *M*⁻¹ sec⁻¹¹⁷ and is only slightly lower than that observed in the absence of fumarate ion. The intercept yields a rate constant of (0.21 ± 0.04) × 10⁻⁴ *M*⁻¹ sec⁻¹ for the EDTA⁴⁻-related term. The reason for this lower value compared with that in the absence of fumarate ion is not known.

In the presence of high concentrations of hydrazine the only important reaction for the disappearance of H₂NOSO₃⁻ is eq 7. This rapid reaction follows the simple second-order rate law, rate = $k_{\text{obsd}}[\text{H}_2\text{NOSO}_3^-][\text{N}_2\text{H}_4]$; the observed rate constants are collected in Table III. The data establish that the reaction rate is independent of hydroxide ion concentration. An average value for the rate constant is 0.010 ± 0.002 *M*⁻¹ sec⁻¹.¹⁷

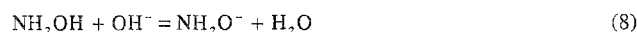
In the presence of high initial concentrations of hydroxylamine the important reaction for disappearance of H₂NOSO₃⁻ is eq 6. At a given hydroxide ion concentration this reaction also follows a second-order rate law, rate = $k_{\text{obsd}}[\text{H}_2\text{NOSO}_3^-][\text{H}_2\text{NOH}]$, and is even more rapid than the hydrazine reaction. Kinetic data are collected in Table IV. Because of the rapid rate of the reaction and the necessity of monitoring the rate by gas evolution, the uncertainty in k_{obsd} values is large. The value of k_{obsd} increases markedly with increasing hydroxide ion concentration. We interpret this to mean that the conjugate base of either H₂NOSO₃⁻ or H₂NOH is important in the reaction. The absence of a hydroxide effect in the reaction of H₂NOSO₃⁻ with N₂H₄ points to the conjugate base of H₂NOH as the active species. This is consistent

Table IV. Rate Data for Reaction of Hydroxylamine-*O*-sulfonate Ion with Hydroxylamine at 26.6°^a

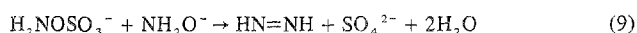
[OH ⁻], M	[H ₂ NOS ₃ ⁻], M	[NH ₂ OH], M	<i>k</i> _{obsd} , ^b M ⁻¹ sec ⁻¹	<i>k</i> , ^b M ⁻¹ sec ⁻¹
0.116	0.078	0.100	0.023	0.13
0.126	0.081	0.200	0.021	0.11
0.153	0.080	0.202	0.032	0.14
0.286	0.081	0.200	0.064	0.18
0.456	0.080	0.200	0.083	0.18
0.518	0.080	0.100	0.090	0.18
0.524	0.079	0.100	0.070	0.14
0.731	0.079	0.100	0.114	0.20
0.789	0.080	0.101	0.124	0.21

^a All runs include added ethylenediaminetetraacetate ion at 5.0 × 10⁻³ M concentration and were done at ionic strength 1.5 M. ^b Uncertainty ±20%.

with the known p*K*_a of 13.7 for hydroxylamine as determined by Hughes, *et al.*,¹⁹ from which a value of 1.9 M⁻¹ for the equilibrium constant for reaction 8 is calculated. In our system



this rapid equilibrium is followed by the rate-determining step



The rate law is therefore

$$\frac{-d[\text{H}_2\text{NOSO}_3^-]}{dt} = k[\text{H}_2\text{NOSO}_3^-][\text{H}_2\text{NO}^-]$$

The amount of NH₂OH in the NH₂O⁻ form is significant at the [OH⁻] in our studies and is given by

$$[\text{NH}_2\text{O}^-] = \left[\frac{K[\text{OH}^-]}{1 + K[\text{OH}^-]} \right] [\text{NH}_2\text{OH}]_T$$

where [NH₂OH]_T is the total hydroxylamine in solution in all forms and *K* = 1.9 M⁻¹. Since our kinetic analysis was done using [NH₂OH]_T, the second-order rate law is

$$\frac{-d[\text{H}_2\text{NOSO}_3^-]}{dt} = \left[\frac{kK[\text{OH}^-]}{1 + K[\text{OH}^-]} \right] [\text{NH}_2\text{OH}]_T [\text{H}_2\text{NOSO}_3^-]$$

and

$$k_{\text{obsd}} = \frac{kK[\text{OH}^-]}{1 + K[\text{OH}^-]} \quad (10)$$

The value of *k*_{obsd} should level off at high [OH⁻], and some evidence of this is seen in Figure 2. Although it should be possible to extract values for both *k* and *K* from our data, the large uncertainties in *k*_{obsd} values do not permit deriving satisfactory values for both. We have therefore taken *K* = 1.9 M⁻¹ and calculated *k* at each [OH⁻] from *k*_{obsd} (Table IV). The average value is 0.16 ± 0.06 M⁻¹ sec⁻¹;¹⁷ the curve in Figure 2 is fit for this value. This curve suggests that the difficulty encountered in following the very rapid reaction at high hydroxide concentrations led to unreliably high values for *k*_{obsd} for the runs near [OH⁻] = 0.8 M.

Although H₂NOSO₃⁻ may also react with the ammonia formed to produce hydrazine, we found this reaction was too slow to be of importance at the ammonia concentrations present in our studies.

Discussion

The mechanism for H₂NOSO₃⁻ decomposition in alkaline solution originally proposed by Schmitz⁷ consists of four steps, eq 1-4. Although no one has yet successfully observed diazene in this system, its presence as an intermediate is amply supported by the hydrogenating ability of an alkaline H₂NOSO₃⁻ solution.²⁻⁵ The formation of diazene by eq 2 is supported by the superior hydrogenating ability of H₂NOSO₃⁻-H₂NOH mixtures⁷ and, more directly, by our synthesis

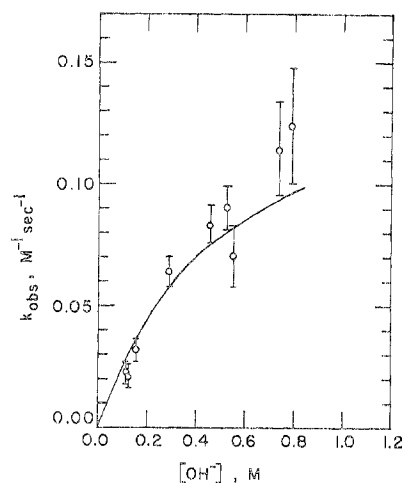


Figure 2. Plot of the observed second-order rate constant for the reaction of H₂NOH with H₂NOSO₃⁻ as a function of [OH⁻] at 26.6° and μ = 1.5 M. The curve is drawn for eq 10 with *k* = 0.16 sec⁻¹ M⁻¹ and *K* = 1.9 M⁻¹.

and isolation of substituted diazenes, RN=NH, using RNHOH.⁶ Initial formation of H₂NOH by eq 1 is harder to demonstrate given our inability to measure it in this complex chemical system. As an alternative approach we attempted to see if the *N*-methyl derivative, CH₃NHOSO₃⁻,¹¹ would provide CH₃NHOH by using nmr to track the methyl group. Unfortunately CH₃NHOSO₃⁻ in strong hydroxide solution reacts preferentially at the methyl group apparently because of the strongly electron-withdrawing character of the group attached to carbon.²⁰ Nonetheless nucleophilic attack at the nitrogen atom in H₂NOSO₃⁻ is now well established,^{9,10} and it is reasonable that OH⁻ should behave similarly. Chloramine, H₂NCl, which is closely related to H₂NOSO₃⁻ and which also produces diazene in alkaline solution,⁷ has been shown to undergo nucleophilic attack by OH⁻. We therefore take eq 1-4 as a reasonable reaction sequence in H₂NOSO₃⁻ hydrolysis.

In exploring the viability of the proposed mechanism we have measured the overall rate of H₂NOSO₃⁻ decomposition in both the absence and presence of a diazene scavenger. In addition we have measured independently the rates of eq 6 and 7. In the presence of excess HONH₂ the rate for eq 6 is determined by the rates of steps 2 and 3, while the rate for eq 7 is determined by the rates of steps 3 and 4. No direct measure of the rate of step 3 is available from either our work or the literature. Since all reported attempts to detect diazene in solution have been unsuccessful, we assume that step 3 is much faster than either step 2 or 4. Thus the rates of eq 6 and 7 are a measure of the rates of step 2 or 4. On the basis of the H₂NOH-H₂NOSO₃⁻ kinetics, step 2 is better represented by a two-step process, eq 8 and 9.^{22,23} Our kinetic data also provide direct measurements for the specific rate constants of steps 4 and 9 as well as a rate constant for the overall rate of decomposition of H₂NOSO₃⁻ alone in alkaline solution. These data show that steps 4 and 8-9 are much faster than the overall rate of H₂NOSO₃⁻ disappearance. We conclude, therefore, that the slow step in the reaction sequence is step 1, the initial reaction of H₂NOSO₃⁻ with OH⁻.

If [H₂NOH], [N₂H₂], and [N₂H₄] all reach steady-state values in the decomposition of H₂NOSO₃⁻, the observed rate constant would be 3 times the rate constant for step 1, *k*₁. From the kinetic data without fumarate present this would mean *k*₁ = 0.61 × 10⁻⁴ M⁻¹ sec⁻¹. However, this estimate of *k*₁ must be too low since periodic assay for N₂H₄ during the kinetic runs shows that [N₂H₄] does not attain steady state but increases throughout the run. In the runs with added fumarate steps 3 and 4 will not be important as most of the

diazene is used to reduce the fumarate. That the rate constant does not drop by one-third (from 1.84 to $1.21 \times 10^{-4} M^{-1} \text{sec}^{-1}$) in the presence of fumarate is consistent with the failure of N_2H_4 to reach steady state.

A better estimate of k_1 may be obtained from the measurements made in the presence of fumarate. If $[H_2NOH]$ attains a steady state, $2k_1 = 1.72 \times 10^{-4} M^{-1} \text{sec}^{-1}$ and $k_1 = 0.85 \times 10^{-4} M^{-1} \text{sec}^{-1}$. This value for k_1 is at least 250 times smaller than the rate constant, eq 10, for the H_2NOH reaction even at the lowest $[OH^-]$ studied. This lends support to the steady-state assumption for H_2NOH in the absence of our ability to follow it directly in the kinetic runs.

The ability of the proposed mechanism and the measured and estimated rate constants to reproduce kinetic data for the decomposition of $H_2NOSO_3^-$ at various $[OH^-]$ values was tested by computer simulation. The steps included were (1) through (4) plus a term for the reaction of $EDTA^{4-}$ with $H_2NOSO_3^-$. The rate constants for the EDTA term and for step 4 were the experimental values of $0.0071 M^{-1} \text{sec}^{-1}$ and $0.010 M^{-1} \text{sec}^{-1}$, respectively, while k_1 was taken as $0.85 \times 10^{-4} M^{-1} \text{sec}^{-1}$ as estimated above. For simplicity step 2 was used to replace steps 8 and 9; the rate constant for step 2 was given by eq 10 at the $[OH^-]$ appropriate in the run. Since step 3 is assumed to be very rapid, it was assigned arbitrarily a moderately large rate constant of $10^4 M^{-1} \text{sec}^{-1}$.

Runs were simulated at three different $[OH^-]$ values with initial concentrations of $H_2NOSO_3^-$ at $0.0120 M$ and of $EDTA^{4-}$ at $4.8 \times 10^{-3} M$. In each case disappearance of $H_2NOSO_3^-$ showed pseudo-first-order kinetics and the calculated first-order rate constant was in good agreement with the experimental values as taken from Figure 1. Results are as follows for $[OH^-]$, $10^4 k_{\text{computed}} (\text{sec}^{-1})$, $10^4 k_{\text{exptl}} (\text{sec}^{-1})$: $0.115 M$, 0.68 , 0.63 ; $0.833 M$, 1.99 , 1.95 ; $1.47 M$, 3.12 , 3.04 . Changing the hydroxylamine rate constant (step 2) by a factor of 2, changing the rate constant for step 3 by an order of magnitude, or assuming the presence of 5% H_2NOH initially present in the H_3NOSO_3 used had no effect on these results. However, changing the initial estimate of k_1 had a comparable percentage effect on the computer-generated rate data. From this we conclude that $0.85 \times 10^{-4} M^{-1} \text{sec}^{-1}$ is a good estimate for the rate constant of step 1 and that the proposed mechanism is consistent with the overall rate of decomposition of $H_2NOSO_3^-$.

Krueger, *et al.*, have recently been using $H_2NOSO_3^-$ as a model to study nucleophilic attack at an sp^3 nitrogen center.^{9,10} In the present study three species, OH^- , N_2H_4 , and H_2NO^- , would appear to react with $H_2NOSO_3^-$ in this manner even though the immediate products of such a reaction cannot be isolated. The case of OH^- was discussed above. That both N_2H_4 and H_2NO^- act as nucleophiles is supported by the form of the rate law and by the intermediate formation of diazene through N-N bond formation. In the case of N_2H_4 Schmitz⁷ has used ^{15}N labeling to show that triazene is an intermediate in the reaction with $H_2NOSO_3^-$.

From our rate data the order of relative nucleophilicities of OH^- , N_2H_4 , and H_2NO^- toward the sp^3 nitrogen of $H_2NOSO_3^-$ is $H_2NO^- > N_2H_4 \gg OH^-$. This order is consistent with Krueger's conclusion that polarizability and

ease of oxidation of the nucleophile play a considerably more important role in determining reactivity toward the $H_2NOSO_3^-$ nitrogen center than does proton basicity. Both hydroxylamine and hydrazine are readily oxidized compared with hydroxide ion. The proton basicities of H_2NO^- and OH^- are comparable but H_2NO^- should be substantially more polarizable. In terms of the present chemistry the relationship between OH^- and H_2NO^- is similar to that observed in studies comparing the peroxide anion HOO^- and OH^- . The anions HOO^- and H_2NO^- are isoelectronic species.²⁴

After the work presented above had been completed and accepted for publication, a paper appeared²⁵ which overlaps in part with our own studies. The two studies differ somewhat in the reaction conditions used in the kinetic work but the results and the conclusions are in agreement.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. W. E. S. and D. H. R. were National Science Foundation undergraduate research participants.

Registry No. $H_2NOSO_3^-$, 41380-12-5; N_2H_4 , 302-01-2; NH_2OH , 7803-49-8.

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